

A NOVEL METHOD FOR DETERMINING FORCING DRIVERS FOR TOTAL
WATER FLOW IN PEM FUEL CELLS INCLUDING ELECTRO-OSMOTIC DRAG,
BACK DIFFUSION, AND SINGLE- AND TWO-PHASE THERMAL OSMOSIS

by

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To my wonderful wife Virginia, and my sons Stefano and Gabriel, I could not have accomplished this without your support, love and patience. My wife Virginia has been there every step of the way and has been my anchor keeping me on my path. She has kept me on the path to achieve my dream. I would like to thank my family for the sacrifices that they have made so I could complete my dream!

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PREFACE

With the push for electrification, people have turned to batteries and have overlooked fuel cell technology. The PEM fuel cell is still in its infancy and need to support in the heat and water management to improve its performance and efficiency. With this research the modes of water transport will be better understood, and this can be implemented into the fuel cell to overcome the existing fuel cell hurdles.

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ABSTRACT

Heat and water management are essential for successful for PEM fuel cell operation, the goal being optimal fuel cell hydration to maximize ionic conductivity. Overhydration can lead to flooding on the cathode side. In experimentation on PEM fuel cells, total water transfer across the membrane is a result of simultaneous fluid drivers present in the experiment, including voltage, chemical potential, thermal and pressure gradients, and is measured indirectly with a high degree of precision.

The conventional process in assigning magnitudes to these simultaneous drivers consists of assuming a water transport coefficient from one the many empirical models to determine one effect and subtracting that effect from the other. In the case of only two drivers, this results in both depending on the empirical coefficient model chosen. As shown in this paper, electro-osmotic drag, back diffusion and thermal osmosis models have significant scatter and a variety of trends making it difficult to assign numeric

values with certainty. The proposed method developed here is to couple the theoretical model to the experimental data and solve for transport coefficients at each data point.

One of the issues seen in experimental data from prior research in the archival literature is an assumption in the negligibility of other fluid drivers. This is sometimes done unintentionally and implicitly when experimental data curve fits are forced through the origin, which is documented to have happened on numerous occasions. The proposed approach here shows explicitly the magnitude of these minor drivers. As a result, several prior research papers included an error borne out of assumptions that weren't quite true. The result of forcing the data trendline through the origin will either result in an overstating of the measured fluid driver which could lead to flooding, or the result could be understating the measured fluid driver which could lead to membrane dry out.

The approach here has also been applied to thermal osmosis experiment data to explain anomalies in data where some researchers claimed that thermal osmosis was only substantial above a certain temperature difference threshold. This was not the case. In fact, specific to thermal osmosis, there appear to be two types: single- and two-phase. These are very different from one another and impact experiments that used liquid on either side of the membrane versus vapor. This too can be uncovered with the proposed method as shown here.

In the end, the current method calculates water transport from each fluid driver, magnitude and direction, increases accuracy and will result in more efficient fuel cell operation by optimizing fuel cell humidification.

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LIST OF ABBREVIATIONS AND SYMBOLS

Alkaline Fuel Cell	AFC
Proton Exchange Membrane Fuel Cell	PEM
Reduction and Oxidation Reaction	REDOX
Platinum	Pt
Carbon Dioxide	CO ₂
Oxygen	O ₂
Gas Diffusion Layer	GDL
Bi-Polar Plate	BPP
Anode Catalysts Layer	ACL
Cathode Catalysts Layer	CCL
Hydrogen Ions	H ⁺
Water	H ₂ O
Electromotive Force (V)	E
Change in Gibbs Energy	ΔG
Number of Molecules of Substance	n
Faraday's Constant	96485 C/mol
Electron	e ⁻
Theoretical voltage at 25°C	E°
Universal Gas Constant	R _u , R
Pressure	a
Activation Energy Losses	$\Delta E_{activation}$

Current density	j
Voltage	V
Ohmic Resistance	r
Charge Transfer Coefficient	α
Absolute Temperature	T
Empirical Mass Transport Loss Coefficient	$m(V)$
Empirical Mass Transport Loss Coefficient	$n(m^2/A)$
Equilibrium exchange current density	j_o
Membrane Hydration State	λ
Membrane Empirical Coefficient	(C_o, C_1, C_2)
Membrane Heat Source Term	S_T
Electro-Osmotic Drag	(EOD)
Back Diffusion	(BD)
Equivalent Weight of Membrane	EW
Perfluoro Sulfonic Acid	(PFSA)
Available Sulfonic Acid Groups Water	(N_{water})
Captured by Sulfonic Acid Groups	$(N_{SO_3^-})$
Relative Humidity	a or RH
Vapor Pressure	p_w
Saturation Pressure	p_{sat}

Balance of Plant	(BOP)
Original Equipment Manufacturer	(OEM)
Microporous Layer	MPL
Phase Change Induced	(PCI)
Polytetrafluoroethylene	(PTFE)
Electric Osmotic Pump	(EOP)
Electro-Osmotic	(EO)
Total Water Flow Transfer Coefficient	b,a
Non-Equilibrium Thermodynamics	(NET)
Thermal Osmosis	(TO)
Chemical Potential	μ
Direct Methanol Fuel Cell	(DMFC)
Total Water Flux Across Membrane	J_{Total}
Mass Flowrate	$\dot{m}$
Electro-osmotic drag coefficient	n_d
Back Diffusion Coefficient	$D(l), D_w$
Concentration	c
Spatial coordinate	x
Stoichiometry	St
Membrane Water Content	c_w
Stoichiometry of cathode	λ_c
Dew Point	T_{dew}

Net Water Drag	(NWD)
Change in Molar Flux	ΔN_y
Methanol	CH ₃ OH
Differential Pressure	DP
Cathode	CA
Anode	AN
Gas Diffusion Layer without MPL	BA
Gas Diffusion Layer with MPL	BC
Molar Flux	N_m
Concentration Difference	DI
Heat Flux	J_q
Electrical Current	I
Temperature Difference	ΔT
Concentration Difference	Δc
Voltage Difference	ΔE
Permeate Flux	J_m
Thermal Osmosis Flux	J_{TO}
Thermal Osmosis Transfer Coefficient	D_T, D_i^o, D^*
Thermal Gradient	∇T
Thermal Osmosis Coefficient	D_T^o
Nafion 112	N112
Gas Diffusion Layer without MPL	SGL 10 AA

Gas Diffusion Layer with MPL	SGL 10 BB
Thermal Osmosis Fluid Flux	J_i^o
Entropy Difference	Δs
Wall Thru Plane	WTP
Anode Temperature	T_a
Cathode Temperature	T_c
Activation Energy	E_a
Osmotic Transport Coefficient	v_o
Osmotic Pressure	$\Delta \pi$
Collodion Membrane	CM
Membrane	I-M-2
Thermal Osmosis Transport Coefficient	B
Membrane Thickness	d
Membrane Cross-Sectional Area	q
Thermal Osmosis Transport Coefficient	B_o
Activation Energy	E_T
Water Transport Across Membrane	J_w
Pressure Flux Transport Coefficient	A
Pressure Transport Coefficient at a Given	A_T
Pressure Transport Coefficient	A_o
Thermal Osmosis Transport Coefficient	B_1
Heat of Transport	Q^*

Volume	V
Phenomenological Coefficients	L_{11}, L_{12}
Specific Volume	v
Thermal Osmosis Transport Coefficient	D^*, D^c
Membrane Temperature	T_m
Pressure Transport Coefficient	L_p
Volume Flow Across the Membrane	J_v
Total water Flow Across the Membrane	J_{Total}
Membrane Thickness	δ
Pressure Transport Coefficient	A
Thermal Osmosis Transport Coefficient	B
Temperature Difference Across the Membrane	ΔT_m
Heat of Transport	Q, Q_m^*
Activation Energy	E_a
Specific Volume	v_o
Volume	V
Membrane Distillation Transport Coefficient	β
Length	L, l
Thermal Osmosis Transport Coefficient	L_{VT}

Pressure Based Transport Coefficient	L_{VP}
Phenomenological Coefficients	$L_{11}, L_{12}, L_{13}, l_{11}, l_{12}, l_{13}$
Membrane Transport Coefficient	A_x, L_{PW}
Concentration water	C_w
Concentration Difference of Water	DC_w
Concentration acetic acid	C_a
Concentration Difference of acetic acid	ΔC_a
Specific volume of water	v_w
Heat of vaporization of water	ΔH_w
Heat of vaporization of Acetic Acid	ΔH_a
Voltage Gradient	$\Delta \phi$
Phosphoric Acid Fuel Cell	PAFC
Molten Carbon Fuel Cell	MCFC
Solid Oxide Fuel Cell	SOFC
Total Water Flux	J
Empirical Coefficients of Total water flow data	a_o, a_1, a_2
Empirical Coefficients of Total water flow data	b_o, b_1, b_2
Empirical Coefficients of Total water flow data	c_o, c_1, c_2

Dry Membrane Density	ρ_{Dry}
Ratio of Electro-Osmotic Drag to Total Flow	R_{EOD}
Ratio of Back Diffusion to Total Flow	R_{BD}
Ratio of Thermal Osmosis to Total Flow	R_{TO}

CHAPTER ONE

INTRODUCTION

1 Introduction

The first fuel cell was discovered in 1839 by Sir William Grove, finding that it is possible to generate electricity through the reverse electrolysis of water. At this time, it was known as a “gas battery”, this discovery leading to fuel cell technology. In the 1960’s NASA adopted the then-common alkaline fuel cell (AFC) but the issue with those was that it required pure oxygen, and carbon dioxide (CO_2) in the environment would poison the liquid electrolyte and ruin the fuel cell. In the late 1960’s, that the Proton Exchange Membrane (PEM) fuel cell was born. The PEM fuel cell was unique because it did not require pure oxygen (O_2); it could run on air, and it could tolerate CO_2 . The PEM fuel cell required platinum (Pt) as a catalyst, and it was costly compared to the nickel (Ni) used in the alkaline fuel cell. The other key difference for the PEM fuel cell was that the electrolyte is a sulphonated organic polymer membrane which requires hydration but was resistant to CO_2 poisoning while the AFC used aqueous potassium hydroxide as the electrolyte.

NASA encountered heat and water management problems with the PEM fuel cell, such as membrane dry out or cathode catalysts layer flooding, and it was forced to go back to the less desired Alkaline Fuel Cell (AFC). The Proton Exchange Membrane (PEM) fuel cell and alkaline fuel cell are electrochemical devices that convert hydrogen (H_2) and oxygen (O_2) into water, electricity, and heat. It was clear that the water transport across the

membrane was not fully understood, and it needed to be better managed. Even with the shortfalls of the PEM fuel cell it is more desirable than the alkaline fuel cell because it can run on air. The performance of the PEM fuel cell depends on the hydration state of the membrane as well as the phase of water. To control the hydration state of the membrane, the total water flow across the membrane needs to be precisely controlled.

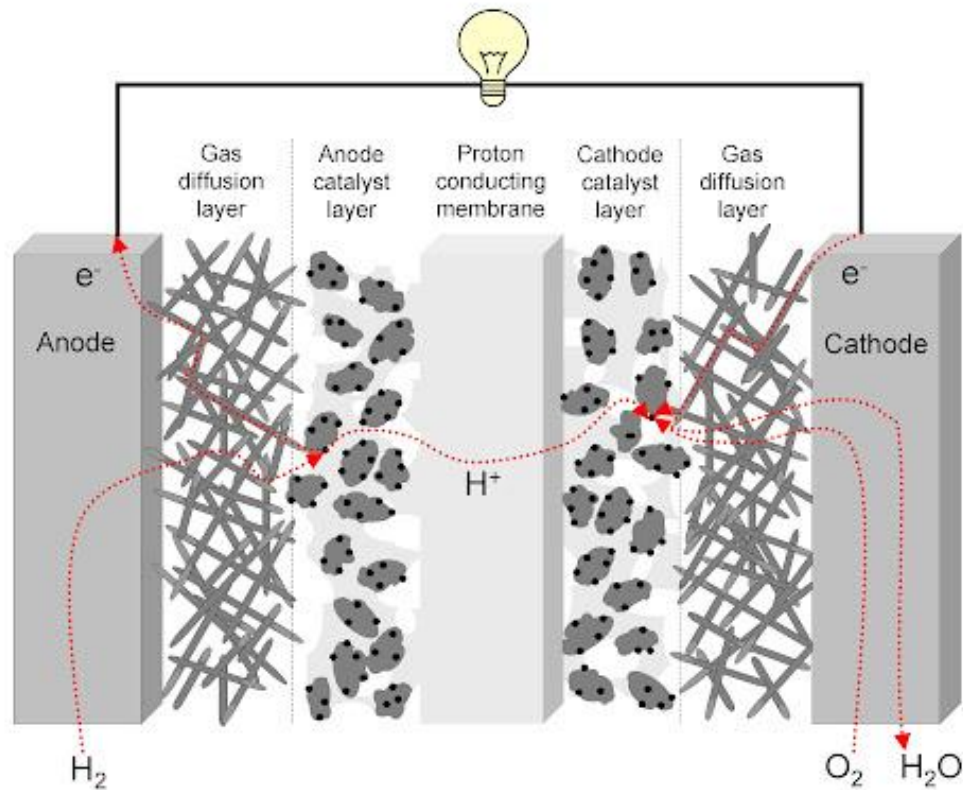


Figure 1.1 Schematic of PEM Fuel Cell [1]

Figure 1.1 shows the internal workings of the PEM fuel cell, particularly what occurs within each layer of the cell. Each individual layer has an essential function for fuel cell operation. The PEM fuel cell contains an oxidation and a reduction reaction. The combination of these two reactions provides voltage and current. Oxidation is when a

substance loses electrons, whereas reduction is when a substance gains electrons.

Oxidation and reduction reactions are also called REDOX reactions. Hydrogen gas is oxidized at the anode catalysts layer (ACL), and the hydrogen side of the PEM fuel cell is considered the anode.



Equation 1 shows that one atom of diatomic hydrogen produces two hydrogen ions and two electrons. The electrons produced in the oxidation reaction are sent outside the fuel cell to the electrical load. Then they are returned to the cathode catalysts layer where the electrons react with the hydrogen ions and oxygen to complete the reduction reaction.



The hydrogen ions are transported through the membrane via process named electro osmotic drag. This process requires water to move the hydrogen ions from the anode to cathode. The hydrogen ions meet with oxygen and electrons to complete the reduction reaction to form water at the cathode catalysts layer (CCL). Equation 2 shows the reduction reaction. The current process for modeling an electro-chemical involves assuming a simple mechanical substance under constant pressure and constant temperature where the only work performed by the system is electrical work. The result of the assumption relates the Gibbs free energy to theoretical electrical work. Gibbs Free energy allows for the calculation of the theoretical voltage of the REDOX reactions.

$$E = \frac{-\Delta G}{nF} \quad (3)$$

As shown in equation 3, the relationship between the change in Gibbs Free energy and the number of electrons in the electrochemical reaction. Where ΔG is the change in Gibbs Free Energy, n is the number of electrons involved in the reaction and F is Faraday constant and E is the maximum voltage that thermodynamics will allow. The maximum voltage a PEM fuel cell can produce is 1.22 V. All electro-chemistry is defined at 25 °C, and at 101.3 kPa and when conditions vary from these conditions the theoretical voltage needs to be recalculated. The theoretical voltage also will change in pressure and/or temperature. By using the Gibbs free energy equation, and the Gibbs Free energy equation of state, the new voltage can be expressed in the Nernst Equation.

$$E = E^o + \frac{R_u T}{nF} \ln \left(\frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) \quad (4)$$

There is also an impact of temperature on the Open Circuit Voltage (OCV), is also obtained by through the Gibbs equation and it is shown in Equation 5.

$$E = E^o - T \left(\frac{\partial s}{\partial q} \right) = E^o - T \left(\frac{\partial E}{\partial T} \right) \quad (5)$$

The relationship of the pressure corrected voltage is shown in equation 4. Where E^o is the voltage at standard temperature and pressure, R_u is the universal gas constant, T is the absolute temperature, and a represents the activity coefficients for the reactants and

products in the gaseous phase. The relationship of the temperature corrected voltage is shown in equation 5. Where E_o is the open circuit voltage, the partial derivative of entropy with respect charge is not directly known but it is equal to the change in voltage with respected to temperature. The voltage calculated through the Gibbs Free Energy is what the second law of thermodynamics permits. Like with friction, there are voltages losses of the fuel cell, and each one is impacted by different parameters. After all the losses in the fuel cell, the resulting voltage is a discharge voltage. There are three types of voltage losses in the fuel cell. Fuel cell voltage losses consist of activation, Ohmic and mass transport losses. Each of these losses is governed by different mechanisms. The activation loss represents the losses for activating any chemical reaction. To lower the activation losses, catalysts are used to lower the activation energy. The activation loss is mainly a function of the catalyst material. The losses from the activation are dependent on the anode and cathode catalysts selected as well as the current. The activation loss is derived from the Butler-Vormer equation. The loss of fuel cell voltage from activation energy is shown in equation 6.

$$\Delta E_{activation} = -\frac{RT}{n\alpha F} \ln \left(\frac{j}{j_o} \right) \quad (6)$$

Where $\Delta E_{activation}$ is the voltage loss due to activation energy, α is charge transfer coefficient n is the number of electrons, j_o is the equilibrium current which varies from catalysts material, and j is the current density. The hydration state of the membrane does not impact the activation losses. The activation losses do depend on the current density. The

second type of voltage loss is Ohmic loss. The Ohmic resistance is computed through Ohm's Law. Ohm's law is the linear relationship between voltage and current. The Ohmic losses depend on the materials selected for the fuel cell. Ohm's Law is shown in Equation 7.

$$V = jr \quad (7)$$

Where V is the voltage drop, r is the area specific resistance and j is the current density. The Ohmic losses mainly depend on the materials selected and the hydration state of the membrane. The Ohmic losses in the material is material is constant, and the membrane of the fuel cell resistance does change based on its water content. As the membrane hydrates increases its resistance decrease. The membrane reaches its highest ionic conductivity when the membrane is fully saturated. This is the main reason of the membrane needs to be hydrated.

As shown in Equation 4, the theoretical voltage is dependent on the pressure of the reactants and products, this is the main reason why the fuel cell is pressurized. As reactants are consumed the partial pressure from the reactants decreases also, and when the pressure reduced the fuel cell voltage will decrease also. The pressure of the oxygen is the limiting factor of the PEM fuel cell, the water is formed on the cathode side further reducing the oxygen pressure, when liquid water is present in the cathode catalysts layer This type of loss is known as mass transport loss. Reactants must move through the gas diffusion layers (GDL) and make it to the catalysts layer. The limiting reaction in the

PEM fuel cell is the reduction reaction. The oxygen (O_2) is being consumed at the cathode catalyst layer, which reduces its concentration. As the concentration decreases, so does the voltage. Therefore, oxygen (O_2) must diffuse fast enough to keep concentration high. One empirical model used to compute mass transport loss is shown in equation 8.

$$\Delta E_{masstransport} = me^{nj} \quad (8)$$

Where $\Delta E_{masstransport}$ is the voltage loss due to mass transport, m, and n are empirical constants and j is the current density. The mass transport losses depend on the operating conditions, and mass transport to the catalyst layer. When liquid water is formed in the cathode, the oxygen transport is greatly reduced, and the mass transport losses increase. The voltage loss from mass transport losses is mainly limited by the cathode because the diffusivity of hydrogen is larger than oxygen which means it takes more time for oxygen to diffuse. In addition, the hydrogen oxidation reaction (HOR) is simpler than the cathode reduction reaction. Lastly, liquid water flooding will occur more at the cathode. The mass transport losses occur when the concentration of oxygen cannot be maintained in the cathode catalysts later.

One of the differences between the PEMFC and the alkaline fuel cell is that in the PEM, the water is formed on the cathode and in the alkaline fuel cell, the water is formed at the anode. This is why flooding hurts the PEM more than the alkaline fuel cells. A polarization curve represents how the output voltage of the PEM fuel cell is affected by

the fuel cell current density. By combining the Nernst equation along with activation, Ohmic and mass transport voltage losses together, a mathematical model of a fuel cell polarization curve is generated. Equation 9 is produced by combining Equations 4 through 8. Figure 1.2 shows a graph of the polarization curve.

$$E = E^o + \frac{R_u T}{nF} \ln \left(\frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) - \frac{RT}{n\alpha F} \ln \left(\frac{j}{j_o} \right) - jr - me^{nj} \quad (9)$$

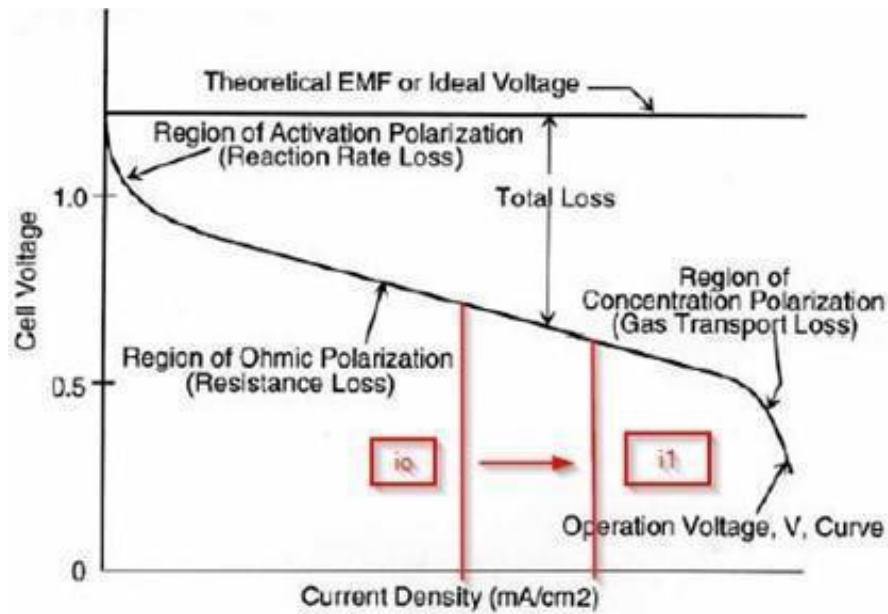


Figure 1.2 Sample of Polarization Curve of PEM Fuel Cell [2]

The polarization curve can be broken down into three regions. The first region is the activation loss. While the second region is the Ohmic region and the last region is the mass transport region. To further understand the limitation of the PEM fuel cell, each layer of the PEM fuel cell must be understood. The goal is to keep the fuel cell in the Ohmic loss region and not to let it go into the mass transport loss region, in the mass

transport loss region the discharge voltage is too low, and the heat generation is very high. It is difficult to determine the transition between the Ohmic and mass transport loss region due to flooding.

The transition of Ohmic to Mass Transport losses does not occur at the same current density for all fuel cells, the transition occurs when the concentration/pressure of oxygen in the catalysts layer cannot be maintained, this occurs when the rate of oxygen consumptions exceeds the rate of oxygen transport in the fuel cell. When liquid water is introduced in the cathode catalysts layer, the mass transport resistance of oxygen further increased and reduces the rate of oxygen transport to the cathode catalysts layer and reducing the oxygen pressure. The fall of the oxygen pressure will start the flooding of the fuel cell, to counter this the liquid water must be removed.

The liquid water must be removed by either pushing it toward the anode, this is ideal because this promotes self-humification but requires precise modeling of the total water flow across the membrane. On the other hand, the water can be pushed toward the bipolar plate and out the fuel cell. This method is not preferred because it requires a humidifier to recover the outlet water to humidify the incoming air. The current approach requires precise modeling of the total water flow across the membrane to deliver the right amount of humidity to promote back diffusion and not to flood. Both cases, the total water flow needs to be accurately modelled.

Also, the Microporous Layer is also added to the fuel cell promote liquid water removal, but the microporous layer can be added to the cathode only, anode only or both the anode and cathode microporous layer. The mechanism of the transport of the MPL are not fully understood and it only functions when it is wet. The water transport of the MPL need to be better models to reflect how it impacts the total water flow.

With proper total water flow modeling, the fuel cells can be designed for higher current densities which will improve the power density, and the bi-polar plate can be properly designed for the supply and remove water. The need of the MPL can also be confirmed.

1.1 Impact of Water Management of the PEM Fuel Cell

There are three types of voltage losses in the fuel cell, the first type is the activation losses, the second type of loss is the Ohmic losses and the last is the mass transport losses as shown in Figure 1.1.2. If too much water is moving toward the cathode there is a risk of flooding because the cathode RH can exceed 100%. The goal is to move the water to the anode to keep the cathode catalysts layer from flooding which is why the water balance across the membrane needs to be reported along with the voltage. Water balance in a PEM fuel cell is essential for fuel cell performance. There is a coupling of moisture content and performance. There are two criteria that must be met to maintain fuel cell performance. The first criteria item is the membrane hydration, and the second criteria is catalysts layer flooding. The output voltage of the fuel cell depends on the total water flow across the fuel cell if the cell is flooded this will impact discharge voltage and if the

cell is too dry then the voltage loss will occur by a different mechanism. Presently the only way to humidify the hydrogen is through back diffusion.

The membrane must be hydrated to increase its ionic conductivity, but it must not be too hydrated to the point where the catalyst's layer will flood. When liquid water accumulates in the catalysts layer and or diffusion media (GDL), the liquid water will prevent gases from reaching the catalysts layer. The loss of oxygen will reduce the concentration of oxygen at the catalysts layer, which will cause the fuel cell to enter the mass transport loss region faster. By entering the mass transport region sooner, the output voltage will be reduced, and the fuel cell will lose efficiency.

Flooding in the PEM fuel cell can occur in three different locations. The first location is the flow channel. Flooding also can occur in the diffusion media (GDL) and the catalysts layer. When the fuel cell is operated at low current densities, the fluid velocity in the channel may not have enough momentum to remove the slugs of liquid water. In instances where the fuel cell is operated at high current densities, the fluid will have enough momentum to remove slugs, but the flooding will occur in the diffusion media (GDL) and/or catalysts layer. The types of flooding are shown in Figure 1.1.1

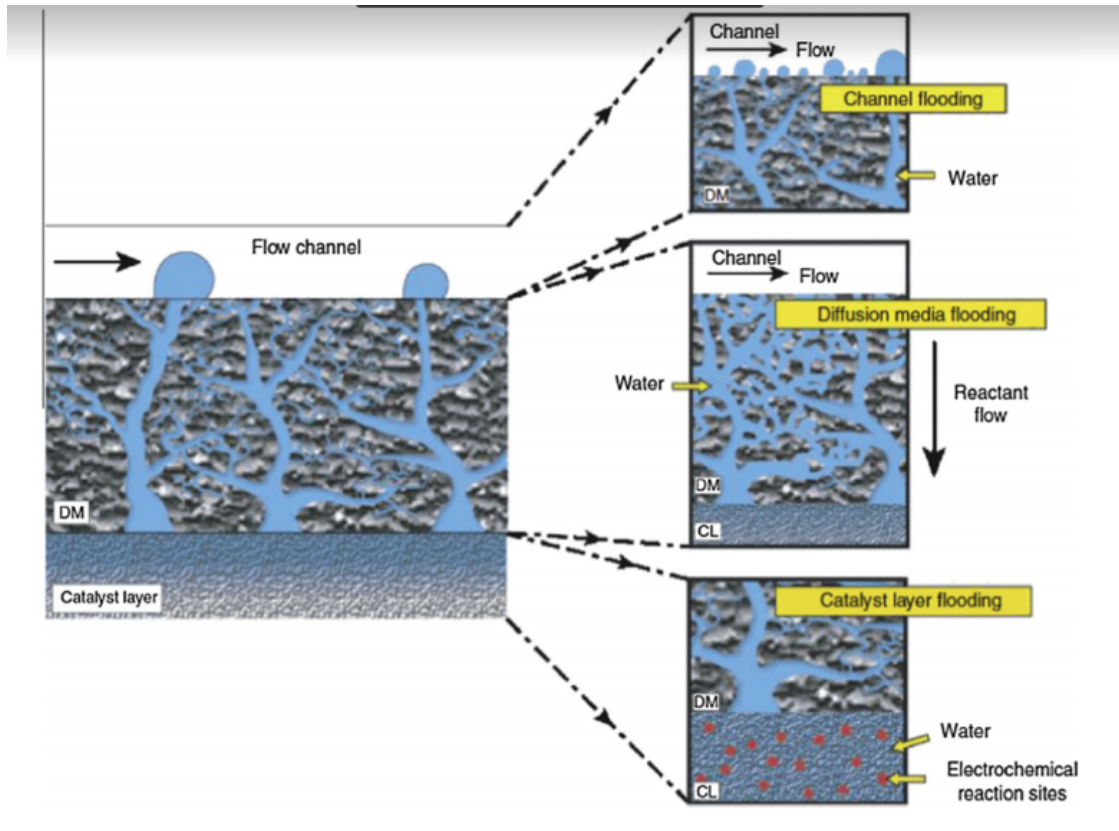


Figure 1.1.1 Types of a PEM Fuel Cell Flooding [3]

The flow channel flooding can be resolved through flow channel design and through fluid velocity. The channels of the bi-polar plate will influence flooding. For the flooding inside the diffusion media (GDL) and catalysts layer, the liquid water will fill the pores. By filling the pores, the reactants will see more hydraulic resistance, which will result in a reduction of concentration at the catalysts layer. The reduction of reactants at the catalyst layer will reduce the fuel cell output voltage. Flooding will impact the cathode much more than the anode. At the anode, only hydrogen and water vapor will be present, whereas on the cathode side, nitrogen, water and oxygen will be present. Water vapor is formed when oxygen is consumed which further reduces the concentration of oxygen.

During fuel cell operation, the formation of water and the water transported through EOD will result in an increase of the partial pressure of water vapor in the catalysts layer. In the meantime, oxygen is which drives down the concentration of oxygen. The reduction in the concentration of oxygen will cause the fuel cell voltage to fall. Therefore, the focus is on removing the water in the cathode catalysts layer to maintain the concentration of oxygen.[3]

1.2 Cathode Catalysts Layer (CCL) Flooding

To understand the impact of flooding on fuel cell performance, Mench [3] ran a polarization curve on a fuel cell at 100 % relative humidity on the anode and cathode. In the instance when the cell was at 80°C, the fuel cell entered flooding at 1 A/cm².

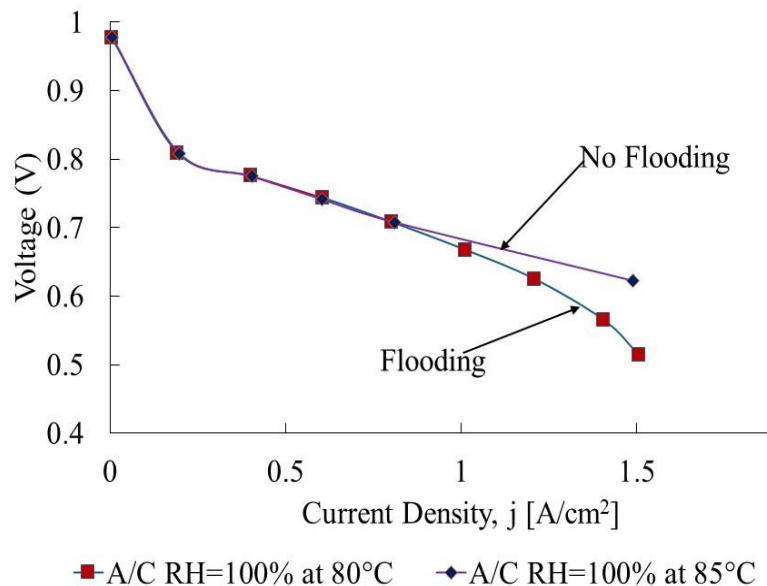


Figure 1.2.1 Flooding Impact on Output Voltage [3]

When the same fuel cell was run at a cell temperature of 85°C, the fuel cell was still in the Ohmic region. When both cells were run at 1.4 A/cm², there was a voltage difference of .115 V. At 85°C, the saturation pressure was higher than at 80°C, which gave the air more capability to hold more water vapor. The additional capacity reduced the amount of liquid water condensing at the cathode catalysts layer. Figure 1.2.1 shows how flooding reduces fuel cell output voltage [3]. The flooding was delayed because of the increase in the capacity of air to hold more water vapor. Figure 1.2.2 shows how the vapor pressure of water changes with temperature. At lower temperature the air is easier to saturate, which leads to condensation at the catalysts layer. The cell temperature needs to be high enough to avoid flooding and low enough to avoid drying out the membrane.

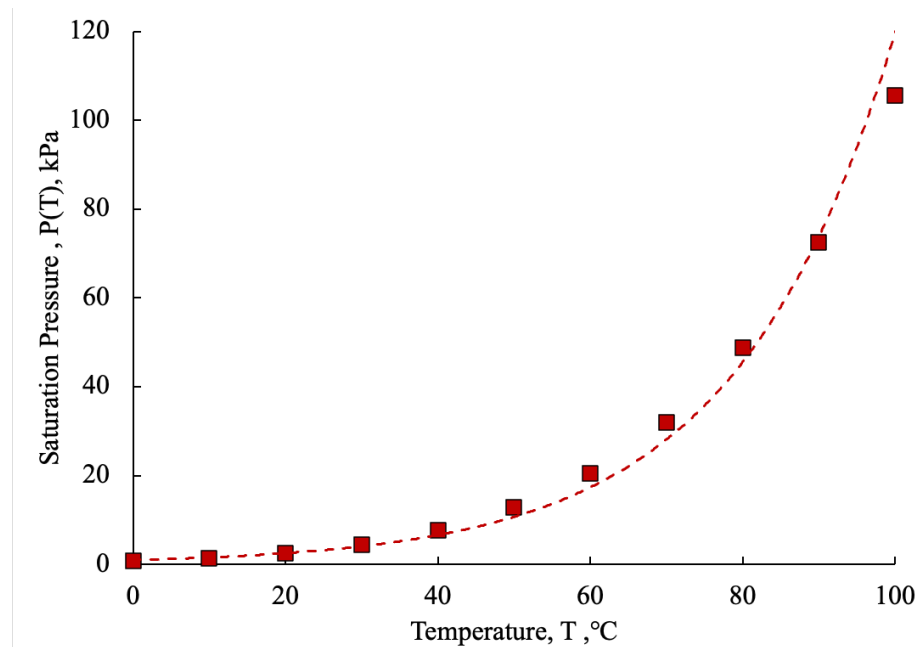


Figure 1.2.2 Saturation Pressure of Water [3]

Like Mench [3], Ijaodola [4] conducted some PEM fuel cell testing to show the impact of flooding. The testing data shows that the polarization curve starts making its transition from the Ohmic region to the mass transport region at lower current densities.

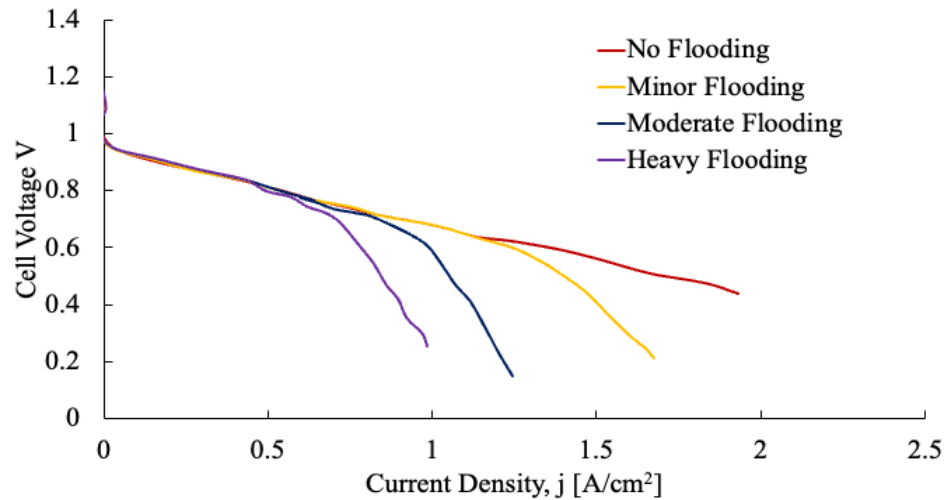


Figure 1.2.3 PEM Fuel Cell Flooding Impact on Voltage Output [4]

Figure 1.2.3 shows how fuel cell flooding reduces the voltage output of the fuel cell. In the no-flooding case, the polarization curve does stay in the linear region. In the case of the minor flooding the fuel cell cannot achieve the same performance as the non-flooding case. As the flooding further increases the maximum cell voltage decreases. The loss of voltage will lead to heat generation in the membrane and lead to more heat removal.

Flooding therefore limits the design current density. If the total water flow is not accurately modelled, then there is a possibility that the fuel cells will not meet its design project. By limiting where flooding takes place, fuel cells can be pushed to a higher

current density and/or efficiency can be gained through improved water management.

The designed current density cannot be achieved when flooding occurs.

1.3 Membrane is Too Dry/Dehydration of the Fuel Cell

One of the water transport modes governed by the Nernst Planck equation is electro-osmotic drag, and Ohm's law relates the voltage gradient to current density. The membrane needs to prevent electrons from passing through it and it as to conduct protons as the same time. This is where the Nafion membrane comes into play, it conducts protons and resists electrons. The protonic conductivity of the membrane is a function of the hydration state and temperature. The lower the hydration state, the higher the membrane Ohmic resistance. Equation 10 shows how conductivity depends on the hydration state and absolute temperature of the membrane.

$$\sigma(\lambda, T) = (C_o + C_1\lambda)e^{(C_2(\frac{1}{T_1}-\frac{1}{T_2}))} \quad (10)$$

The ionic conductivity is both a function of temperature and water content of the membrane. The higher the ionic conductivity the lower the Ohmic resistance of the membrane will be. The goal is to hydrate the membrane to maximize its ionic conductivity, and this is the reason the hydrogen needs to be humidified. If the membrane is not hydrated enough, its resistance will be high and lead to loss of voltage and additional heat generation.

The only source of heat generation in the membrane is Joule heating. As the membrane dries, the membrane resistance increases along with the internal heat generation. The local heat generation will lead to hot spots. The local heating also leads to further water evaporation and accelerated membrane drying, which will increase the rate of destruction of the membrane [6]. The Joule heating term is inversely proportional to the conductivity as shown here in equation 11:

$$S_T = \frac{j^2}{\sigma} \quad (11)$$

Where S_T is the source term of heat generated, j is current density and σ is the conductivity of the membrane. To minimize the heat generation the ion conductivity of the membrane needs to be maximized. Electric Osmotic Drag (EOD) only moves water in the direction of anode to cathode because of this mechanism, the hydrogen (H_2) must be humidified to prevent the membrane from drying out. Since EOD is mainly a function of current density, the amount of water required increases along with current density. If there is not enough water at the anode inlet, the membrane will begin to dry out because there is insufficient water to move the hydrogen ions. Some of the water generated by the electrochemical reaction can diffuse toward the anode but this mode is not enough to keep the fuel cell hydrated. Presently the only method to humidify hydrogen is through back diffusion.

1.4 The PEM Fuel Cell Operating Window

The hydrogen needs to be humidified to support electro-osmotic drag, and this is done through back diffusion. Water is generated on the cathode, and the water must be kept in vapor form. The fuel cell hydration state must be maintained such that the cathode catalyst layer does not flood and where the hydration state must be high enough to minimize the resistance of the membrane and to maximize EOD and BD. If the water removal rate is less than the rate of water generation then flooding will occur. In instances where the water removal is greater than the water generation, then the membrane will begin to dry out. The goal is to maintain the moisture content by getting water generation to equal the rate of water removal. Although the PEM fuel cell has many advantages, one of the disadvantages is that the PEM fuel cell requires active water management. There is also a thermal gradient present in the fuel cell and this thermal gradient

1.5 Current Countermeasures for PEM Fuel Cell Flooding

Several countermeasures have been implemented to improve heat and water management of the PEMFC, these design considerations range from membrane thickness all the way to an electro-osmotic drag pump. There are advantages and disadvantages to all of them. The different methods are thickness of the membrane and equivalent weight (EW), a cathode humidifier on the Balance of Plant (BOP), the addition of the Microporous Layer MPL or an electro-osmotic pump.

1.6 Membrane Parameters (Thickness and Equivalent Weight (EW))

The membrane of the PEM fuel cell has two design parameters: they are equivalent weight (EW) and thickness. The membrane is composed of hydrophobic and hydrophilic regions. The hydrophobic regions are designed to move water away from the catalysts layers while the hydrophilic regions are that permit water flow between anode and cathode. The membrane structure is shown in Figure 1.6.1.

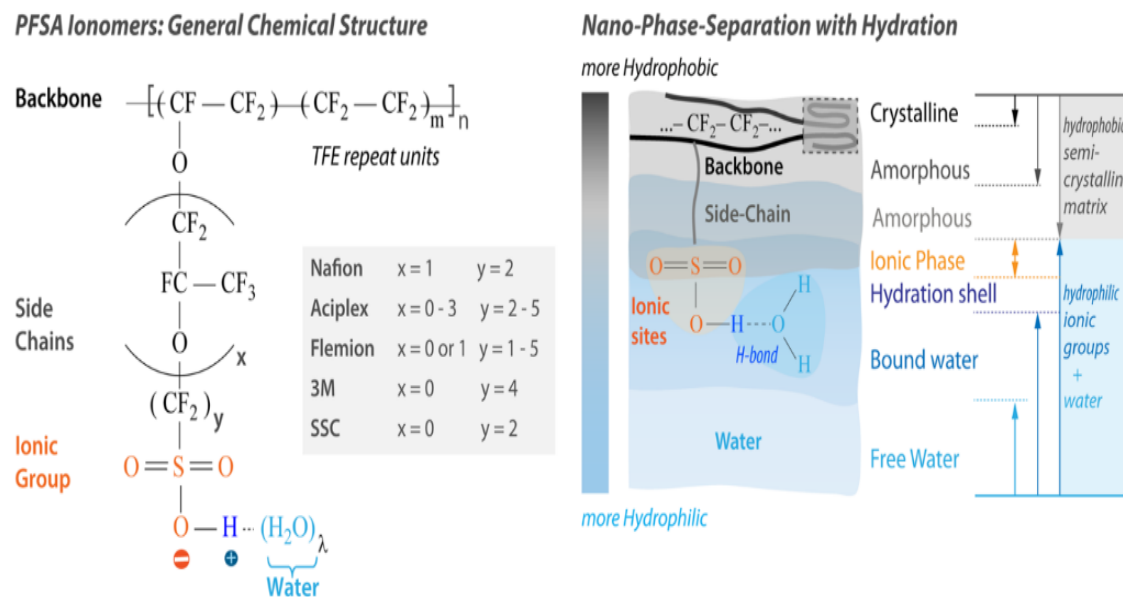


Figure 1.6.1 Fuel Cell Membrane Structure [5]

The membrane structure is shown in Figure 1.6.2. The membrane properties change as it is wetted or dried.

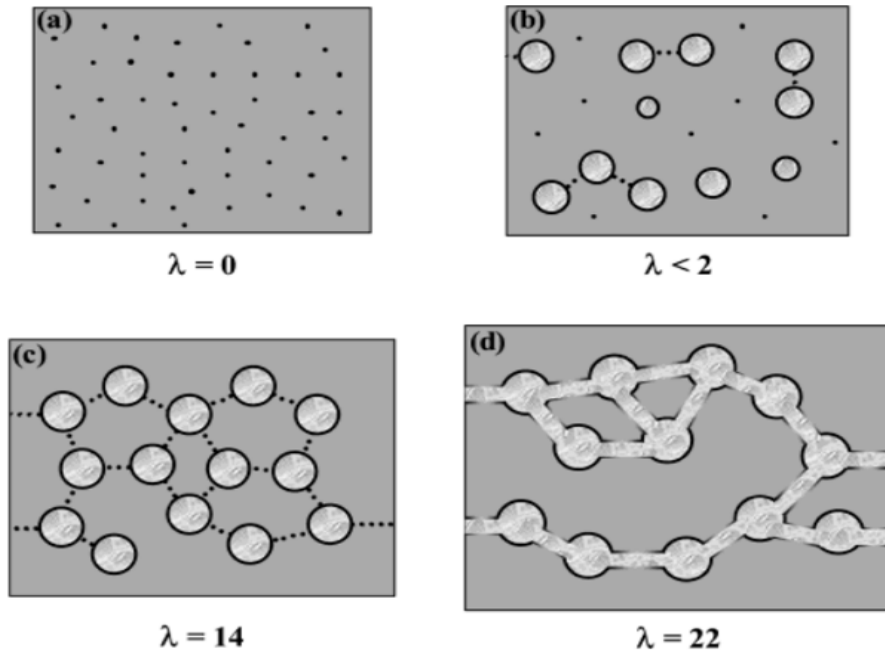


Figure 1.6.2 Fuel Cell Membrane Structure with Hydration [6]

The sulfonic acid groups of the membrane attract water and begin forming clusters as shown in Figure 1.6.2. As a result of the increased hydration, the membrane becomes less hydrophobic and more hydrophilic as shown by the contact angle change in the membrane as it is wetted as shown in Table 1.6.-1.

Table 1.6-1 Contact Angle Change of PFSA based on Hydration State [7]

Water Content λ	P _{water} /P _{water}	Contact Angle (Advancing/Receding)
0	0	116/30
2	.14	115/0
4	.58	114/0
9	.82	107/0
14	1	98/14

Contact angles above 90° are considered hydrophobic, but as the membrane hydrates the angle decreases from 116° to 98° indicating its properties change with its hydration state. The membrane becomes more hydrophilic as it hydrates. This indicates the membrane properties are dependent on the hydration state of the membrane. The hydration state is the measured amount of occupied sulphonic acids groups versus unoccupied sulphonic acid groups as shown in Equation 12.

$$\lambda = N_{\text{water}} / N_{\text{SO}_3^-} \quad (12)$$

The hydration state needs to be linked to relative humidity. An empirical relationship exists for Nafion/ PFSA membranes establishing a relationship between hydration state and relative humidity. The relative humidity (RH) and hydration state relationship is established by substituting Equation 12 into Equation 13. If Equation 12 and 13 are combined, then the hydration state of the membrane is a function of relative humidity; thus,

$$a = \frac{p_w}{p_{\text{sat}}(T)} = RH \quad (13)$$

$$\lambda = 0.043 + 17.18a - 39.85a^2 + 36a^3 \quad 0 < a < 1 \quad (14)$$

The saturation pressure of air is only a function of temperature. Since the hydration state is a function of relative humidity it is indirectly a function of temperature. The incoming gas temperatures can be used to impact the water management of the fuel cell, but the heat and water management are coupled together. The hydrophobic regions are composed of fluorocarbon polymer which makes it chemical resistant. The hydrophilic region is composed of a sulfonic acid group (SO_3) to promote a path for hydrogen ions through the membrane. The equivalent weight is a ratio of fluorocarbon polymer to sulfonic acids groups. The higher the equivalent weight the more hydrophobic the membrane is; therefore, the membrane will have a low protonic conductivity. To increase protonic conductivity, a lower equivalent weight membrane is needed. Lower equivalent membranes are more conductive but hydrophilic because they have more sulphonic acid groups. The thickness of the membrane and equivalent weights are two parameters that can be used as design parameters in the PEM fuel cell. Thicker membranes tend to reduce back diffusion as well as increasing the membrane resistance. The membrane cannot be made too conductive because electrons will pass through the membrane instead of going to the electrical load. Thinner membranes will promote more back diffusion to the anode.

1.7 Adding Cathode Side Humidifier to the Balance of Plant (BOP)

To humidify the hydrogen, water vapor is introduced into the cathode to promote back diffusion, and the outlet hydrogen is humidified where it is mixed with dry hydrogen, and this humidification will support electro-osmotic drag. The balance of plant (BOP) are components that provide reactants to the fuel cell stack. To control the humidity of the

inlet gases a humidifier can be used to humidify cathode air. A humidifier is used to transfer water vapor from wet gas to a dry gas. The outlet air is run through a humidified to humidify the inlet air coming into the fuel cell. Most fuel cell systems will place a humidifier at the cathode inlet to humidify the membrane. This is due to the inability to accurately model total water flow across the membrane. The humidified gas can either be from the cathode exhaust or an auxiliary source of water to support humidification. The humidifier is an additional component in the balance of plant (BOP) which will add extra cost and weight. Figure 1.7.1 shows how the humidifier takes exhaust gas from the cathode and uses this gas to humidify the incoming cathode air.

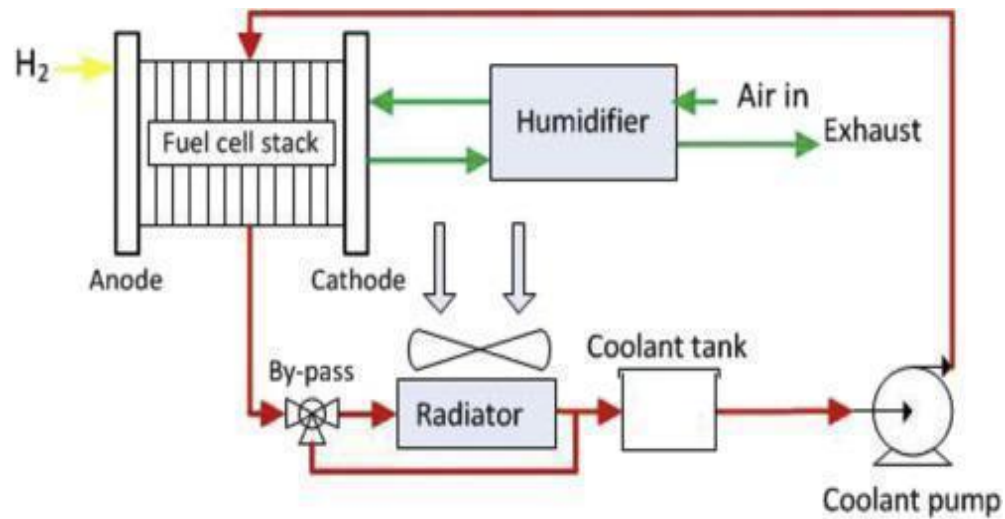


Figure 1.7.1 Humidifier Addition to Balance of Plant (BOP) [8]

The addition of the humidifier to the balance of plant (BOP) does not impact the water removal in the catalysts layer. The humidifier provides humidification for the cathode so the water can back diffuse toward the anode to promote hydrogen humidification. The humidifier impacts the water delivered to the cathode inlet. The water vapor must make

its way from the catalysts layer through the gas diffusion layer and to the bi-polar plate and out of the fuel cell stack. The humidifier mainly keeps the cell hydrated with the water generated in the PEM fuel cell. The humidifier takes up space and adds additional cost to the system. Fuel cell system OEM often a humidifier but wish to eliminate the component to promote self-humidification. The humidifier also is not needed all the time; there are instances of when it is needed so the balance of plant needs to control flow to the humidifier. The temperature of the inlet gases also be controlled also. The total water flow needs to be properly modelled to determine the humidification requirements and to properly size the humidifier.

1.8 The Addition of the Micro-Porous Layer (MPL)

A microporous layer (MPL) is a hydrophobic material which is added to the fuel cell which will aid in the removal of liquid water. Typically, the MPL is added to the cathode side of the fuel cell to help remove the liquid water. Figure 1.8.1 shows the MPL in the PEM fuel cell. Some fuel cell manufacturers that add MPL to both the anode and cathode.

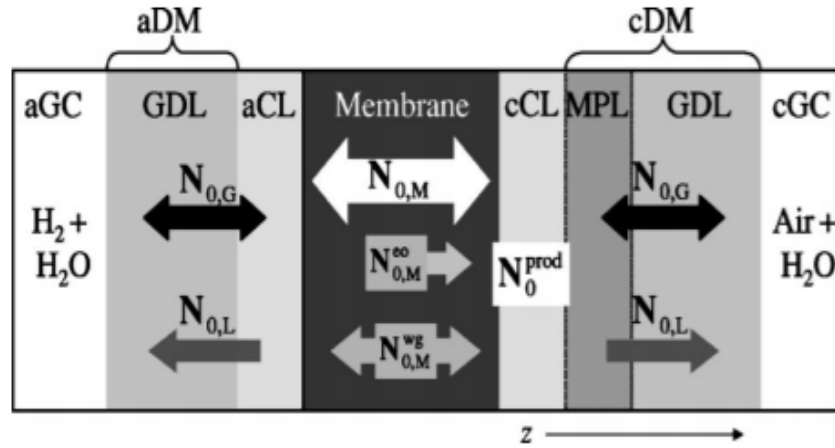


Figure 1.8.1 Schematic of PEM Fuel Cell with Microporous Layer [9]

The MPL helps eliminate liquid water from the fuel cell, which will reduce cathode flooding. Weber [69] has performed modeling and testing with a standard fuel cell, a cell with an anode and cathode MPL and a cell with a cathode MPL only. The cathode MPL has the best impact on fuel cell performance. The MPL adds Ohmic resistance to the PEM fuel cell, but it also reduces the resistance of the membrane. Figure 1.8.2 shows how the additional MPL impacts voltage and water movement in the PEM fuel cell.

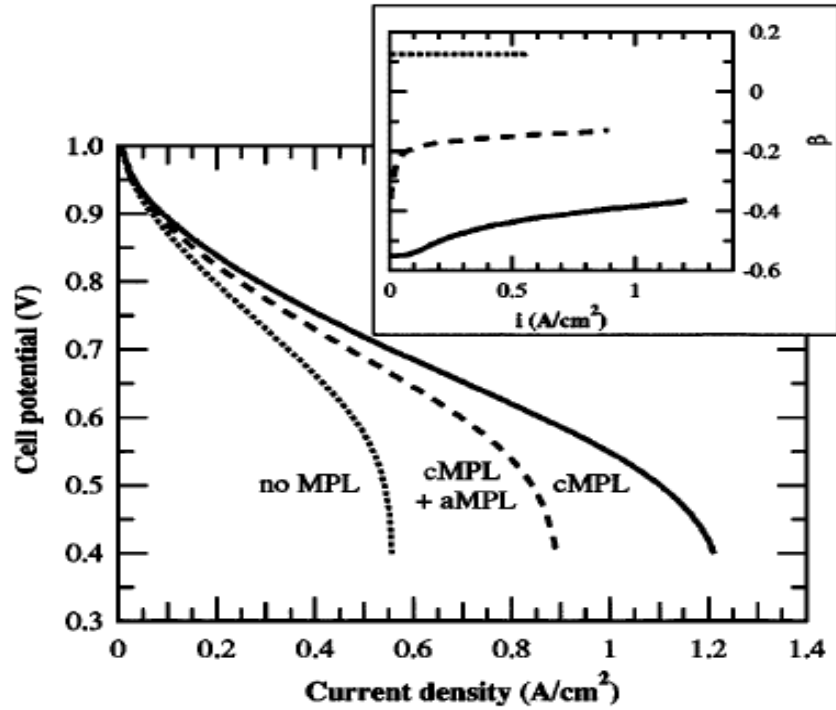


Figure 1.8.2 Polarization Curve and Water Transfer with MPL [9]

In the first case where there is no MPL, the water flow is in the direction of anode to cathode, and when the cathode and the fuel cell was only able to operate at a maximum current density of 0.6 A/cm^2 . When the MPL was added to the cathode, the water flow across the membrane reversed and the water flow was in the direction of cathode to anode and the maximum current density achieved was 1.2 A/cm^2 . In the case where the anode and cathode MPL was added the flow was also reversed and the flow was in the direction of cathode to anode and the maximum current density is approximately 0.9 A/cm^2 . Both the anode and cathode were fully humidified. The explanation for the water flow toward the anode, was that the MPL acts as a valve pressurizing the cathode and pushing the water away from the cathode. The MPL in both cases did improve the flooding by pushing the water toward the anode, this transport mechanism needs to be

better modelled and understood. The MPL needs to be examined when the cathode is dry and partially humidified. The water transport mechanism of the MPL is not fully understood.

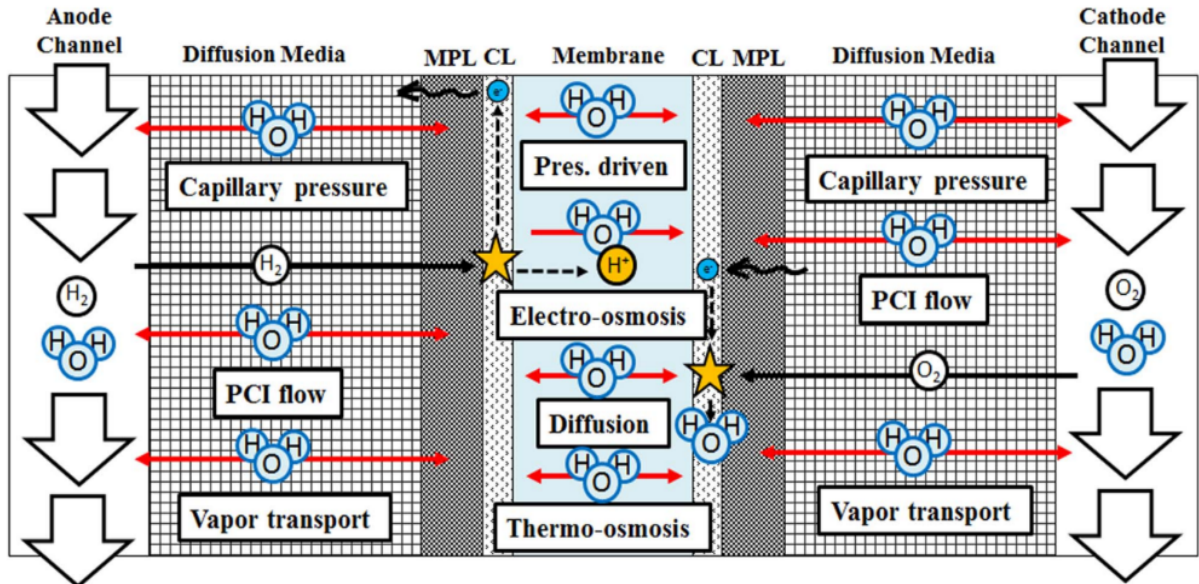


Figure 1.8.3 Proposed Water Flow Through PEM Fuel Cells [10]

Gandomi et al [10] theorized that Phase Change Induced (PCI) flow will occur to move water as shown in Figure 1.8.3. The main difference in Gandomi et al [10] work was that the thermal gradient will induce water flow, presently the Nernst-Planck equation does not consider these effects. The thermal effects introduce thermal osmosis, but its magnitude and direction are not known, and it also introduces Phase Changing Flow (PCI) which is water that evaporates to pass through the membrane and then condenses. In the PEM fuel cell, there is a thermal gradient, and it must be understood to predict these new modes of water transport. The thermal effects need to be better understood.

Zhou et al [11] had noted that the MPL needs to be hydrophobic and when the MPL is dry it does not impact the performance and water management, but when the MPL is wet it impacts the water management and performance. Zhou et al [11] also noted that there is two-phase water flow. The MPL is dependent on how hydrophobic the material is. The MPL only performs well when the fuel cell is wet, and its flow mechanism is not understood. Sarker et al [12] had also noted that the impact of polytetrafluoroethylene (PTFE) and MPL on fuel cells operating conditions is not fully understood and requires additional information. Sarker et al [12] noted that the addition of the MPL has an impact on the fuel cell operating in wet conditions. In some prior research, as current density increased, the net water flow changed direction. In other cases (pending on MPL configuration) the direction stayed 1-way and was not impacted by the current density. The impact of the MPL needs to be understood and addressed. The impact of the MPL on the cathode vs the anode needs to be better understood. The MPL impacts the total water flow but its transport mechanism is not fully understood, it must be understood to understand how the MPL functions on the anode and the cathode and does it need to be more hydrophobic or hydrophilic.

1.9 Electro-Osmotic Pump

The Electric Osmotic Pump (EOP) is a pump which requires electric power to induce an electric field that will move water generated from cathode to the anode. Figure 1.9.1

shows how the EOP is integrated into the PEM fuel cell:

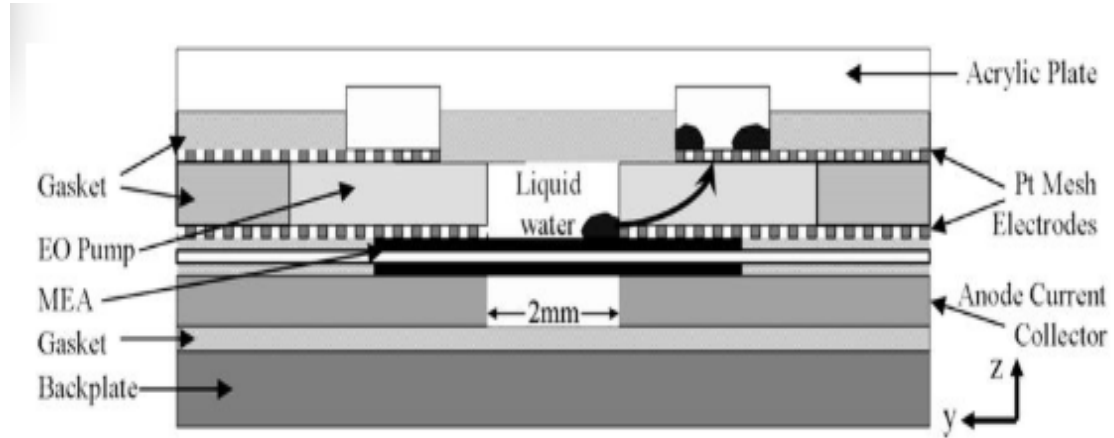


Figure 1.9.1 Schematic of EO Pump in the PEM Fuel Cell [13]

The testing results from the EOP show the pump increases the fuel cell output voltage, which is a sign that the fuel cell was not flooding, unfortunately the EOP requires power to remove water. Figure 1.9.2 shows how the EO pump impacts the fuel cell voltage.

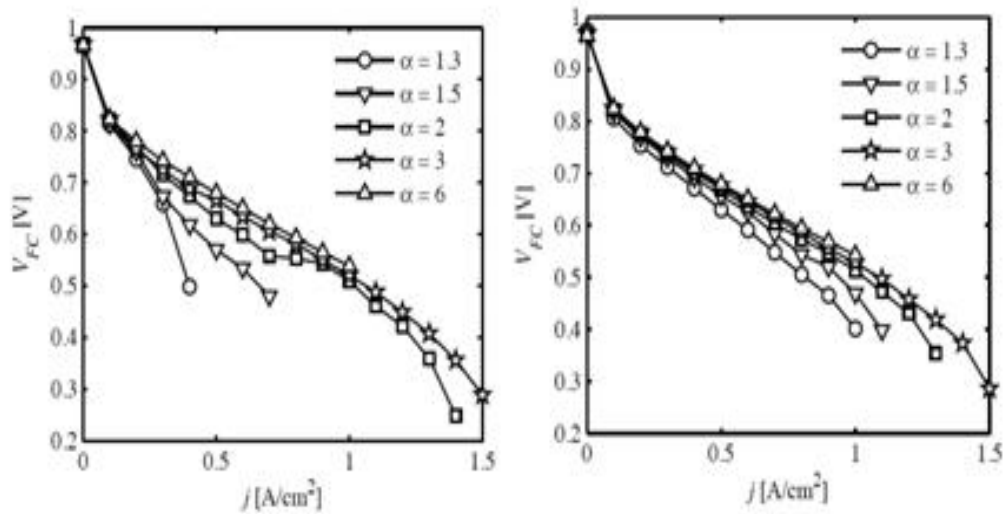


Figure 1.9.2 Voltage Impact with EO Pump [13]

1.10 Cathode Flooding Countermeasure Summary

In each of the countermeasures, the goal was to keep the net water flow direction biased toward the anode. The fuel cell performance goal is to keep the water away from the cathode catalyst layer (CCL). The net water flow through the membrane will change with current density. It would therefore be hard to optimize a passive element for all the possible operating conditions.

The humidifier helps keep the membrane hydrated by adding moisture to the incoming air thus the addition of the humidifier does not impact the water removal from the fuel cell. This effect on the front end does not therefore affect conditions on the back end. The addition of the microporous layer (MPL) changes the net water flow through the membrane. The MPL changes the net direction from cathode to anode to anode to cathode. The solution requires an additional component to the fuel cell. The MPL is a passive element however, and thus its operation does not change with various fuel cell operating conditions. The EO pump solution requires parasitic power to push the water from the cathode to the anode, which is not ideal because additional power and packaging are required.

One solution that has not been implemented is water transport control via thermal osmosis. Thermal osmosis is fluid transport through a porous media driven by a temperature potential. To further understand fuel cell behavior, theoretical models must be developed to understand fuel cell behavior. Counter measures need better

understanding to better integrate them. It should be noted that thermal osmosis is not being used as counter measure of flooding of the fuel cell. Also, since the Nerst-Planck equation does not consider the thermal effects, presently the thermal effects may be lumped either into electro-osmotic drag and/or back diffusion.

1.11 Modeling PEM Fuel Cells and Water Flow Across the Membrane

In each of the countermeasures, the goal was to keep the net water flow direction biased toward the anode. The fuel cell performance goal is to keep the water away from the cathode catalyst layer (CCL). The net water flow through the membrane will change with current density. It would therefore be hard to optimize a passive element for all the possible operating conditions.

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1.12 Modeling PEM Fuel Cells and Water Flow Across the Membrane (Isothermal)

A sample isothermal model was by Abdin et al [14] where they used MATLAB and Simulink to model the performance of the PEM fuel cells. Their model was assumed to be isothermal, and Abdin et al [14] stated that this neglects thermal osmosis. Their water flow model only consisted of electro-osmotic drag and back diffusion and hydraulic pressure. For the case of the electro-osmotic drag Abdin et al [14] had chosen the Springer et al [15] and there are several different electro-osmotic drag models, and it is not known if this model is best one for the fuel cell. In addition, an isothermal model is not recommended for fuel cell modeling, but it may be applicable for a first attempt as an approximation. The models are very simple but do not address the heat and water management.

1.13 Modeling PEM Fuel Cells and Water Flow Across the Membrane Non-Isothermal Single Phase

PEM fuel cells can operate at different temperatures and current densities. Some of these operating conditions will only have gaseous water flowing in the fuel cell while other operating conditions could have two phase flow. Single phase models will be effective when the fuel cell is running with an outlet relative humidity on the cathode less than 100%. In cases where the cathode outlet relative humidity is greater than 100% multi-phase models are required, in these cases liquid water and water vapor will be present. When liquid water is present, water evaporation and condensing needs to be considered.

Siemer et al [16] developed a single-phase non-isothermal model using Non-Equilibrium Thermodynamics to model the fuel cells. Siemer et al [16] water flow model consisted of electro-osmotic drag, back diffusion and thermal osmosis, unfortunately they neglected the effects of thermal osmosis as well as the Soret, Dufour and thermal electric effects. There was no reason for neglecting thermal osmosis. Siemer et al [16] had also selected the Springer et al [15] electro-osmotic drag model. Siemer et al [16] did attempt the voltage with experimental data but neglected to include the water balance.

Bhaiya [17] used classic thermodynamics to model the PEM fuel cells to develop a single phase and two-phase non-isothermal model. The model assumed that no liquid water present. and the model considered electro-osmotic drag, back diffusion and thermal

osmosis. For electro-osmotic drag the Springer et al [15] empirical coefficient model was used.

1.14 Modeling PEM Fuel Cells and Water Flow Across the Membrane Non-Isothermal Two Phase

Bhaiya [17] had used classic thermodynamics to model the PEM fuel cells too. For the water through the membrane Bhaiya [17] had considered electro-osmotic drag and back diffusion and thermal osmosis. For the electro-osmotic drag, Bhaiya [17] had used Springer et al [15] model for the electro-osmotic drag coefficient and included thermal osmosis in their water flow model and for back diffusion Bhaiya [17] used Motupally et al [18] empirical model for back diffusion. For the thermal osmosis portion of water flow across the membrane, Kim and Mench's [19] thermal osmosis empirical model was used for thermal osmosis, and the thermal osmosis model is assumed to flow in the direction cold to hot.

Bhaiya [17] has assumed that the Soret and Dufour Effects in the fuel cell based on Newman [20] and Bird [21] statement Newman "This process is called thermal diffusion, whereby a temperature gradient maintained across a solution can lead to a variation in composition. **Thermal diffusion is not, however, usually important in industrial systems.**" This reference did not have any data or analysis to back up the claim. R Byron Bird [21] said: "**The Dufour term is normally small and often neglected,**" without any data to validate this claim. The phase of the fluid may impact Soret and Dufour effects.

Falcao et al [22] had developed a one-dimensional single-phase model with heat transfer. The water flow through the membrane was modeled with electro-osmotic drag and back diffusion. The single-phase model will work if liquid water is not present, it is important to know when liquid water is formed because the model will not be valid when it is present.

1.15 Modeling PEM Fuel Cells and Water Flow Across the Membrane Non-Isothermal Two Phase

Bhaiya [17] had also developed a non-isothermal model to accommodate water in the liquid phase and water vapor. The two-phase model does account for liquid water in the fuel cell. Liquid water is transported through Darcy's law and there is a phase change term to account for evaporation and condensation. Bhaiya [17] also noted that the electro-osmotic drag coefficient was assumed to be 1. Bhaiya [17] had noted that two phase model predicts liquid water accumulation, mass transport limitation due to flooding and drying of the membrane at higher current densities compared to the single-phase model. The two-phase model does show a drop in performance at higher current densities. The single-phase model is easier to compute.

The two phase model is required when liquid water is present, the single phase will be sufficient also as there is no liquid water, the goal is known when to switch from the single to two-phase model, this is impacted by the balance of plant and the humidification of the fuel cell as well as the total water transport across the membrane this is the main

reason why the transport coefficient accuracy is required. The two-phase should handle liquid water and water vapor.

1.16 Nernst-Planck Equation

The water flow across the membrane must be properly modeled across the membrane, and this is essential to prevent the fuel cell from flooding or the membrane from drying out. The equation that is typically used is the Nernst-Planck equation and it consists of two terms electro-osmotic drag and back diffusion.

In one instance of fuel cell modeling Abdin et al [14] had used an equation which consisted of four terms, the first term was electro-osmotic drag, the second term is back diffusion, and the third term is thermal osmosis, and the last one was due to hydraulic pressure. Since their system was isothermal thermal osmosis was neglected, Siemer et al [16] started their fuel cell modeling with non-equilibrium thermodynamics (NET), there were three terms, the first one was thermal osmosis, the second term was back diffusion and third consisted of electro-osmotic drag. The three terms were common in the models, but it is not known if both forms are equivalent. Bhaiya [17] had used an equation for the water flow consisting of electro-osmotic drag and back diffusion and thermal osmosis. In some of the cases thermal osmosis was added to the Nernst-Planck equation it is not known which application is the best for fuel cell modelling. The Nernst-Planck equation is derived from the Stefan-Maxwell diffusion equation so there are assumptions and limitation behind the Nernst-Planck equation. It is also possible that the Nernst-Planck

equation is valid for liquids and not valid for water vapor, the previous fuel cell was an Alkaline fuel cell that had a liquid electrolyte. The PEM fuel cell has the membrane as its electrolyte.

1.17 Electro-osmotic Drag

One of the terms in the Nernst -Planck equation is electro-osmotic drag as shown in Figure 1.8.3; electro-osmotic drag is the process hydrogen ions are moved from the anode to cathode. The hydrogen ions bond with water to move hydrogen from the anode to cathode. Also shown in Figure 1.8.3 is back diffusion. The back diffusion is driven by the concentration gradient so the flow can go in the direction of anode to cathode or cathode to anode.

There are several methods in determination of the electro-osmotic drag coefficients and there is scatter with all the methods also. There is not agreed upon technique. The current EOD techniques are applied potential, fuel cell operation, hydrogen pump, streaming potential, chemical potential and Nuclear Magnetic Resonance (NMR). In addition, the phase of water will impact the electro-osmotic drag coefficient. Some experiments focused on liquid and others focused on vapor. The table of experiments is shown in Table 1.17-1

Table 1.17-1 Electro-Osmotic Drag Coefficients, Methods and Phase of Fluid [23]

Table 1

Literature references for proton electro-osmotic drag coefficients and techniques

Technique (driving force)	Measured quality	Aqueous solution	Membrane	Proton drag coefficient	Non-proton drag coefficient	Cell electrodes	Source
Electro-osmotic drug cell (applied potential)	Volume change	Halogenic salts	Anion/cation exchange	2.6–2.77	Many	Ag/AgCl	Breslau and Miller, 1971
		DI water	Nafion 117, Membrane C, Dow experimental	0.9, 2.0–2.9, 2.6–4.0, 1.4–2.0		Pd/Pd-H	Zawodzinski et al., 1993 (two papers)
		KCl	Cation exchange			Ag/AgCl	Mayer and Woermann, 1997
Radiotracer method (applied potential)	Isotope concentration	H ₂ SO ₄ , H ₃ PO ₄ , HCl	Nafion 117, Cation, Polybenzimidazole	3–8, 1.5–2.3, 0–1.05		Pd/Pd-H	Pivovar et al., 2005
		H ₂ SO ₄	Nafion 117	3.2–8		Pt/H ₂ O	Verbrugge and Hill, 1998
Fuel cell (electro-chemical)	Water crossover	MeOH	Nafion 117, Membrane C, Dow experimental	2.0–5.1, 3.0–5.0, 2.0–3.1		Pt–Ru anode, Pt cathode	Ren et al., 1997; 2001
		MeOH	Nafion, BPSH, sPI, 6FCN	3.3–3.9, 1.4–3.0, 0.5–0.8, 1.3		Pt–Ru anode, Pt cathode	Pivovar et al., 2001; Hickner, 2003; Kim et al., 2004
Hydrogen pump (applied potential)	Pressure change	Vapour	Nafion 117/H ₃ PO ₄ , PBI/H ₃ PO ₄	0.2–0.6, <0.01–0.09		Pt anode, Pt cathode	Weng et al., 1996
Electrolysis (applied potential)	Unclear, likely water crossover	HCl	Nafion	0.2–9.5		High surface area/ catalytic	Balko et al., 1981
Streaming potential (applied pressure)	Water crossover Electro-chemical potential	HCl/water vapor	Nafion 115	3.5–3.8	Many	Pt anode, Pt cathode	Motupally et al., 2002
		Halogenic salts	Cation/anion exchange			Ag/AgCl	Trivijitkasm and Osvoid, 1980
Activity gradient (chemical potential)	Electro-chemical potential	HCl/KCl	Cation exchange	2.3	11.2	Ag/AgCl	Okada et al., 1992
		Vapour	Nafion 117	1.4		Pt–H ₂	Fuller and Newman, 1992
Electrophoretic NMR (applied potential) SECM (applied potential)	NMR shift Conc. of electro-active species		Nafion 117, Membrane C, Dow experimental	1.0, 1.1, 0.95		Pt–H ₂	Zawodzinski et al., 1995
		DI water	Nafion, PEEKK	1.5–2.8, 0.5–50		Pt–H ₂ O	Ise et al., 1999
		NaCl	Nafion		3.7–6.4 (Na ⁺)	Ag/AgCl	Bath et al., 1998

One of ways to determine electro-osmotic drag is through the water cross over, this technique, this approach does reflect the nature of the PEM fuel cell. For the water cross over the results depend on the data analysis of the total water flow. The electro-osmotic drag coefficients range from 0.2 up to 50. Some of the cases may not fully reflect the fuel cell usage, others may, and it is not known if the work with liquid will carry over to vapor and if the work with vapor will carry over to liquid. There is not an agreed upon method for measuring electro-osmotic drag.

The electro-osmotic drag coefficient does not change with temperature for vapor but does change with temperature when liquid is present. The dependency of electro-osmotic drag

on temperature needs to be better understood. Experimentation is needed where the thermal gradient is known to determine why electro-osmotic drag is dependent on temperature for only liquids. The variation in the electro-osmotic drag coefficient could be a result of how the total water flow was analyzed; there are assumptions made in data analysis by forcing the data trendline through the origin or even the type of trendline used

1.18 Back Diffusion

The next mode of water transport from the Nernst-Planck equation is back diffusion, this is the model, the typical model of diffusion used is back diffusion or Fickian diffusion, this is a form of diffusion that simplifies from the Stefan-Maxwell equation. There are also classifications of diffusion, the first is steady state diffusion which is driven by the concentration gradient and the second type is a transport coefficient driven by the chemical potential difference [24]. It is not known if these two methods are equivalent or if one method is better than the other.

1.19 Current Testing (Measuring the Total Water Transfer)

The discharge voltage of the fuel cell depends on the total water flow. The total water flow is measured through a mass balance on the fuel cell. The total water is often expressed in terms of the total water transfer coefficient. As a result of the modes of water transport and the differences in electro-osmotic drag and back diffusion, the test results are reported as total water transfer coefficient which will reflect on the direction of

water flow, but information obtained by individual drivers cannot be obtained because the total water flow is the summation of all the present fluid drivers. For instance, one researcher Yan et al [25] wanted to understand how operating condition and flowrates. A sample of the total water transfer coefficient is shown in Figure 1.19.1:

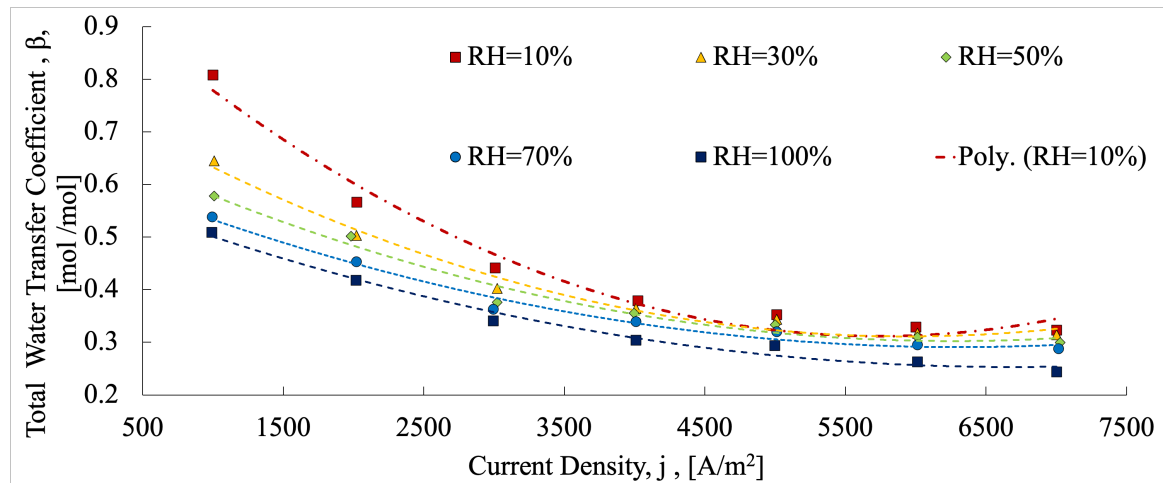


Figure 1.19.1 Sample Total Water Transfer Coefficient [25]

Note the water transfer coefficient does need to be converted to the water transfer across the membrane. This only tells the direction of the total water flow. It can only tell you if the flow is anode to cathode or cathode to anode. It is not known if the total water flow will flow a linear trend or a polynomial trend. If the Nernst Planck equation is used it only assumes the only fluid drivers are electro-osmotic drag and back diffusion. The thermal effects are not considered, and the thermal effects will either be lumped into electro-osmotic drag or back diffusion pending on the direction of the thermal effects.

By keeping everything in terms of the total water transfer coefficient it does not allow for the understanding of the total water flow. The electro-osmotic drag and back diffusion

coefficient are not known, and the theoretical fuel cell model cannot be validated. A way is needed to determine the actual electro-osmotic drag and back diffusion coefficient from the experimental data. The current process is good for a comparison between fuel cells but does not provide a better understanding of the fuel cell water transport. It also makes it difficult to validate fuel cell models, it is not known if the error is coming from the back diffusion model or electro-osmotic drag model or if the fluid flow is coming from thermal osmosis. The total water flow needs to be further analyzed to determine each component. Also, the thermal effects need to be considered if the Nernst-Planck equation is used.

1.20 Temperature Profile Across the Fuel Cell

The electrical work is derived from the Gibbs free energy with an assumption of constant pressure and constant temperature conditions, this may be valid for a battery, but a fuel cell is an open thermodynamic system which will have a pressure gradient and concentration gradient. In the PEM fuel cells heat is not generated uniformly, there is Ohmic heating in the resistance in each part of the fuel cells, there is also evaporation and condensation and there is the heat of the reduction reaction, as a result there will be a temperature profile across the fuel cell as shown in Figure 1.20.1:

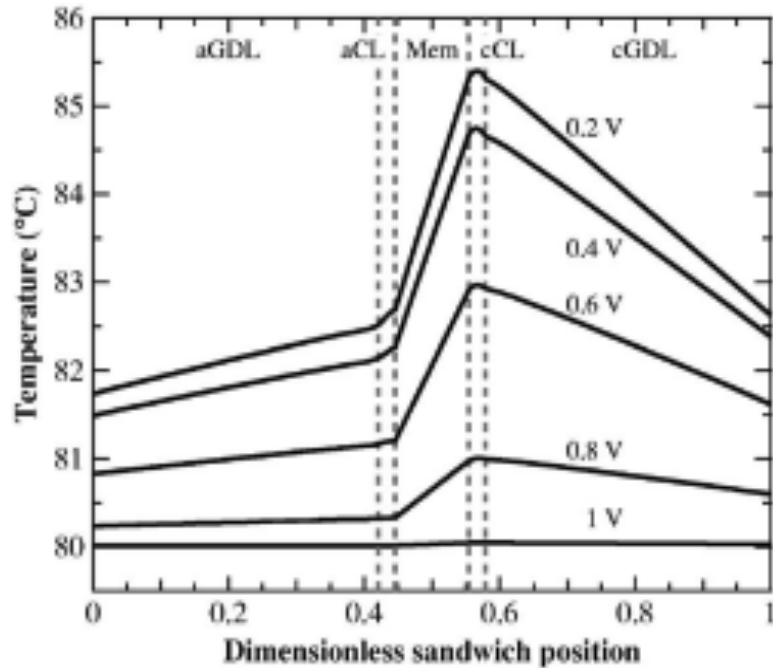


Figure 1.20.1 Temperature Profile in the Fuel Cells [26]

In the PEM fuel cells heat is not generated uniformly, there is Ohmic heating in the resistance in each part of the fuel cells, there is also evaporation and condensation and there is the heat of the reduction reaction, as a result there will be a temperature profile across the fuel cell. The thermal gradient is dependent on the discharge voltage which is also dependent on the hydration state of the membrane.

1.21 Thermal Osmosis

Siemer et al [16] has introduced Non-Equilibrium Thermodynamics (NET) which has three gradients that are capable driving fluid flow, the gradients are voltage gradient concentration and thermal gradient. The Nernst-Planck equation only considered electro-osmotic drag and back diffusion. The temperature driven flow needs to be understood

into fully integrate it into fuel cell models, but the temperature driven flow is not fully understood. There is no agreement on the magnitude and direction thermal osmosis, it is also not known if thermal osmosis is neglectable of a substantial fluid driver, it has not been compared to electro-osmotic drag and back diffusion. In general, thermal osmosis moves liquid water in the direction of hot to cold when the membrane is hydrophobic and moves liquid water in the direction of cold to hot for hydrophilic membranes. It is not known how this transfers to water vapor. Some membranes are not fully hydrophobic or hydrophilic; these membranes are hybrid and the behavior on hybrid membrane needs to be further understood because they contain both regions. It is also unclear if thermal osmosis rules for liquid are the same for gases.

Fu et al [27] had conducted an experiment with a fixed temperature difference and variable concentration difference across the membrane. Fu et al [27] had used the Motupally et al [18] back diffusion model and in their model and did good correlation up to a 65% RH but at higher humidity did not have good correlation. To add further complications there are several back diffusion models. The thermal osmosis results are based on the Motupally et al [18] model and would change if a different back diffusion model was selected. The back diffusion component was not determined based on the experimental data. Fu et al [27] stated that thermal osmosis is neglectable compared to back diffusion but did not separate the thermal osmosis portion of the flow from the total flow. The original data was not expressed in terms of the concentration gradient. It is not known if this assumption is applicable. Without thermal osmosis transport coefficients

being known it cannot be easily separated from other fluid drivers. The impact of the phase of water as well as the membrane material impact on thermal osmosis needs to be determined.

1.22 Schroeder Paradox

One unexplained phenomenon in PEM fuel cells is the Schroeder Paradox. The membrane will transport liquid water at a faster rate than water vapor. There is no explanation for this phenomenon.

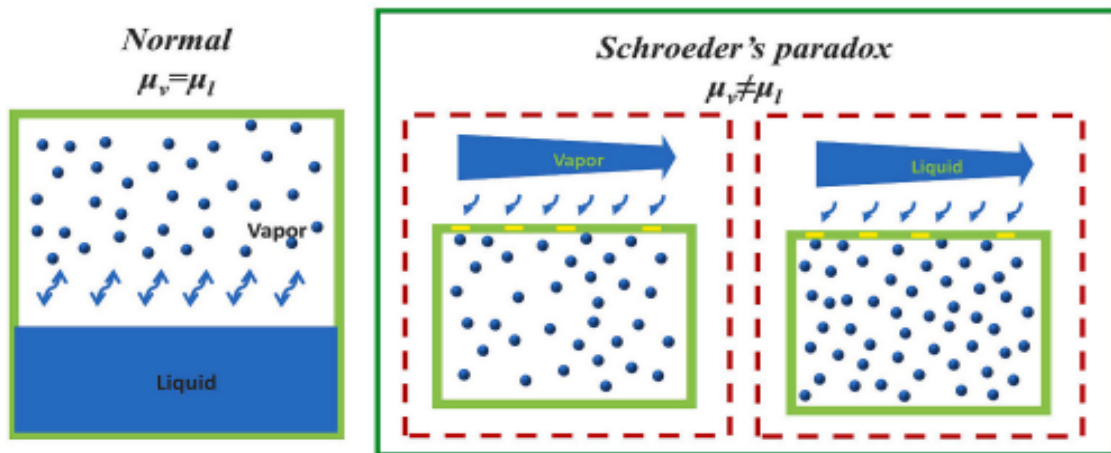


Figure 1.22.1 Schroeder Paradox – Chemical Potential Difference [28]

An anomaly that is seen in porous media is the Schroeder Paradox as shown in Figure 1.22.1. The Schroeder paradox relates to a membrane absorbing more water when exposed to liquid compared to vapor. For the case of the membrane exposed to vapor should move more fluid but instead the membrane will move more when liquid is present. This concept is not explainable by classical thermodynamics. With classical thermodynamics, liquid and vapor will form a natural equilibrium with one another as

shown in the Normal portion of Figure 1.17. The equilibrium is known as vapor pressure which is mainly a function of temperature. When the vapor is in contact with the membrane, the membrane will absorb a portion of the vapor, but when the membrane is in contact with liquid water, the membrane will absorb more fluid compared to the vapor case as shown in Figure 1.22.1. The chemical potential of the liquid in contact with the membrane does not equal the chemical potential of the vapor in contact with the membrane thus violating the chemical potential equilibrium shown in Schroeder's Paradox in Figure 1.22.1

The chemical potential of the liquid does not equal the chemical potential of the vapor. If the chemical potentials were equal, then the membrane would uptake more with vapor compared to liquid. Schroeder discovered this phenomenon in 1903 and at that time it was considered a violation of the laws of thermodynamics. It is not fully understood how the Schroeder Paradox impacts electro-osmotic drag, back diffusion and thermal osmosis. By understanding the Schroeder Paradox, it can be used to improve the heat and water management of the fuel cell. This phenomenon is seen in PEM fuel cells. Based on the paradox the membrane will respond differently when exposed to liquid water compared to when the membrane is exposed to water vapor. It is not known why the membrane will transport more liquid water compared to water vapor.

1.23 Summary

The PEM fuel cell needs to overcome the heat and water management issues to move forward, this is done by better understanding the governing equation for total water flow along with understanding electro-osmotic drag, back diffusion and thermal osmosis. The Schroeder Paradox as well as the Microporous Layer needs to be better understood.

If electro-osmotic drag is overstated, then there will not be enough water to maintain the hydration of the membrane, and it will dry out. On the other hand, if the electro-osmotic drag is understated then more water will be present in the cathode, and this will introduce flooding. The same could be said for back diffusion, if the back diffusion coefficient from an existing back diffusion coefficient model is greater than the actual value then the back diffusion will be overstated, and if the back diffusion coefficient is less than the original result then back diffusion will be understated. This is the main reason why accuracy and precision are required. It is not fully known if the thermal effects are lumped into electro-osmotic drag and back diffusion because the Nernst-Planck equation only accounts for electro-osmotic drag and back diffusion. For thermal osmosis if it is understood it could be used as a mode of water transport to mitigate flooding and membrane dry out. The magnitude and direction of the flow need to be understood as well as when single phase and two-phase thermal osmosis are present.

CHAPTER TWO

LITERATURE REVIEW

2 Literature Review

Porous media is used in fuel cell technology such as Proton Exchange Membrane (PEM), Alkaline Fuel Cells (AFC), Direct Methanol Fuel Cells (DMFC), electrolyzers and humidifiers, it is required to accurately predict the cross-over flow because this will control the hydration state/wetting of the membrane as well as the fluid transport properties of the membrane. If the total flow is under-predicted or over predicted there could either be poor transport across such as the membrane being too dry or other fluid drivers will appear and hurt the system performance.

The total water flow across the membrane is not measured directly, it is indirectly calculated. The difference between the inlet and outlet mass flow rate. The mass flow calculated is the summation of all the fluid drivers present and is not an individual driver. The desired fluid driver will need to be extracted from the total water flow. The total water flow equation is shown in equation 15.

$$J_{Total} = \dot{m}_i - \dot{m}_o \quad (15)$$

Where J_{Total} is the mass flow across the membrane, $\dot{m}_i$ is the inlet mass flowrate and $\dot{m}_o$ is the outlet mass flowrate. The electro-osmotic drag portion of the total water needs to be extracted, and the contribution of the other fluid driver also needs to be addressed. One

common error made in data analysis is to assume no other fluid drivers are present or if they are present that they are neglectable without quantifying them. In the case of fuel cells, the total water flow across the membrane can be expressed in terms of current density. The total water flow can be divided by the current density and multiplied by Faraday's constant to obtain the total water transport coefficient β . The total water transport coefficient can be used to compare different fuel cells to one another. The total water flow is calculated with β and current as shown in equation 16. [29][30]

$$J_{Total} = \beta \frac{j}{F} \quad (16)$$

Note that the total water transfer coefficient does not tell anything about electro-osmotic drag or back diffusion coefficient, it only tells the direction of the total water flow. In the case of PEM fuel cells, the Nernst Planck equation is used to model the water flow across the membrane as shown in equation 17.

$$J_{Total} = n_a(\lambda) \frac{j}{F} - D(\lambda) \frac{\partial c}{\partial x} \quad (17)$$

The Nernst-Planck equation does not consider the effects of electro-osmotic drag and back diffusion, and it does not consider the thermal effects. As a result, the total water flow is the summation of the electro-osmotic drag and back diffusion as shown in equation 18. [29][30]

$$\beta \frac{j}{F} = n_a(\lambda) \frac{j}{F} - D(\lambda) \frac{\partial c}{\partial x} \quad (18)$$

The total water transfer coefficient does indicate the direction of the total water flow, if β is positive the flow is in the direction of anode to cathode and if β is negative the total water flow is in the direction of cathode to anode. The total water transfer coefficient does not give provide the electro-osmotic drag and Fickian diffusion coefficient and the total water flow needs to be reduced to individual fluid drivers. The MPL does impact the total water flow, so it is not known how the Nernst-Planck equation accounts for the MPL as Webber et al [9] has shown the MPL does change the direction of the total water flow when it is added. If one of the coefficients is known the other one can be determined. For instance, if the electro-osmotic drag coefficient is known then the back diffusion be calculated as shown in equation 19.

$$J_{BD} = J_{Total} - J_{EOD} \quad (19)$$

To separate out the total water flow the electro-osmotic drag coefficient needs to be known. If the electro-osmotic drag coefficient is known, then it can be isolated, but it is not the known it must be determined. In the case of modeling the fuel cell, the models will have to be validated, and a technique is needed to experimentally determine the electro-osmotic drag coefficient so models can be validated. The next step involves

examining the electro-osmotic drag and back diffusion coefficient models. When the mass flow is indirectly measured it is summation of all the simultaneous fluid drivers present, the total water flow must be broken down into its fundamental fluid drivers. The total water flow will contain the measured fluid driver but how much it contributes to the total water flow needs to be determined.

2.1 Total Water Flow Across the Membrane

The total water flow across the membrane of the fuel cell will impact the fuel cell performance, if the membrane is too dry, the Ohmic losses will be higher, and the fuel cell will lose efficiency due to increased voltage resistance. If too much water is on the cathode, then the mass transport losses will be increased, and this will cause a loss of voltage due to loss of oxygen pressure. This is the main reason why an accurate electro-osmotic drag and back diffusion coefficient are needed.

Yan et al [25] built a 25 cm² Proton Exchange Membrane (PEM) Fuel Cell with a Nafion 117 membrane and tested it under various operating conditions. Yan et al's [25] objective was to understand water transport in the PEM fuel cell under different operating conditions. In the first set of experiments, the anode was fully humidified, and the cathode relative humidity varied from 10%-100% Pure hydrogen was used on the anode side and pure oxygen was used on the cathode side. Yan et al [25] reported that the electro-osmotic drag coefficient ranges from 1.5-2.6 depending on the operating conditions. To eliminate the flow related to pressure gradient, the pressure across the

membrane was kept the same. Even though the pressure difference is the same across the membrane, if liquid water is present, the effects of the Schroeder Paradox will be present.

Additional runs were performed with current, and the diffusion was measured with respect to the concentration gradient. By combining the experiments with and without current the electro-osmotic drag coefficient was obtained. The total water transfer coefficient vs current density is shown in Figure 2.1.1 This run one of the once with the current density so electro-osmotic drag and back diffusion are present.

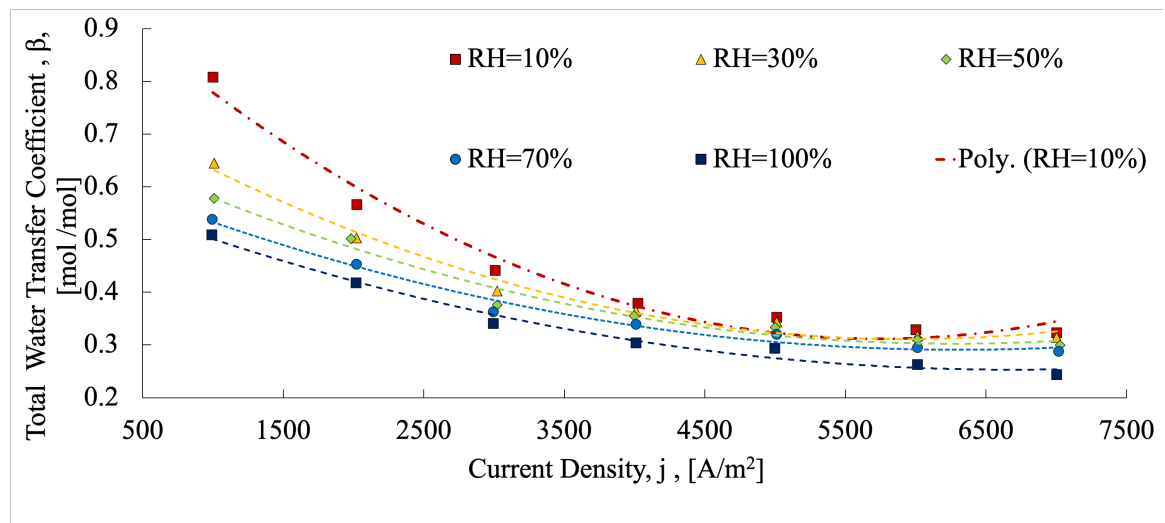


Figure 2.1.1 Water Flow Transfer Coefficient for Variable Relative Humidity [25]

For all cases the total water transfer coefficient is decreasing with current density, the total water flow across the membrane needs to be obtained by using equation 16. The total water flow coefficient does not tell how the total water will change with respect to current density. The output voltage of the fuel cell is also dependent on current density also. As previously shown, the temperature profile is dependent on discharge voltage.

The total water transfer coefficient does not provide any insight on the electro-osmotic drag and back diffusion coefficient, and the data must be further analyzed to extract electro-osmotic drag and back diffusion. The total water flow can be decomposed into its fundamental fluid drivers without assuming a fluid transport coefficient. An electro-osmotic drag coefficient cannot be assumed to determine the back diffusion portion of the total water flow, because of the scatter of the existing electro-osmotic drag models and the back diffusion will be dependent on the electro-osmotic drag coefficient model.

As the Nafion membrane hydrates, its structure changes, it becomes for hydrophilic. The total water flow is changing because the transport properties are changing with each operating point. The membrane properties will be impacted by the phase of water by in contact with the membrane. All the data points indicate that the water is moving in the direction of anode to cathode, and the only conclusion that can be made is electro-osmotic drag exceed back diffusion. The electro-osmotic drag and back diffusion coefficients are not known nor is the percentage of the flow that is electro-osmotic drag and back diffusion. The existing processing does not allow for model validation because it is not known if it is the electro-osmotic drag or back diffusion model is accurate.

A proposed method was developed to determine the composition of the total water flow.

In the experiment, the total water flow across the membrane was not separated into its electro-osmotic drag and into its Fickian diffusion components everything was kept in terms of the total water transfer coefficient. Yan et al [25] also ran another total water

flow experiment with fixed anode relative humidities and variable cathode relative humidities and the current density was fixed 5,000 A/m² at as shown in Figure 2.1.2:

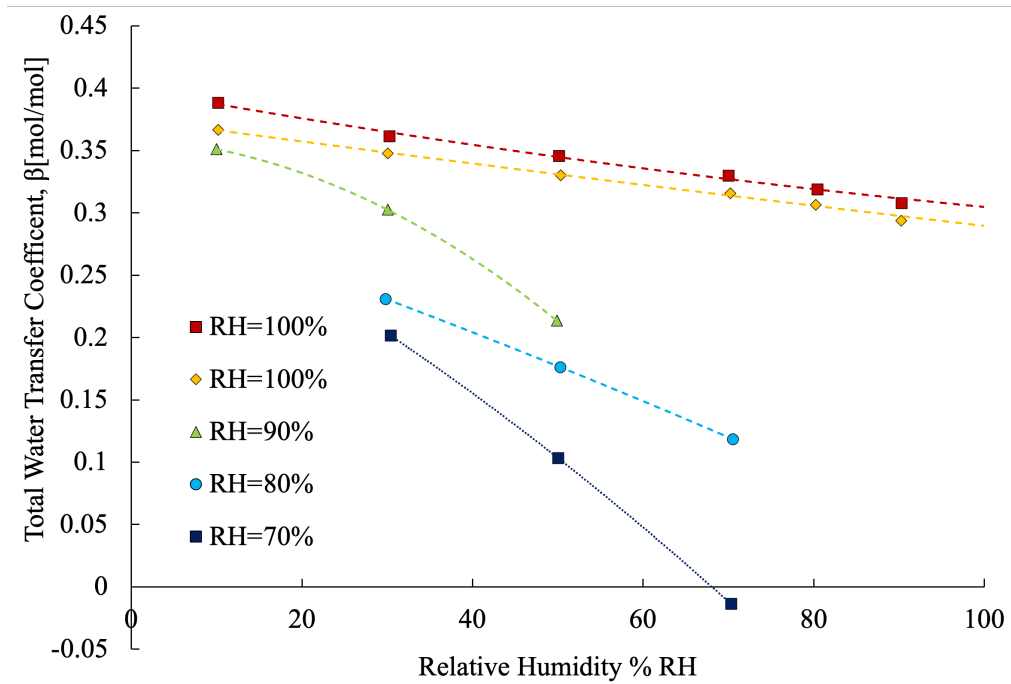


Figure 2.1.2 Water Flow Transfer Coefficient with Variable Concentration Gradient [25]

The data in the present form does not express the total water transfer coefficient in terms of the concentration gradient. The total water flow data needs to be plotted in terms of the concentration gradient. The data shows how the total water transfer coefficient changes as the inlet relative humidity changes. The total water transfer coefficient is mainly positive but the trendline are different when the inlet cathode is at 100% RH. The other cases have trendlines that are decreasing with an increasing relative humidity. The experimental data does shows that the cathode relative humidity does impact the total water flow across the membrane.

The total water flow data was not broken down into its electro-osmotic drag and back diffusion components. The only conclusion that can be made is that electro-osmotic drag does exceed back diffusion. By keeping the data in terms of the total water transfer coefficient it does not show how the total water flow changes with respect to the concentration gradient. It is not known if the total water flow follows a linear trendline like the Nernst-Planck equation indicates it would or if it follows a non-linear data fit. The electro-osmotic drag and back diffusion coefficient are not known therefore it is difficult to assume an electro-osmotic drag coefficient to determine the electro-osmotic drag portion of the total water flow. The theoretical model of the fuel cell cannot be validated it is not known because none of the transport coefficients were determined experimentally. Yan et al [25] did not separate the total water flow into its individual fluid drivers, and it is not known what percentage of the fluid flow electro-osmotic drag is and which portion is back diffusion. It is possible to separate the total water flow into its fundamental fluid drivers. It is possible to isolate the electro-osmotic drag and back diffusion portion of the total water flow without making an assumption of a fluid transport coefficient.

As shown in the previous experiments, the total water flow depends on the inlet conditions of the reactants, Yan et al [25] also examined how the flowrate of hydrogen impacts the total water flow. Yan et al [25] performed an additional experiment with the scenario where the hydrogen relative humidity was fixed at 20% and the air side relative

humidity is fixed at 100% and the in this scenario mass flow rate of hydrogen was varied as shown in Figure 2.1.3:

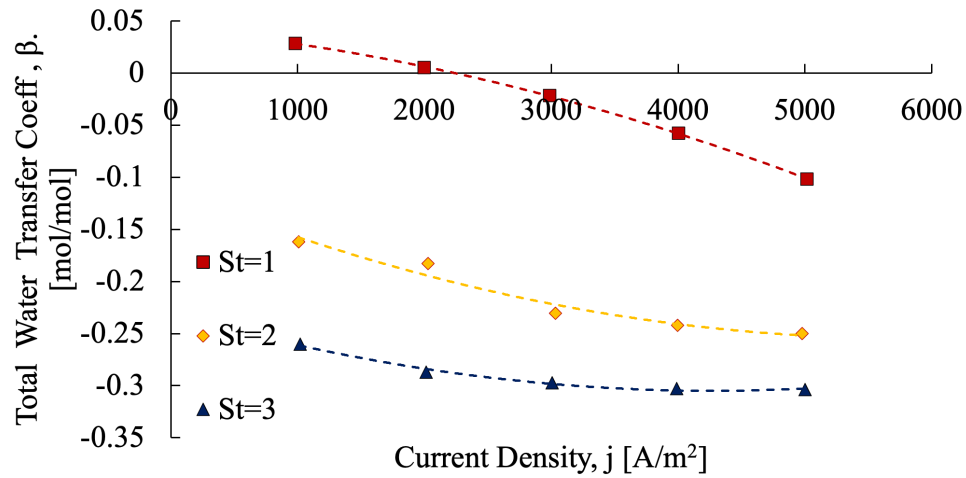


Figure 2.1.3 Water Flow Transfer Coefficient with Variable Hydrogen Flowrate [25]

Two of the three cases have a negative total water transfer coefficient; this indicates that back diffusion is exceeding electro-osmotic drag. It is not known how much of the total water flow is electro-osmotic drag and how much is back diffusion. The data in the current form does not show how the total water flow changes with respect to the current density. It is not known if the total water flow trendline will follow a linear or non-linear trend. The electro-osmotic drag and back diffusion coefficient are not known. The mass flowrate of hydrogen does impact the total water flow across the membrane. As before the electro-osmotic drag and back diffusion components were not extracted from the total water flow. The total water flow across the membrane needs to be determined, and it can be broken down into its electro-osmotic drag and back diffusion components without assuming a transport coefficient.

In another Yan et al [25], experiment, there were two experiments performed where one was aimed at getting the back diffusion coefficient and this was subtracted from the total water flow experiment to compute the electro-osmotic drag coefficient. The process relies into two experiments to isolate the electro-osmotic drag coefficient. The back diffusion experiment was performed with a variable current density, and with humidified hydrogen on the anode and liquid water on the cathode. The back-diffusion results are shown in Figure 2.1.4:

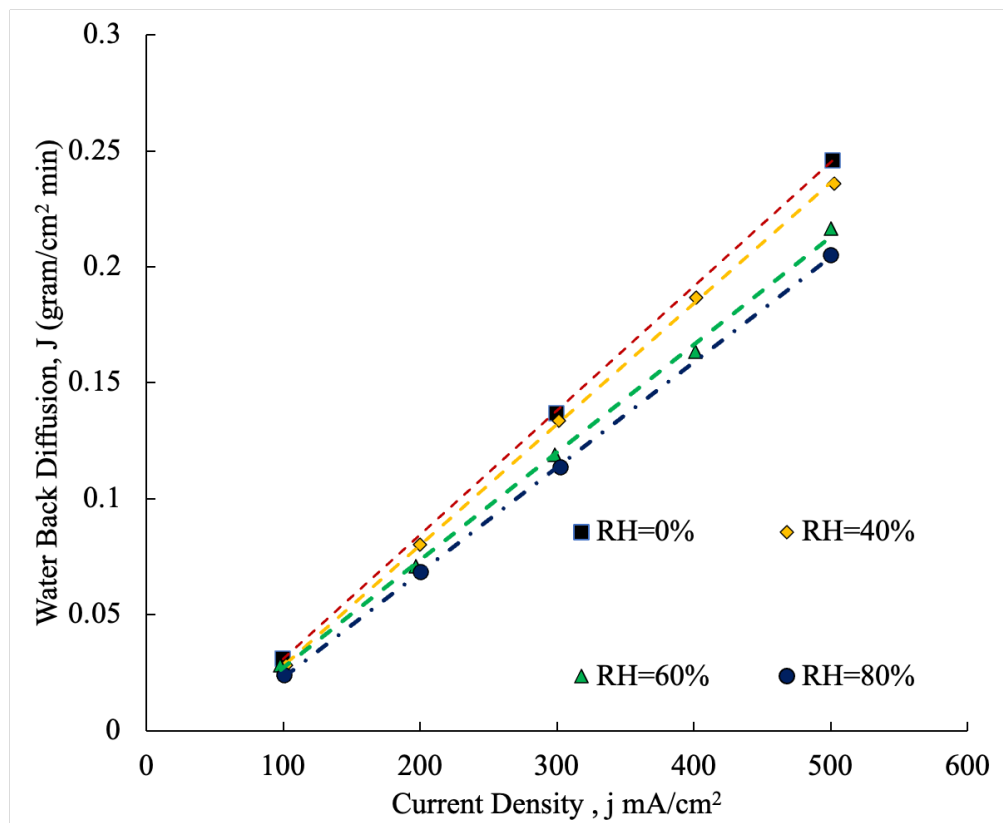


Figure 2.1.4 Back Diffusion Experiment with Variable Current Density [25]

The total water flow across the membrane was reported in terms of the total water flow instead of the total water transfer coefficient. The total water flow seems to fit a linear

trendline. The direction of the water flow is in the direction of was from liquid to vapor. The experiment was conducted with a variable inlet relative humidity and a fixed current density and the water flow across the membrane will contain electro-osmotic drag and back diffusion.

According to the data the total water flow across the membrane is a function of current density. The total water flow was not broken down into its electro-osmotic drag and back diffusion components. The existing data can be broken down into its electro-osmotic drag and back diffusion components without assuming a fluid driver. The experiments data can be used to determine how much of the fluid flow is from electro-osmotic drag and back diffusion without assuming a transport coefficient. The second part of the experiment consists of running the fuel cells with humidified hydrogen and liquid water on the cathode, the total water flow is shown in Figure 2.1.5:

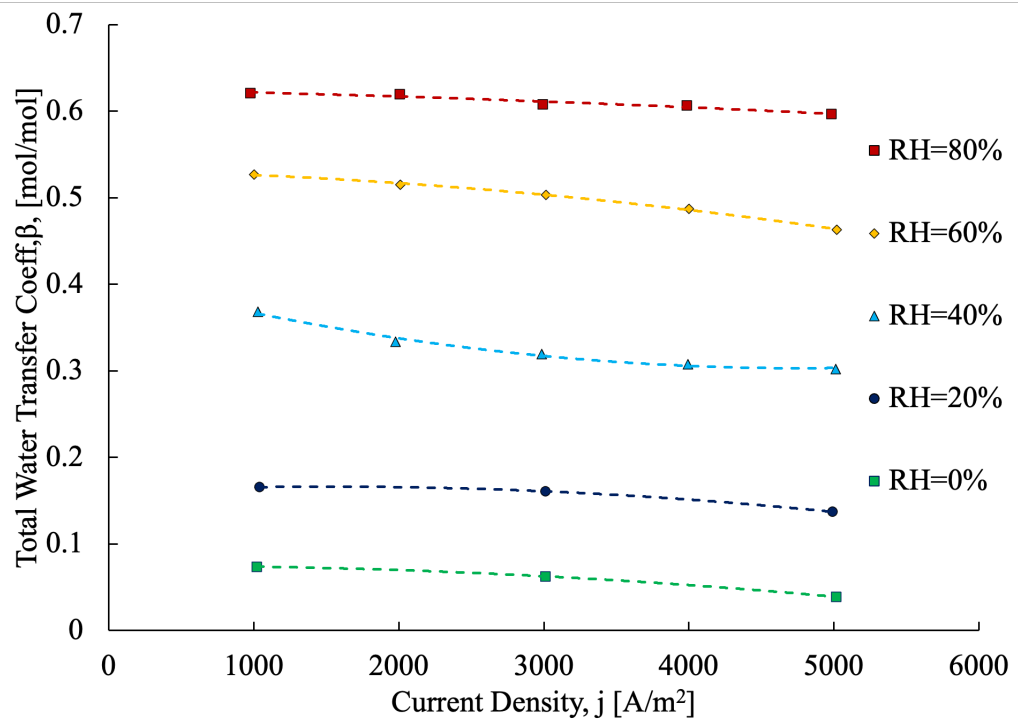


Figure 2.1.5 Total Water Transfer Coefficient with Variable Current Density [25]

The experimental results were reported out in terms of total water transfer coefficient. Based on the total water transfer coefficient, the total water flow was in the direction of anode to cathode. The total water transfer coefficient does not provide the electro-osmotic drag and back diffusion coefficient. This approach makes it difficult to validate total water flow theoretical models. The total water flow needs to be obtained from the total water transfer coefficient. The data trendline needs to be obtained on how the total water flow varies with respect to the current density, it is not known if the total water flow trendline will follow a linear or non-linear fit. Yan et al [25] only reported the total water transfer coefficient and did not report the total water flow.

Yan et al [25] had noted the water flow direction when liquid water was present on the cathode, the direction of water flow was toward the water vapor. Yan et al [25] had used the back diffusion from Figure 2.1.4, and Figure 2.1.5 to compute the electro-osmotic drag and back diffusion coefficients, note that liquid water was on one side of the membrane and water vapor was on the other side, there were no results for the vapor/vapor scenario. The back diffusion experiment shown in Figure 2.1.4 contains electro-osmotic drag and back diffusion. It is not known if these results will transfer over to a vapor/vapor scenario. The calculated electro-osmotic drag coefficient from Yan et al [25] ranged from 1.5 to 2.4. It required two experiments to extract electro-osmotic drag and back diffusion, and it would be ideal to obtain results from one experiment.

Yan et al [25] experimental results show that the total water transfer coefficient through the membrane depends on the current density, anode relative humidity, cathode relative humidity and the mass flux of hydrogen. The current density contributes to the water generated at the fuel cell and the inlet relative humidity will impact the hydration of the membrane. It is clear the inlet relative humidity, mass flowrate of reactants and current density impacts fuel cell performance. The total water transfer coefficient does not tell how the electro-osmotic drag and back diffusion coefficient change with current density, it requires breaking down the total water flow into its electro-osmotic drag and back diffusion components. The breakdown of the total water flow must be done without assuming a transport coefficient until there is an agreed upon electro-osmotic drag and back diffusion coefficient model.

Cai et al [31] had run a 128 cm² active area PEM fuel cell with an anode dry and the cathode partially humidified and a case where the anode and cathode were humidified. Cai et al [31] wanted to demonstrate the ability to run the anode without humidification to support fuel cell operation. The fuel cell did contain an anode and cathode Microporous Layer. As before the water transport across the membrane was reported as the total water transfer coefficient as shown in Figure 2.1.6 Note the total water transfer coefficient is negative where the direction of the total water flow is in the direction of cathode to anode.

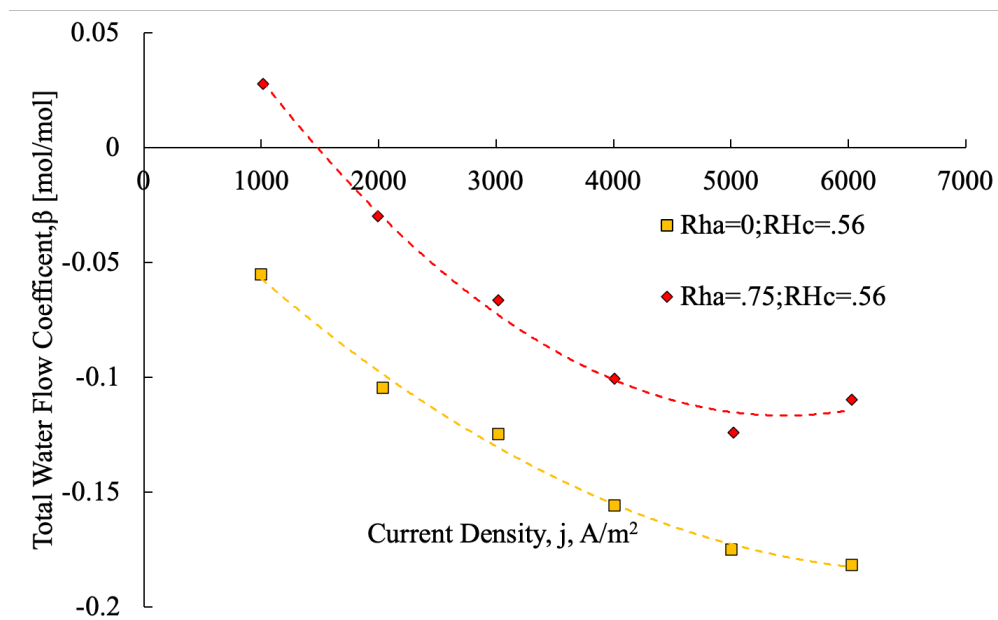


Figure 2.1.6 Total Water Transfer Coefficient Dependence on Current Density [31]

The total water flow transfer coefficient is more negative when the anode is dry, this would reduce the electro-osmotic drag because of the low ionic conductivity of the membrane. As the anode relative humidity increases, the ionic conductivity will increase,

and the electro-osmotic drag will increase. The experimental results were reported out as the total water transfer coefficient instead of the total water flow across the membrane. The total water transfer coefficient was negative noting the direction of the water flow was in the direction of cathode to anode. This is an indication that the back diffusion exceeds electro-osmotic drag; this could be a result of the difference in the cathode and anode relative humidity. The total water transfer coefficient does not provide the electro-osmotic drag coefficient, and it does not provide the back diffusion coefficient. The total water transfer coefficient does not provide how the total water flow changes with current density. The hydrophobic Microporous Layer (MPL) could have also impacted the total water flow.

The total water flow was not reported, and it was not reduced to its electro-osmotic drag and Fickian diffusion components, it is difficult to obtain what percentage of the flow is electro-osmotic drag and which portion is back diffusion because of the scatter of the electro-osmotic drag coefficient and back diffusion coefficient models. The electro-osmotic drag and back diffusion coefficients were not obtained and as a result insight into electro-osmotic drag and back diffusion cannot be obtained. In these experiments the total water flow was in the direction of the cathode due to the anode being less humidified. This experiment does introduce the MPL. It is possible if electro-osmotic drag and back diffusion are understood better then running a dry anode could be a possibility. It is not known how the total water flow changes with current density, it is not known if the total water flow follows a linear or non-linear relationship.

To better understand total water flow and humidification, Nguyen and White [32] also developed a fuel cell model for a Proton Exchange Membrane fuel cell to support humidification. Nguyen and White [32] utilized the model to understand heat and water management model of the PEM fuel cell and they wanted to understand how electro-osmotic, back diffusion and heat transfer impacts fuel cell performance. In their experiments the total water transfer across the membrane was measured but an empirical model was used for the electro-osmotic drag coefficients. The empirical model originated from Springer et al [33] and are shown in equation 20 and 21.

$$n_d = \begin{cases} \{.0049 + 2.02a_a - 4.53a_a^2 + 4.09a_a^3\} (a_a \leq 1) \\ 1.59 + .159(a_a - 1) (a_a > 1) \end{cases} \quad (20)$$

Note this is one of the many electro-osmotic coefficient models. The electro-osmotic drag coefficient does change when relative humidity exceeds 1 or when liquid water is present. The electro-osmotic drag coefficient does change with the hydration state of the membrane when the membrane is exposed to liquid water. The presence of liquid water does improve electro-osmotic drag on the anode.

$$D_w = \begin{cases} \{(.0049 + 2.02a_a - 4.53a_a^2 + 4.09a_a^3)D_0e^{(2416(\frac{1}{303}-\frac{1}{T}))}\} (a_a \leq 1) \\ (1.59 + .15(a_a - 1))D_0e^{(2416(\frac{1}{303}-\frac{1}{T}))} (a_a > 1) \end{cases} \quad (21)$$

The back diffusion coefficient does change when the relative humidity exceeds 100% or when liquid water is present. The back diffusion properties do change as the membrane hydrates; this is when the membrane is exposed to water vapor. The phase of water does impact the electro-osmotic drag and the back diffusion coefficients.

Nguyen and White [32] had also used Springer et al [33] back diffusion model also, noted that Springer et al [33] back diffusion model was inappropriate because it values independent of the water content of the membrane and when the expression was used, the model predicted that at high current density ($j > 1 \text{ A/cm}^2$) without humidification for the anode the fuel cell would run. Due to the lack of data, Nguyen and White [32] made an assumption about the back diffusion coefficient, the assumption made is the back diffusion coefficient depends on the water content of the membrane in a similar matter to electro-osmotic drag. The equations used to by Nguyen and White [32] is shown in equation 22.

$$c_w = \begin{cases} \frac{\rho}{EW} (.043 + 17.8a_k - 39.8a_k^2 + 36a_k^3)(a_k \leq 1) \\ \frac{\rho}{EW} (14 + 1.4(a_k - 1) (a_k > 1) \end{cases} \quad (22)$$

Nguyen and White [32] had modelled three cases, the first one consisted of gases at 90°C, 105°C and 90°C with liquid water. Two of the scenarios consist of water vapor at different temperatures and the other one consist of liquid water. The total water transfer

coefficient and the calculated electro-osmotic drag coefficient are compared to one another.

The scenario Nguyen and White [32] ran was the 90°C with water vapor as shown in Figure 2.1.7 The electro-osmotic drag coefficient is decreasing with current density, and the total water transfer coefficient is following a polynomial trend with increasing at lower current densities and decreasing at higher current density. The total water was in the direction of anode to cathode, thus indicating that electro-osmotic drag exceeds back diffusion.

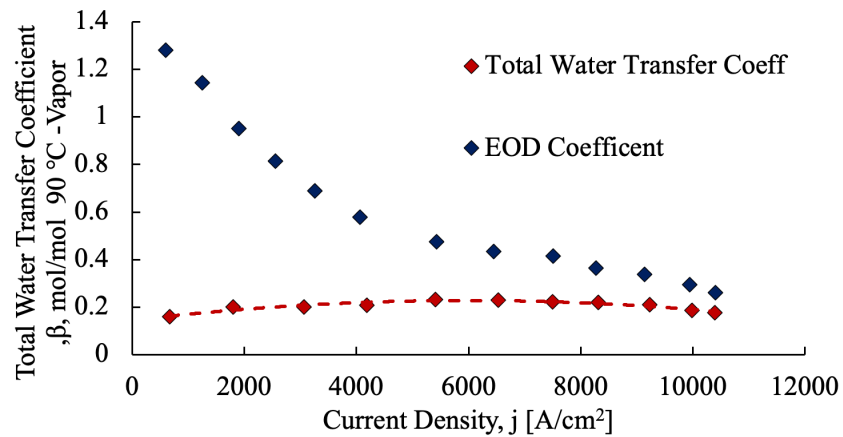


Figure 2.1.7 Comparison of Total Water Transfer Coefficient and EOD Across the Membrane -95 °C Water Vapor [32]

The total water flow was reported as the total water transfer coefficient, it is not known how the total water flow changes with current density. The predicted electro-osmotic drag is decreasing as the current density increases; it starts at 1.3 and decreases to 0.4. The change in the electro-osmotic drag coefficient indicates that electro-osmotic drag coefficient is a function of current density. It is not known if the electro-osmotic drag

coefficient changes because of the voltage gradient or is it changing because of the hydration state of the membrane.

It may be possible that Springer et al [33] did not fully isolate the electro-osmotic drag flow from the total water flow. This could be one of the issues why Nguyen and White [32] model stated that the fuel cell did not require humidification up to 1.5 A/cm^2 . It is possible in the electro-osmotic drag experiments that the total water was not broken down into its electro-osmotic drag and back diffusion components. The total water flow experiment will have other fluid drivers present; it is not known if the other fluid drivers are extracts or the data was used as is.

Barragan et al [34] measured the total water transport across the membrane, their research focus on liquid water transport under different currents and pressures. The experiment was conducted in an aqueous environment. Barragan et al [34] wanted to understand how voltage and pressure will impact water flow through a Nafion membrane. Barragan et al [34] ran experiments at fixed pressures and variable current as shown in Figure 2.1.8. Their total water flow data was **not** forced through the origin, but the change in pressure does shift the data points above the origin. The trendline that is closest to going through the origin is the no pressure case. The data trendline do exhibit linear properties. The current does influence direction of the total water flow, when the current is negative the total water flux is negative and when the current is positive the total water flow is positive.

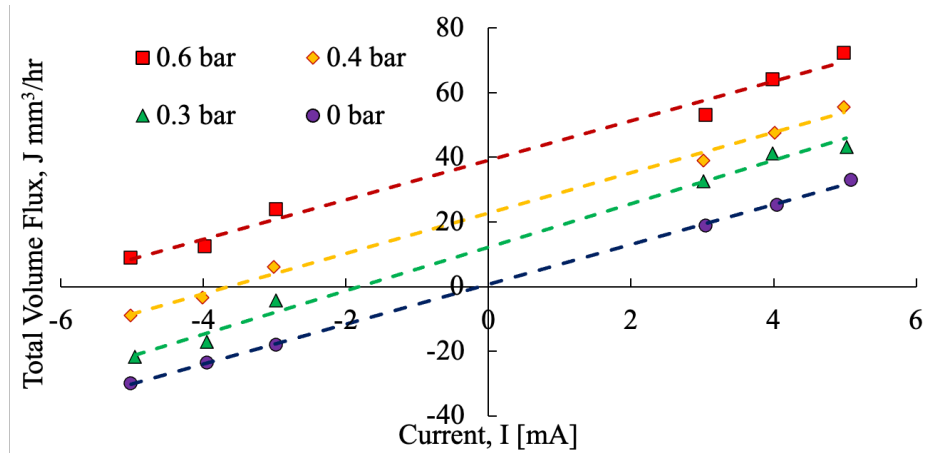


Figure 2.1.8 Total Water Across Nafion at Fixed Pressures [34]

The total water flow varies linearly with current density, the change in pressure causes the linear trendline to shift further away from the origin, the 0-bar case is the closest case to going through the origin while the 0.6 bar case is shifted furthest from the origin. The increase in pressure also adds another fluid driver to the total water flow. In a liquid environment the total water flow varies linearly with current density, the total water transfer cases need to be transformed into the total water flow. The total water flow in a water vapor environment needs to be examined because of the water vapor cases had the total water flow reported as the total water transfer coefficient. The total water flow was not separated into its voltage base component and pressure base component. No insight is gained into the electro-osmotic drag coefficient along with the pressured based coefficient. The electro-osmotic drag portion of the total flow can be obtained through analysis of the experimental data.

Choi et al [35] experiment involved understanding the total water drag or total water flow across the membrane. The fuel cell was run at fixed inlet conditions and variable current density; the total water flow was measured but only the total water transfer coefficient was recorded. The total water flow across the membrane is the summation of electro-osmotic drag and back diffusion. There was no attempt to separate the total fluid flow into its electro-osmotic drag and back diffusion-based components, and the transport coefficients were not obtained.

Choi et al [35] objective was to investigate the influence of water transport properties on the performance of the fuel cell, specifically the study was aimed at how the membrane resistance and water balance affects the fuel cells performance. Choi et al [35] had run experiments to determine the total electro-osmotic drag coefficient in Nafion and Hanwha membranes. Choi et al [35] has examined three scenarios, the first one is with the cathode is humidified, the second one is with a Hanwha membrane with the cathode humidified and the last one with the Nafion with the cathode was not humidified. The electro-osmotic drag nor the back diffusion was obtained as shown in Figure 2.1.9:

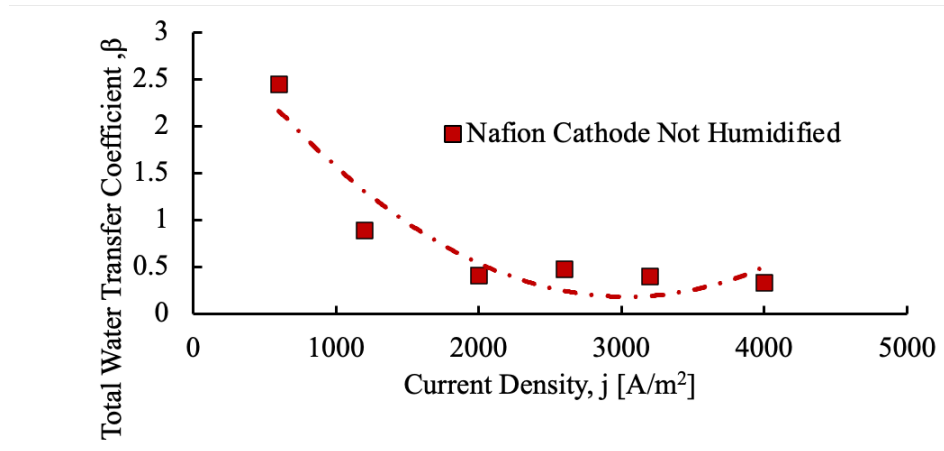


Figure 2.1.9 Total Water Transfer Coefficient on Nafion [35]

The exact relative humidity was not provided, and it is not possible to obtain the back diffusion coefficients, but the back diffusion portion of the total water flow can be extracted by determining the electro-osmotic portion. It is not possible to understand the electro-osmotic drag and back diffusion with the data in this format. The data in this format does not show how the total water flow changes with current density. The total water transfer coefficient needs to be converted into total water flow across the membrane to obtain electro-osmotic drag.

Colinart et al [36] objective was to investigate water transport in the PEM fuel cell by measuring the total water transport coefficient and to understand how operating conditions impact the fuel cell. Colinart et al [36] had tested at 25 cm² without a microporous layer. Colinart et al [36] had noted that other researchers reported results as total water transfer coefficient as shown in Table 2-1

Table 2.1-1 Experiments Reviewed By Colinart [36]

Table 1
Literature review of the water transport coefficient α , defined as the net water flux across the membrane divided by the water production. The arrows indicate the evolution of α with an increase of each parametric value.

Authors	Material	$T(^{\circ}\text{C})$	$P_a - P_c$ (bar)	λ_{H_2}	RH_{H_2}	λ_{Air}	RH_{Air}	i (A.cm ⁻²)	Remarks
[27] Mennola et al.	GORE Primea 25 cm ²	40 - 60		1.5 - 2.5 $\alpha \nearrow$	0	1	0.1 ... 0.2	0.1 - 0.2 $\alpha \nearrow$	Free-breathing PEMFC
[34] Lu et al.	GORE 30 μm 6 cm ² co-flow	80	2	2	1	2	0.3	1	Study on spatially resolved water crossover coefficient
[35] Liu et al.	GORE 30 μm 6 cm ² co-flow	80	2	2 $\alpha \searrow$	0 - 0.42 $\alpha \searrow$	2	0 - 0.42 $\alpha \nearrow$	1	Study on spatially resolved water crossover coefficient
[30] Murahashi et al.	Nafion 112 25 cm ² counter-flow	70 - 80 $\alpha \nearrow$		1.43	0.42	2	0.42 - 0.8 $\alpha \nearrow$	0.3	
[32] Atiyeh et al.	Nafion 112 100 cm ²	60	1.35	1.4	0.6 - 1	2 - 3	1 - 0.6	0.3 - 0.7 $\alpha \searrow$	Investigation of the role of a microporous layer
[33] Karan et al.	Nafion 112 100 cm ²	60	1.35	1.4	0.6 - 1	2 - 3	1 - 0.6	0.3 - 0.7 $\alpha \searrow$	Investigation of the role of a microporous layer at the cathode
[25] Janssen and Overvelde	Nafion 105 - 112 50 cm ² counter-flow	60	1.5 - 3	1.5 - 4 $\alpha \nearrow$	0	2	1	0.4 - 0.6 $\alpha \nearrow$	Wide range of operating conditions Different types of MEA
[28] Cai et al.	Nafion 112 - 115 128 cm ² Co-flow	60	2	1.1 $\alpha \nearrow$	0 - 0.75 $\alpha \nearrow$	2.5	0.56	0.1 - 0.6 $\alpha \nearrow$	Tanaka electrodes Liquid water at the cell outlet
[22] Büchi and Srinivasan	Nafion 115 50 cm ² counter-flow	40 - 75 $\alpha \nearrow$	1 - 1.7	1.7 - 4.4 $\alpha \nearrow$	0	1.2 - 4.5 $\alpha \rightarrow$	0	0.1 - 0.3 $\alpha \searrow$	E-tek electrodes Hydrogen saturated at the cell outlet
[26] Ciureanu and Badita	Nafion 105 250 cm ² 5-cells stack	52	1	?	0	4	0.4	0.04 - 0.4 $\alpha \nearrow$	Wide range of operating conditions Liquid water at the cell outlet
[29] Yan et al.	Nafion 117 25 cm ²	80	1	1 - 3 $\alpha \nearrow$	0.1 - 1 $\alpha \nearrow$	2	0.1 - 1 $\alpha \searrow$	0.1 - 0.7 $\alpha \nearrow$	E-tek electrodes
[31] Jeong et al.	Nafion 221 25 cm ²	25 - 35 $\alpha \searrow$		2.5 - 5 $\alpha \nearrow$	0	1	0.3 - 1 $\alpha \nearrow$	0.05 - 0.2 $\alpha \nearrow$	Free-breathing PEMFC

Thickness of the membrane: Nafion 112: 50 μm ; Nafion 105 or 115: 125 μm ; Nafion 117: 170 μm .

The referenced material shows that other researchers do not come to a consensus on the electro-osmotic drag coefficient, it is not known if it is from the method or if it is from the data analysis. No explanation is given for the scatter on electro-osmotic drag. It is possible that the electro-osmotic drag was not extracted from the total water flow.

Colinart et al [36] has run water transport experiments on PEM fuel cells, with a variable current and a fixed relative humidity. In one specific instance Colinart et al [36] had run the fuel cell with dry hydrogen and a relative humidity of 70% on cathode as shown in Figure 2.1.10:

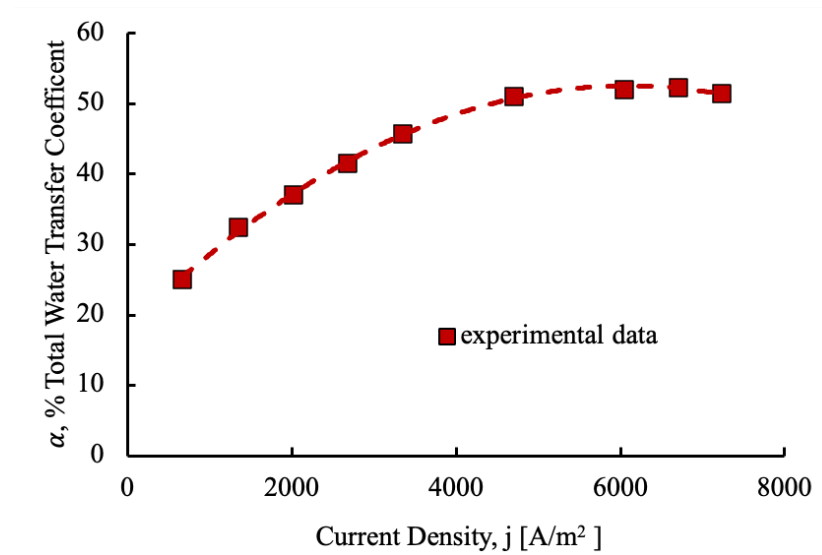


Figure 2.1.10 Total Water Transfer Coefficient for a PEM Fuel cell with dry hydrogen [36]

The total water flow across the membrane was reported as the total water transfer coefficient and not the total water flow across the membrane, it does not tell how the total water flow changes with current density. The total water flow across the membrane was not broken down into its electro-osmotic drag and back diffusion component and it is not compared to any electro-osmotic drag/ back diffusion model. The only conclusions that can be made is that the direction of the water flow is in the direction of anode to cathode. It is not known how the total water flow across the membrane changes with current density. The total water transfer coefficient data requires further analysis.

Adachi [37] ran water transport experiments on the PEM fuel cell with Nafion membrane, his objective was to understand water permeability of Nafion under different conditions specifically when the membrane is exposed to liquid water, water vapor or both. Adachi [37] ran water transport experiments with Nafion membranes. The total water flow scenarios consisted of experiments with Nafion with variable current density at different relative humidities, and different scenarios where liquid water was on one side of the membrane and another case where water vapor was on both sides. In the experiments an electro-osmotic drag coefficient was assumed compared to being calculated from the experimental data. The first case consisted of total water flow was plotted again a variable current density as shown in Figure 2.1.11.

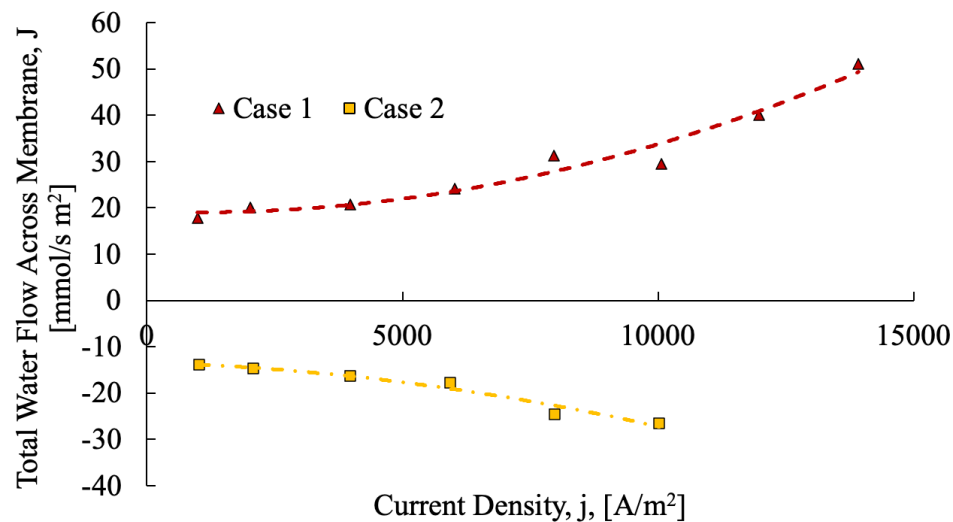


Figure 2.1.11 Total Water Transfer Flow Across Nafion with Variable Current [37]

The total water flow across the membrane was reported and the electro-osmotic drag and back diffusion coefficients are unknown. The electro-osmotic drag coefficient was assumed to compute the electro-osmotic drag portion of the water flow, the coefficient

chosen was either 0.5 or 1.0, the value was not determined based on the experimental data. The assumption of the electro-osmotic drag coefficient also was not validated.

Adachi [37] referenced an electro-osmotic drag model by Ye et al [38] and this is one of many electro-osmotic drag models. Any calculated results depend on the electro-osmotic drag model chosen.

In case 1, the total water flow is in the direction of the anode to cathode and in case 2, the total water flow is in the direction of cathode to anode. If the total water flow is in the direction of anode to cathode, electro-osmotic drag exceeds back diffusion, and the transport coefficients are not known. Case 2 shows back diffusion exceeding electro-osmotic drag. The total water flow can be broken down into its electro-osmotic drag and back diffusion components without assuming an electro-osmotic drag model or a back diffusion model. The electro-osmotic drag portion of the total water flow can be obtained without assuming a transport coefficient and it can be obtained by analyzing the experimental data. If the electro-osmotic drag is extracted from the experimental data, it can be compared to the assumed electro-osmotic drag coefficient.

Adachi [37] performed multiple experiments with the PEM fuel cell, the next experimental set up involved varying the membrane thickness. The inlet relative humidity was fixed where the cathode was humidified, and the anode was dry. The thickness of the membrane will impact the back diffusion portion of the total water flow; the thicker membranes will promote less back diffusion. The thinner membranes will promote more

back diffusion. The total water flow at variable current density and at different membrane thicknesses as shown in Figure 2.1.12:

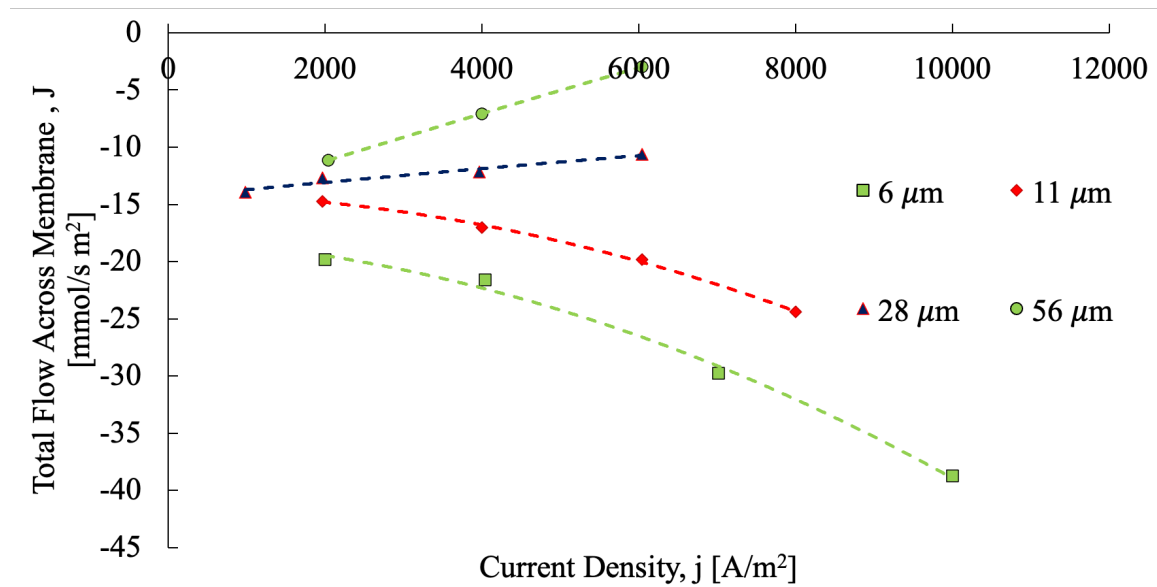


Figure 2.1.12 Total Water Transfer Flow Across Nafion with Different Membrane Thicknesses [37]

As in the other experiment, the total water flow was reported instead of the total water flow transfer coefficient. The total water flow across the membrane is impacted by the membrane thickness, in cases where the membrane was thicker the total water flow is becoming less negative. In the cases with a thinner membrane the total water flow is becoming more negative. The membrane thickness does impact the total water flow. The total water flow is more linear when the membranes are thicker and more non-linear when thinner membranes are present. The thinner membranes will promote more back diffusion while the thicker membrane will reduce the impact of back diffusion. The total water flow was not broken down into its electro-osmotic drag and back diffusion

components. The data requires further analysis to extract the electro-osmotic drag and back diffusion components of the total water flow.

Adachi [37] also examined the impact of liquid water on one side of the membrane and water vapor on the other side. The direction of the water flow was in the direction of liquid to vapor just in the Yan et al [25] experiment as shown in Figure 2.1.4.

Adachi [37] also ran the total water flow experiment with water vapor on both sides of the membrane. Both the liquid water and water vapor scenario are shown in Figure 2.1.13:

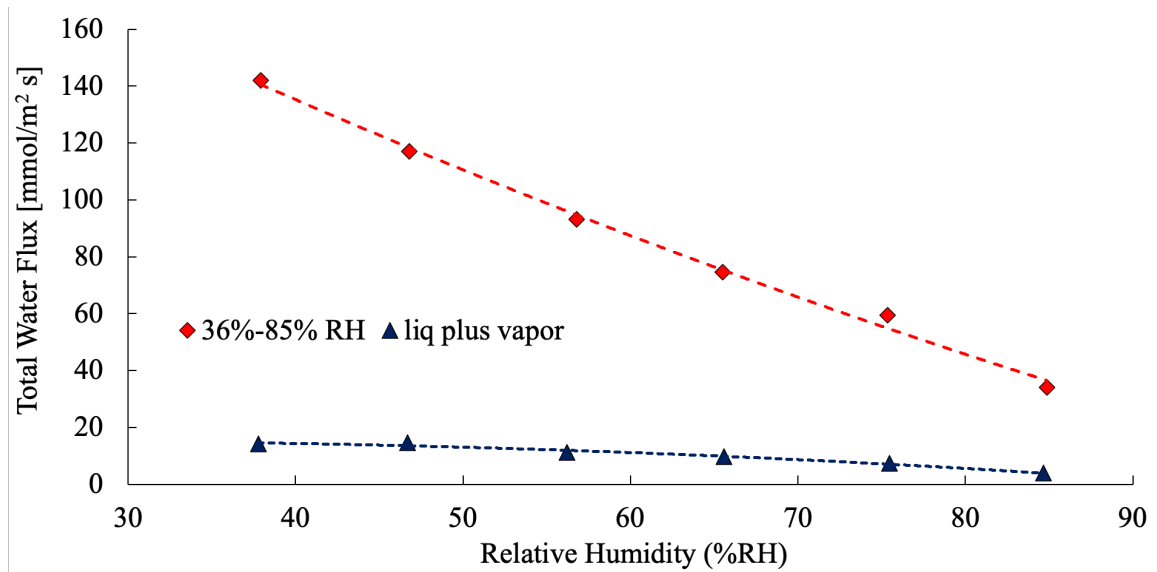


Figure 2.1.13 Total Water Flow with Liquid Water and with Water Vapor

The experimental results are expressed in terms of the total water flow and not the total water transfer coefficient. The current set up does not express the total water flow across the membrane with respect to the concentration gradient and the back diffusion portion cannot be computed. The data need to be reexamined to extract the back diffusion portion

of the total water flow across the membrane. The theory was that the chemical potential was the driving mechanism, but Schroeder Paradox shows that a membrane will move more liquid water compared to a membrane exposed to water vapor. This experiment must be examined further examined to determine the back diffusion portion of the total water flow and to understand why the direction of liquid to vapor.

The other total water flow that was examined was with liquid on both sides of the membrane. Adachi [37] conducted an experiment with liquid water on both sides of the membrane just water permeation with liquid water as shown in Figure 2.1.14. In this experiment liquid water was on both sides on the membrane at different pressures.

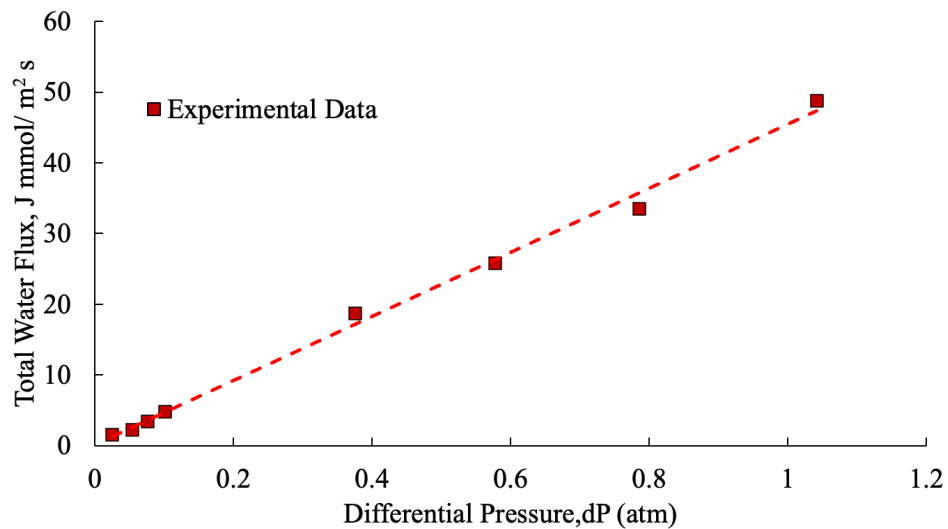


Figure 2.1.14 Total Water Flow with Liquid Water at Different Pressures [37]

The total water flow trendline varies linearly with pressure difference and this indicates that pressure difference does impact total water flow. It is not known if can be translated into D'Arcy Law. The current processes assumes that the total water flux across

membrane is all from the pressure differential, the data was not broken down into its fundamental components to determine how much of the total water flow is from the pressure gradient. The total water flow data needs to be refitted to a linear trendline that is not forced through the origin to account for other fluid drivers, the strength of other fluid driver is unknown. The other fluid drivers need to be determined if it is neglectable or if it has a major influence on the total water flow.

Adachi [37] experimented at various relative humidities and at various cathode pressures. As before, the separation of the total water flow requires an assumption of an electro-osmotic drag coefficient to determine the electro-osmotic drag portion of the total water flow. The total water flow coefficient vs current density is shown in Figure 2.1.15:

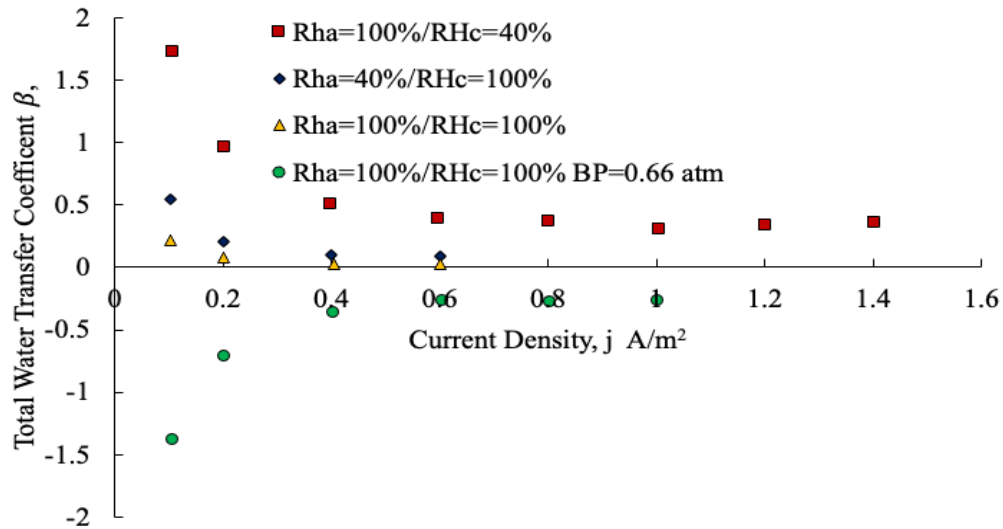


Figure 2.1.15 Total Water Flow at Difference Inlet Conditions [37]

The total water flow transfer coefficient is positive when the anode is fully humidified, and the cathode was partially humidified. The total water transfer coefficient is

decreasing with current density. When the anode was partially humidified and the cathode was fully humidified the total water transfer coefficient starts off positive and decreases with current density. When the cathode and anode were fully humidified and there was no back pressure, the total water transfer coefficient starts off positive and decreases with current density. In the last case where the anode and cathode were both fully humidified and back pressure was applied; the total water flow transfer coefficient was negative and increased with current density. It is difficult to gain insight with the data in this form without knowing the electro-osmotic drag coefficient and the back diffusion coefficient. The data needs to be converted the total water flow across the membrane and the total water flow needs to be broken down into its electro-osmotic drag and back diffusion components.

The total water transfer coefficient was reported and not the total water flow, and it is not known how the total water flow changes with respect to the current density. The experimental data need to be converted to the total water flow to understand how much of the fluid flow is from electro-osmotic drag, back diffusion and how much is pressure based. The total water flow can be obtained, and it can be broken down into its electro-osmotic drag and back diffusion components without assuming an electro-osmotic drag or a back diffusion coefficient and more insight can be gained.

The other fluid flow configuration that was examined was the permeation with water vapor on both sides of the membrane. In this scenario the pressure varied, and the total

water flow was recorded. Adachi's [37] water vapor permeation result with water vapor on both sides of the membrane is shown in Figure 2.1.16:

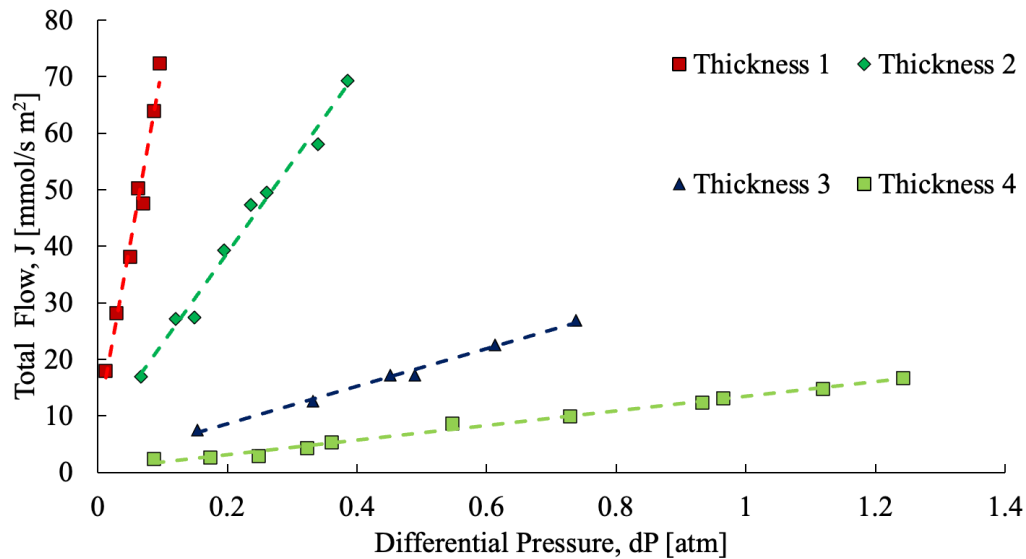


Figure 2.1.16 Total Water Flow with Water Vapor at Different Pressures [37]

The thickness of the membrane does impact the pressure drop of the membrane. All the total water flow cases, the total water flow was fit to a linear trendline that is forced through the origin, this assumes that no other fluid driver is present. The data in its existing form assumes that all the total fluid flow is from the pressure difference, the total water flow needs to be broken down to see if this assumption is true. The total water flow needs to be further examined to see how much of the total flow is pressure based. The total water flow data was not broken down its fundamental components.

One of the goals of the PEM fuel cell balance of plant (BOP) engineers is to eliminate the need of the cathode humidified, to fully eliminate the humidified the water generated from the fuel cells must be pushed toward the anode. To accomplish this each fluid driver

needs to be fully understood. The transport coefficient for both electro-osmotic drag and back diffusion need to be confirmed for better modeling. Both accuracy and precision are required. Ito's et al [39] objective was to experimentally evaluate the total water drag coefficient under dry cathode conditions to support self-humidification. The dry cathode assumes that no humidifier is in the balance of plant and the water generated by the fuel cell will maintain the humidification of the membrane.

Ito et al [39] run experiments where only the total water flow was measured, their main goal was to keep the anode humidified and keep the water flow in the direction of cathode to anode. In this case back diffusion would exceed electro-osmotic drag. In these scenarios. Ito et al [39] referenced Ye et al [38] electro-osmotic drag model but did not compute the electro-osmotic drag coefficient but rather worked with the total water transfer coefficient as shown in equation 23.

$$J_{NET} = \alpha \frac{j}{F} \quad (23)$$

The first set of experimental data consisted of the anode humidified to a relative humidity of 37% and the cathode was run dry. The water generation of the fuel cell is proportional to the current density. The goal is to keep the total water flow in the direction of the anode. The total water transfer coefficient is shown in Figure 2.1.17:

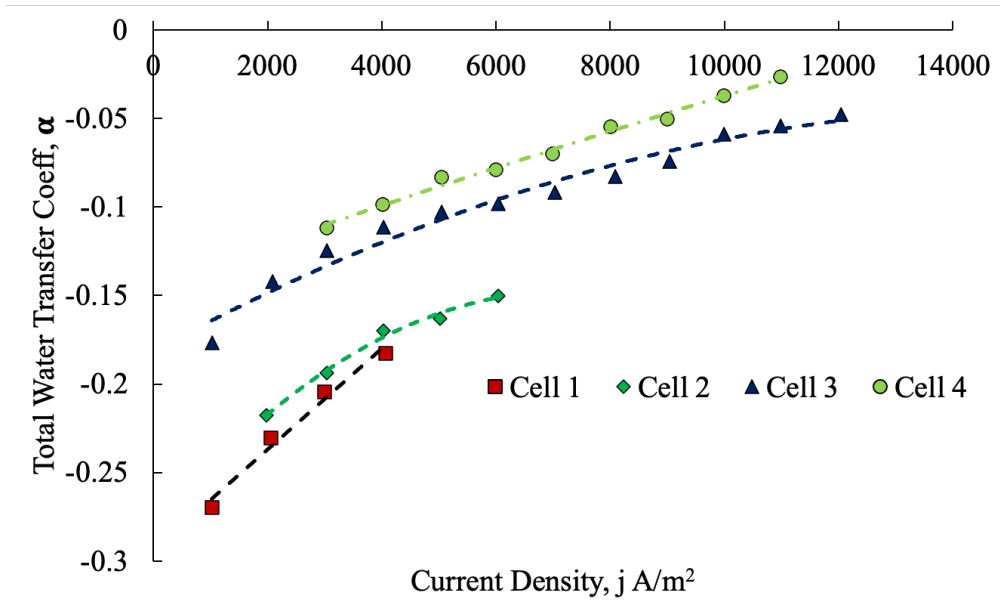


Figure 2.1.17 Total Water Transfer Coefficient vs Current Density [39]

Ito et al [39] was able to keep the total water flow in the direction of cathode to anode but did not reduce the total water flow into its electro-osmotic drag and back diffusion components. The reported results were expressed in terms of the total water transfer coefficient and not the total water flow. The total water transfer coefficient is negative indicating that the back diffusion is exceeding electro-osmotic drag. The existing data does not show how the total water flow changes with current density, it is not known if the total water flow will change linearly with current density. The results need to be converted into the total water flow. The total water flow needs to be decomposed into its electro-osmotic drag and back diffusion components. The electro-osmotic drag coefficients and back diffusion component need to be determined. The total water flow data needs to be further analyzed.

Ge et al [40] wanted to evaluate how high current density will impact membrane hydration of the fuel cell using a 15 μm thick membrane. The thinner membrane does promote back diffusion compared to the thicker membranes. The study examined how inlet conditions along with current density influence the membrane hydration. For the water transport experiments the fuel cell had a 5 cm^2 active area. The total water flow across the membrane was reported instead of the total water transfer coefficient. Note with such small mass fluxes measured, accuracy is required. The total water flow across the membrane is shown in Figure 2.1.18.

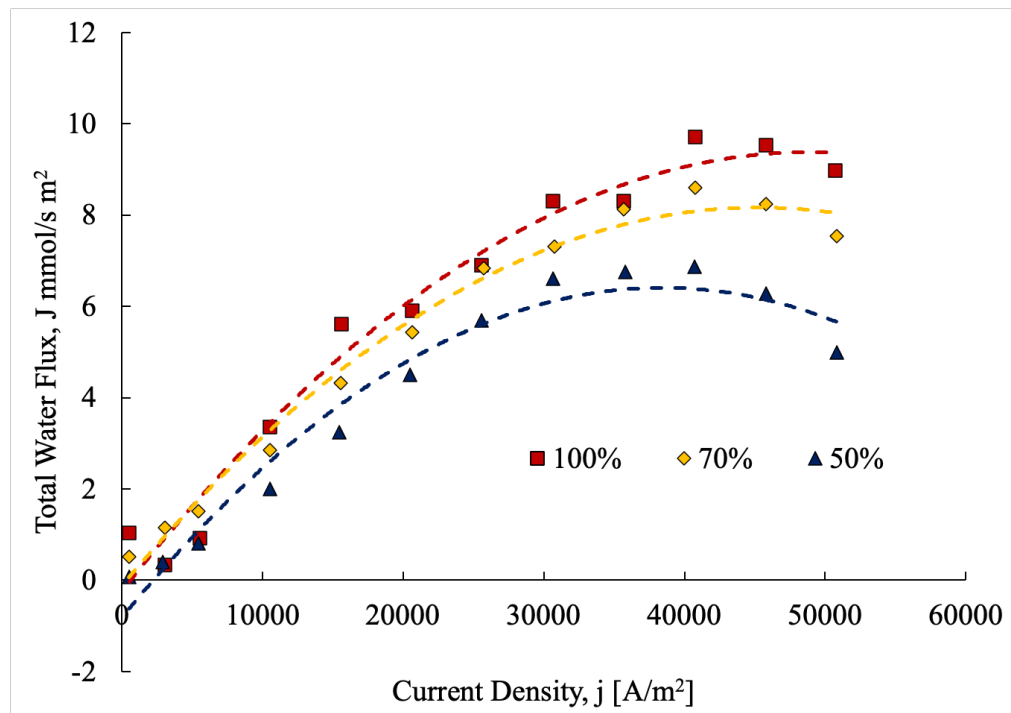


Figure 2.1.18 Total Water Flux Across Membrane (Cathode to Anode) [40]

The total water flow data was fit to a polynomial and not a linear trendline. It is expected trendline follow a linear trendline just like the Nernst-Planck equation. Ge et al [40] had noted that total water flow was always in the direction of cathode to anode, indicating

that back diffusion exceeds electro-osmotic drag. There was no clear separation of the total water flow into the electro-osmotic drag and back diffusion. It is not known why the total water across the membrane following a non-linear trendline.

Without knowing the electro-osmotic drag and back diffusion coefficients it is hard to evaluate why the flow was in the direction of cathode to anode. The total water flow needs to be broken down to understand why the total water flow follows a non-linear trend. Ge et al [40] had noted that the electro-osmotic drag does increase with water content, and when the membrane is in constant with liquid water, temperature has a greater impact on the electro-osmotic drag coefficient and temperature has minimal impact on water vapor.

Bezamalinnovic [41] had run experiment on 50 cm² active area high temperature PEM fuel cell to quantify water transport across the membrane under different operating conditions such as mass flow of hydrogen and inlet relative humidity. The mass flow of hydrogen was fixed and dry and the mass flow of air was varied. The original results were reported at a total water flux and not total water transfer coefficient. The first experiment was performed with different mass flowrate of air entering the fuel cell as shown in Figure 2.1.19:

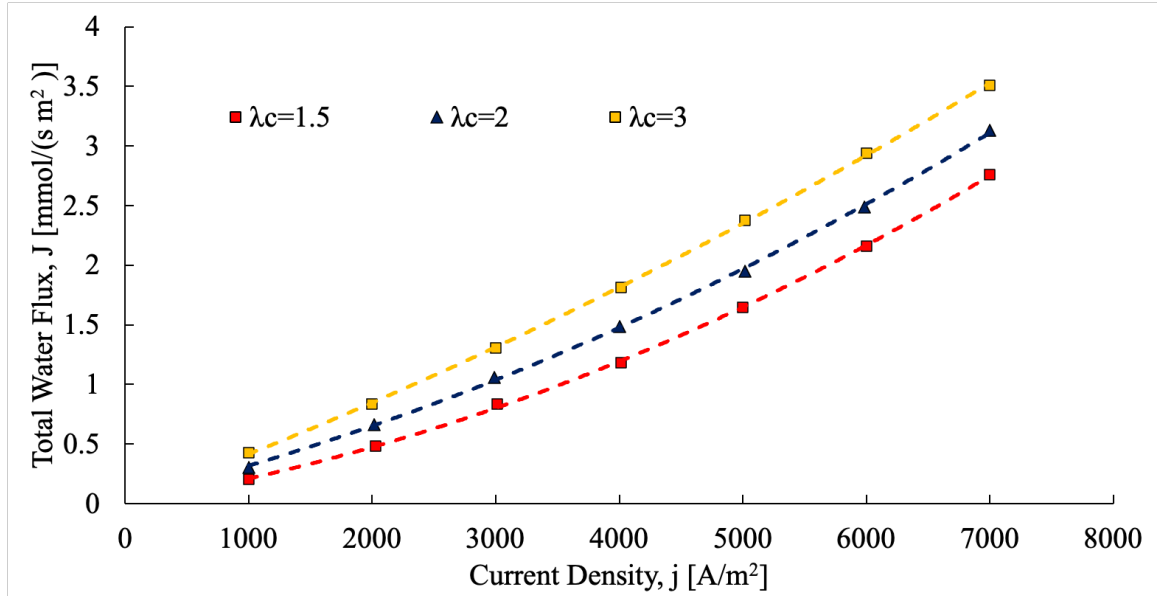


Figure 2.1.19 Total Water Flux Across Membrane with variable air flow [41]

In the high temperature PEM fuel cell, the goal is to keep the temperature high enough to prevent liquid water from forming. The total water flow was reported, and the data can be directly analyzed. The total water flow across the membrane is non-linear and linear behavior was expected based on the Nernst-Planck equation. The total water flux was in the direction of anode to cathode. The mass flux indicates that electro-osmotic drag exceeds back diffusion. The total water flow was not separated into its electro-osmotic drag and back diffusion components. The total water flow needs to be analyzed to determine how much was electro-osmotic drag and how much was back diffusion. The total water flow composition can be obtained without assuming an electro-osmotic drag or a back diffusion coefficient.

Reid [42] examined the total water drag (NWD) on a 5 cm^2 to examine how water moves through the membrane. The total water drag is same as β from equation 16. Reid [42] had used the term net water flow across the membrane which is the same as the total water flow across the membrane. The anode and cathode were both humidified to a relative humidity of 50%. The total water flow was not broken down into its individual components. The total water drag dependences on current density is shown in Figure 2.1.20:

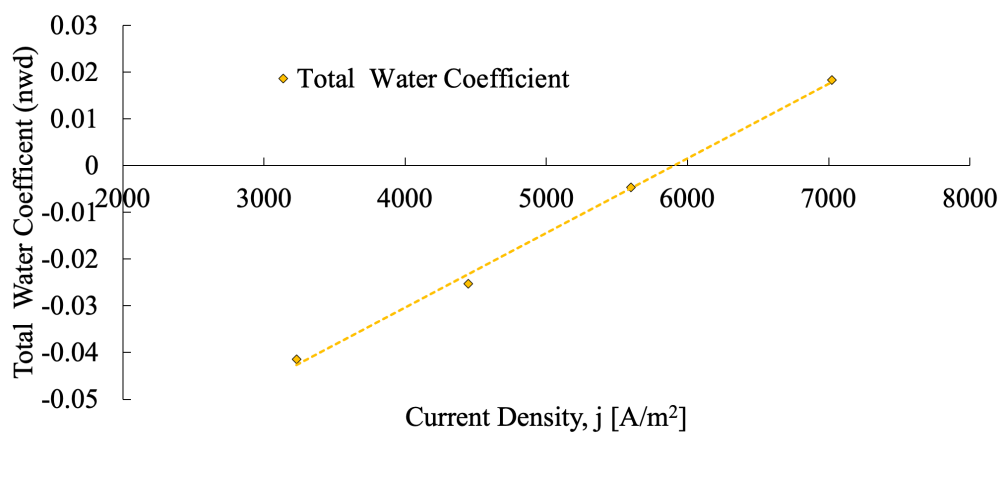


Figure 2.1.20 Total Water Drag for 50%/50% RH [42]

The total water flow transfer coefficient starts of negative and becomes positive as current density increases. The total water transfer coefficient does not show how the total water flow changes with current density, it is not known is the total water flow varies linearly with current density. The total water flow was not broken down into its electro-osmotic drag and back diffusion components. The experimental results show that for low current density, the back diffusion exceeds electro-osmotic drag and at higher current density electro-osmotic drag exceeds back diffusion. The total water flow is changing

direction as the current density changes. The total water flow could be broken down into its electro-osmotic drag and back diffusion components without assuming either a back diffusion or electro-osmotic drag coefficient model, it is not known how much of the total water flow comes from electro-osmotic drag.

Anotani et al [43] set up at 25 cm² active area PEM fuel cell and used a hydrogen pump to represent electro-osmotic drag. The total water flux across the membrane was measured. The purpose of the experiment was to understand water transport in the PEM fuel cells. The water flux across the membrane was reported as shown in Figure 2.1.21:

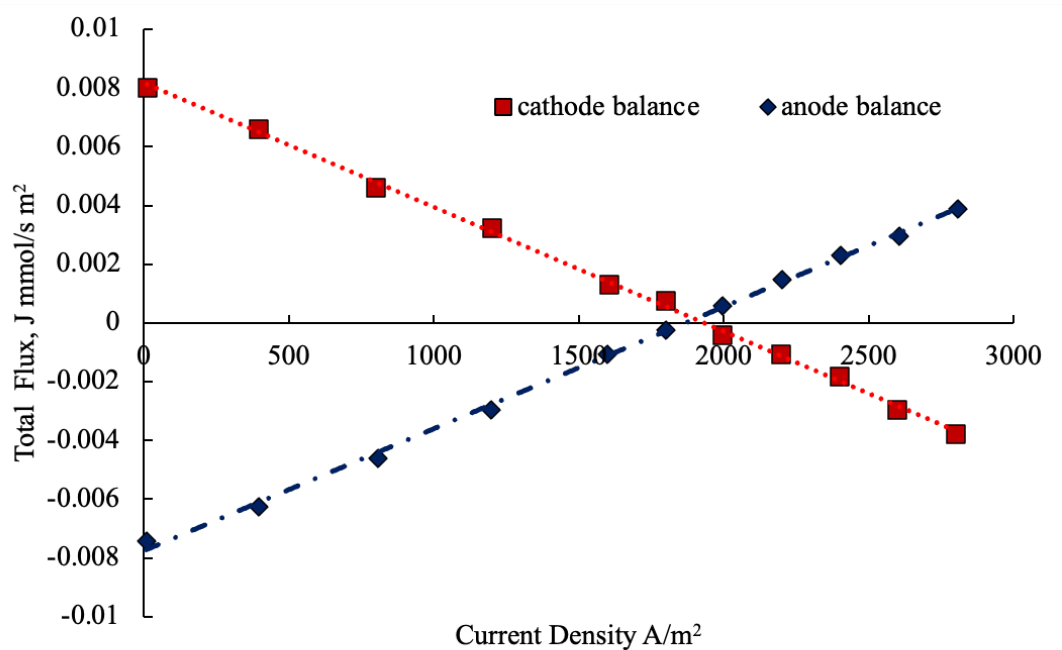


Figure 2.1.21 Total Water Flow across the Membrane by Anode and Cathode Water Balance [43]

The total water flow across the membrane was reported and the data can be used as is.

The total water flow varied linearly with current density. Anotani et al [43] had

determined the electro-osmotic drag coefficient with equation 24. when the current crossed the x-axis. Both the cathode and anode trendlines do not start at 0 A/m², 0 mmol/s m² indicating that back diffusion contributes to the total water flow.

$$n_d = \frac{\Delta N_y F}{I} \quad (24)$$

The total water transfer coefficient was not reported, only the total water flow. The total water flow seems to follow a linear trendline that does not go through the origin. As previously stated, the total water is the summation of all fluid drivers present, and electro-osmotic drag is a portion of the total water flow. The electro-osmotic drag and back diffusion portion of the total water flow needs to be determined. The total water flow data need to be further analyzed to determine the electro-osmotic drag and back diffusion contributions to the total water flow.

At the point where there is no total water flow across the membrane, the electro-osmotic drag portion of the total water flow is equal to the back diffusion portion. This will only work if the total water flow varies linearly with current density, but in cases where it does not a different approach is needed. There needs to be consistent way to determine electro-osmotic drag and back diffusion. The next step is breakdown the total water flow to determine the electro-osmotic drag along with the back diffusion components of the total water flow without assuming a transport coefficient.

2.2 Inconsistent Electro-Osmotic Drag and Back Diffusion Empirical Model

The main agreed upon drivers of water flow from the Nernst Planck equations are the voltage gradient which is expressed in the form of current and the concentration gradient as shown in equation 17. The variations in the water transport comes from the scatter in the electro-osmotic drag coefficient and back diffusion models. The variation on the models comes from the coefficient models for electro-osmotic drag coefficient and the back diffusion coefficient as shown in Figure 2.2.1 and Figure 2.2.2:

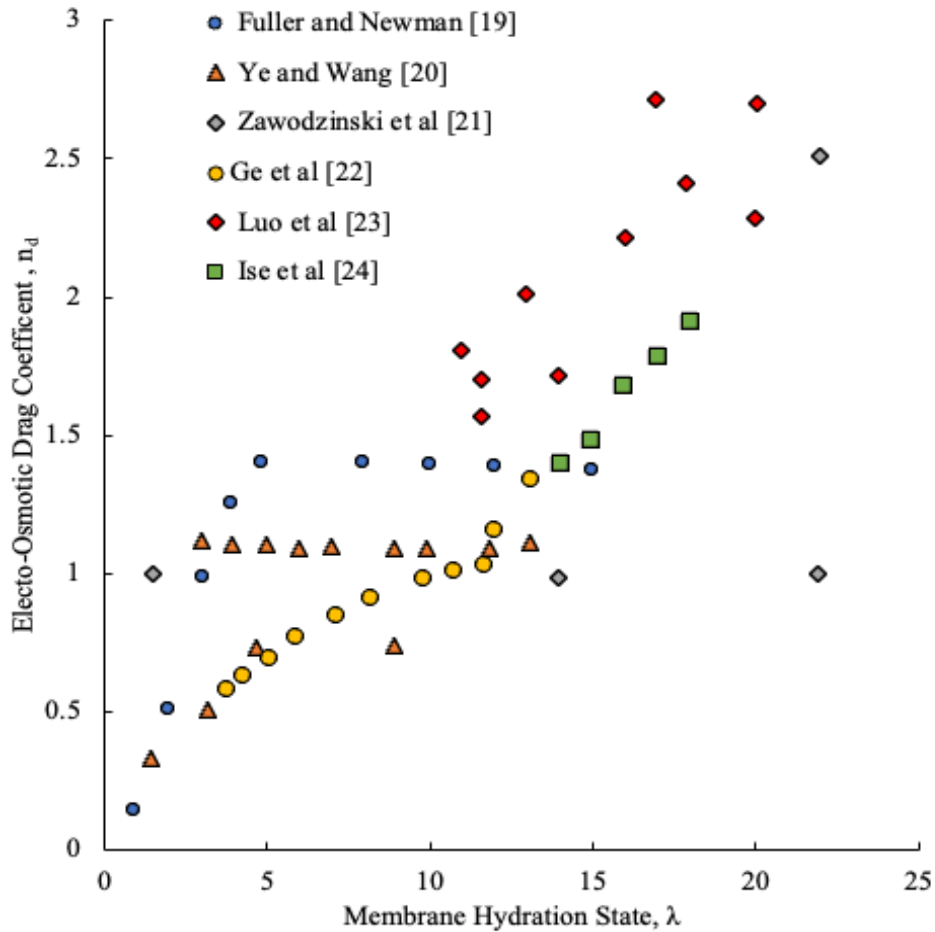


Figure 2.2.1 Electro-Osmotic Drag Coefficient Models [5]

The range of the coefficient and how the coefficient changes with hydration state varies by models. For instance, Ye and Wang [46], Fuller and Newman [45], Zawodzinski [47] show the electro-osmotic drag does not change with hydration state while Ge et al [48] show that the electro-osmotic drag increases with hydration state. It is unclear which trend is correct. In cases where the hydration state is greater than 14, liquid water will be present, and when the hydration state is less than 14, water vapor will be present in the fuel cell. The electro-osmotic drag coefficient is a function of hydration state of the membrane. It is not known if the electro-osmotic drag coefficient is a function of current density.

Luo et al [49], and Ise et al [50] have run their experiments with liquid water only so their models may only be applicable when liquid water is present but there is scatter between the two models. The cases with electro-osmotic drag are run with liquid water the electro-osmotic drag coefficient is much higher than the cases with liquid. The coefficient ranges from 1.5 to 3 compared to the water vapor cases where the coefficient ranges from 0.1 to 1.5. More water is being transported when liquid water is present. The electro-osmotic drag coefficient models assume electro-osmotic drag is only a function of hydration state, it is not known if the electro-osmotic drag is also a function of current density and could be determined by plotting the electro-osmotic drag coefficient as a function of current density.

Ge et al [48] had also noted that when the membrane is exposed to water vapor, the electro-osmotic drag coefficient is independent of temperature. When the membrane is exposed to liquid water the electro-osmotic drag coefficient varies linearly with temperature. Temperature will play a role when liquid water is present in the fuel cell. It is not known how which model is best for electro-osmotic drag. The other fluid driver of the Nernst-Planck equation is back diffusion; it depends on the concentration gradient. The back diffusion coefficient also impacts the back diffusion portion of the total water flow. There is not agreement on the back diffusion coefficient as shown in Figure 2.2.2:

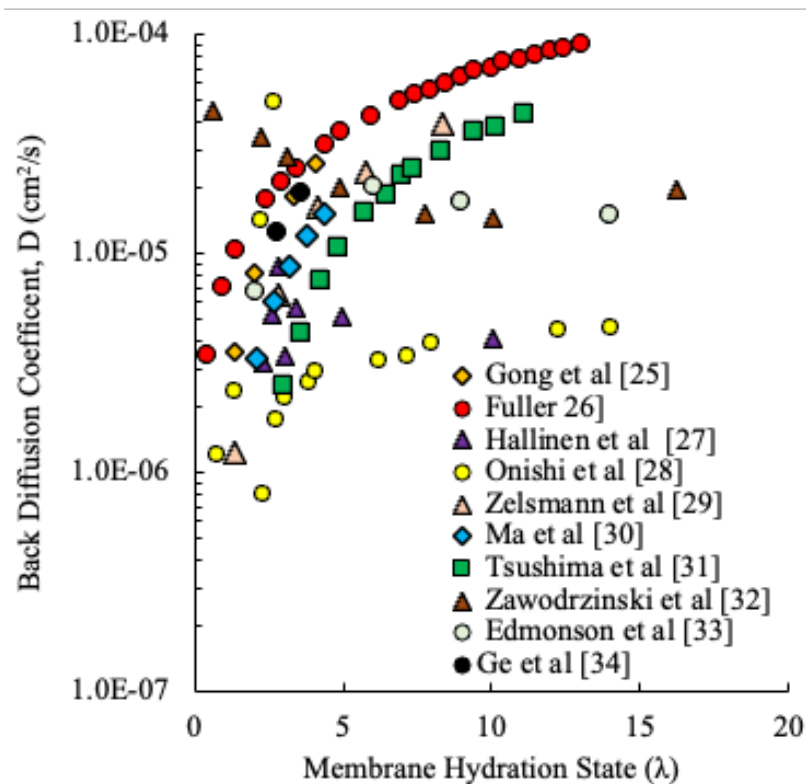


Figure 2.2.2 Back Diffusion Coefficient Models [5]

Like with the electro-osmotic drag the back diffusion model have scatter as well. All the data shows and increase in diffusion coefficient with hydration state but the scatter ranges

from $1 \times 10^{-6} \text{ cm}^2/\text{s}$ to $1 \times 10^{-4} \text{ cm}^2/\text{s}$. The back diffusion coefficient is a function of the hydration state of the membrane; it is not known if it is also a function of the concentration gradient. It is not known which model is applicable for the application. The back diffusion scatter does it make it difficult to determine the back diffusion portion of the total water flow. With the scatter in the electro-osmotic drag coefficient and back diffusion coefficient, a model cannot be selected to determine the electro-osmotic drag coefficient or back diffusion coefficient unless the model is validated against experimental results. With results reported as the total water transfer coefficient it makes it difficult to validate the electro-osmotic drag coefficient model and back diffusion coefficients.

2.3 Electro-osmotic drag and Back Diffusion

The first electro-osmotic drag model examined by Ren et al [61] where Ren et al [61] ran a total water flow experiment with a 5 cm^2 active fuel cell with a Nafion membrane. The experiment consisted of liquid methanol (CH_3OH) on the anode and humidified air on the cathode. The objective of the experiment was to determine the electro-osmotic drag coefficient. The total water flow vs current density is shown in Figure 2.3.1

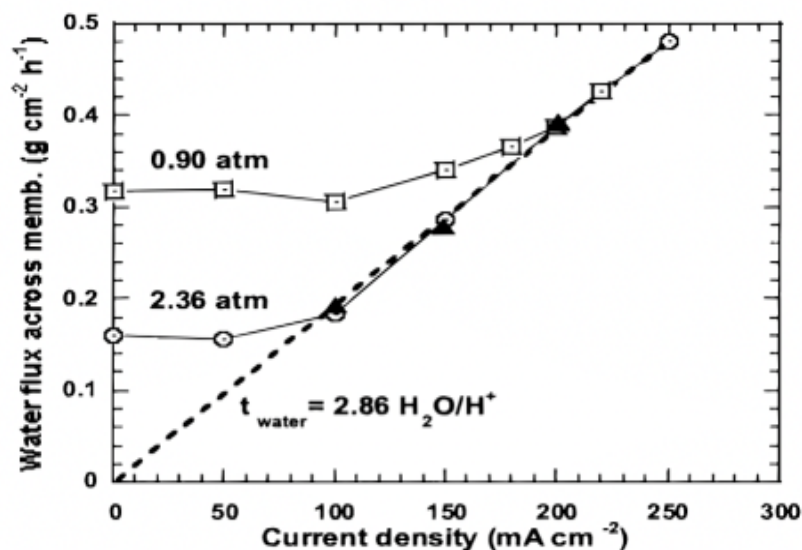


Figure 2.3.1 Total Water Flow vs Current Density [61]

The original data did include runs at two different pressures and these non-linear points were excluded because the contributions of electro-osmotic drag was low, the only data that was examined was the linear portion at high current density, it was assumed that electro-osmotic drag would dominate. Ren et al [61] stated the total water flow should yield a straight trendline that crosses the origin if the electro-osmotic drag coefficient is not a function of current density. The linear trendline was also forced through the origin assuming that all the fluid flow originates from electro-osmotic drag.

The total water flow data was fit to a linear trendline, which coincides with the Nernst-Planck equation. The Nernst-Planck equation has two components the electro-osmotic drag and back diffusion component. The slope of the trendline was used to determine the electro-osmotic drag coefficient but the slope of the existing trendline does include the back diffusion portion of the total water flow. It is not known if it is neglectable or a

major fluid driver. The total water flow needs to be broken down to determine how much of the total water flow is from electro-osmotic drag and how much is from back diffusion. In the direct methanol fuel cell cases, the total water flux was in the direction of anode to cathode or in the direction of liquid to vapor. In a methanol fuel cell liquid is present on the anode and water vapor is present on the cathode so this scenario contains liquid and vapor. Based on Adachi's [37] work water transport was in the direction of liquid to vapor, and the Schroeder Paradox could be impacting electro-osmotic drag.

Biesheuvel and Dykstra [62] also noted that electro-osmotic experiments contain volume flow from two components, the first component is flow from hydrated ions and the flow of water. Biesheuvel and Dykstra [62] also noted it takes two experiments to compute the electro-osmotic drag coefficient. One experiment is run with variable osmotic pressure different to determine the flow from osmotic pressure difference, the second experiment is run with electro-osmotic flow. The difference between the two will yield the electro-osmotic flow component. A second experiment was not seen for water flow without a voltage gradient. Ren et al [61] only conducted the one experiment to determine the electro-osmotic drag coefficient.

By forcing the trendline through the origin this will neglect the back diffusion component, this would imply that back diffusion does not contribute. The Nernst Planck equation shown in equation 17 has two components, the electro-osmotic drag and back

diffusion. By forcing the total water flow through the origin equation 25 is obtained from equation 17.

$$J_{Total} = n_d(\lambda) \frac{j}{F} - D(\lambda) \frac{\partial \epsilon}{\partial x} \quad (25)$$

This is will either overstate or understate electro-osmotic drag pending on the behavior of other fluid drivers. If the back diffusion component is in the opposing direction of electro-osmotic drag, then the electro-osmotic drag will be understated and when the back diffusion is in the same direction of electro-osmotic drag then the electro-osmotic drag will be overstated.

Ren et al [62] ran a similar experiment to the previous one but this time focused on the temperature effects in a DMFC. The total was flow across the membrane was measured. The membrane used was a Nafion membrane. The total water flow vs current density is shown in Figure 2.3.2. The active area of the DMFC is 5 cm². With a small active area fuel cell will result in small amount of water flow crossing the membrane.

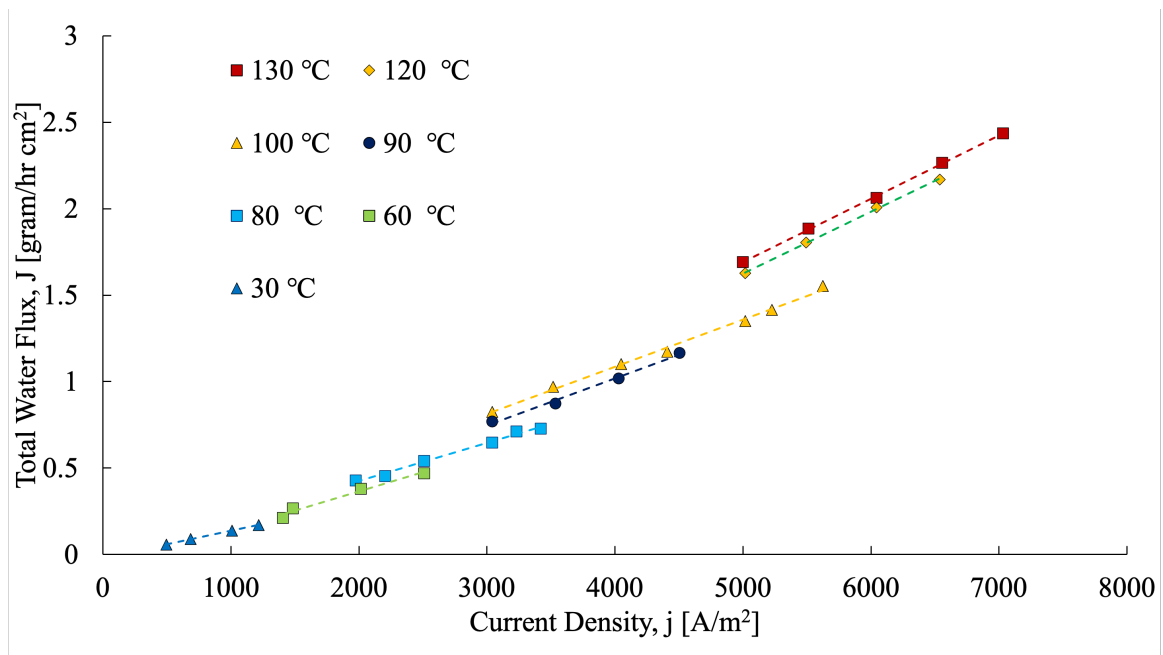


Figure 2.3.2 Total Water at Different Temperature [63]

The total water flow across the membrane was increasing with temperature and with current density. The total water flow data was reported, the total water transfer coefficient was not used. The original plot of the total water flow data shows that the total water flow trendline is forced through the origin which neglects contributions of other fluid drivers. The total water flow across the membrane is increasing with cell temperature, as a result the electro-osmotic drag coefficient will increase also. Not all the fluid flow is from electro-osmotic drag; the electro-osmotic drag portion of the total water flow needs to be determined. The direction of the water flow was in the direction of anode to cathode, indicating electro-osmotic drag exceeds back diffusion. The other fluid drivers need to be evaluated to see if forcing through the origin was a good assumption.

The total water flow is increasing with an increase in the cell temperature. The total water flow data needs further analysis. This experiment has water flow in the direction of anode to cathode and there was liquid on the anode. This case may have the Schroeder Paradox because liquid water is present at the anode. The total water flow needs to be analyzed to better understand how the electro-osmotic drag is changing with temperature.

Lee et al [64] used a hydrogen pump to simulate electro-osmotic drag on a fuel cell and ran two different fuel cells with different membrane thickness a 144 μm and an 18 μm Nafion membrane. The objective was to determine the electro-osmotic drag coefficient of the fuel cell. Lee et al [64] noted that the back diffusion was more apparent in the 18 μm Nafion membrane compared to the 144 μm membrane. The slope of the trendline was used to determine the electro-osmotic drag coefficient. The total water flow vs current density is shown Figure 2.3.3.

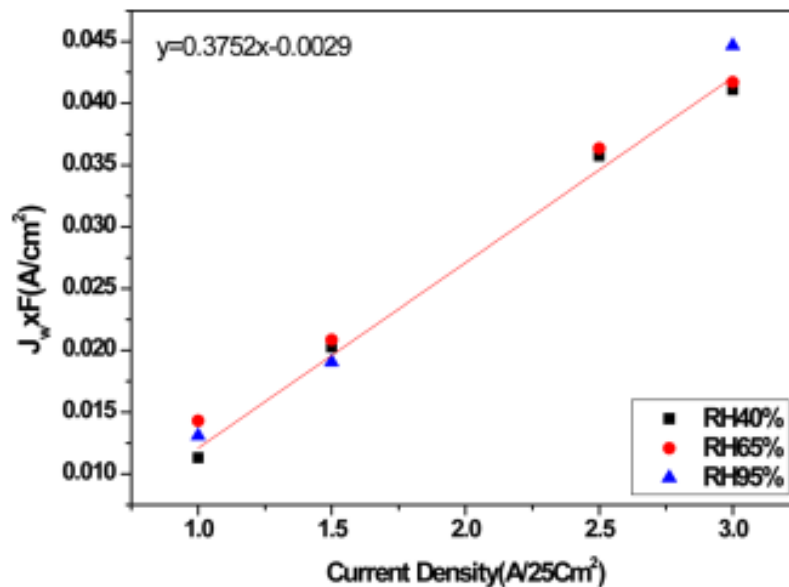


Figure 2.3.3 Electro-Osmotic Drag Coefficient Models [64]

The total water flow was not forced through the origin this approach is different from what Ren et al [61]. Lee et al [64] had forced the trendline through all three relative humidities, the membrane properties do change with the hydration state of the membrane based on the empirical electro-osmotic drag and back diffusion coefficient models. The electro-osmotic drag coefficients are dependent on the hydration state of the membrane; it is not known if it is a function of current density. There needs to be three trendlines, one for each relative humidity. A data fit is needed for each relative humidity to see if each case is linear.

The initial equation of shows electro-osmotic drag and back diffusion. The slope of the line is positive indicating that the water flow is in the direction of anode to cathode. The constant from the trendline is negative indicating it is in the direction of cathode to anode which corresponds to back diffusion. The relative humidity of the inlet gases will impact the hydration state of the membrane which will impact the electro-osmotic drag coefficient. The experimental data need to be further analyzed to by separating out each case and look at it individually.

Husar et al [65] attempted to understand water transport through the membrane due to individual fluid mechanisms such as electro-osmotic drag and back diffusion and hydraulic permeation in an operational fuel cell. The study is aimed at isolating the different mechanism by imposing special boundary conditions. It is believed that this method is better than total water transport across the membrane. The active area of the

fuel cell is 50 cm^2 . The fuel cell did have a micro-porous layer present. One of the assumptions made is that all the fluid flow comes from the measured fluid driver.

The first experiment by Husar et al [65] consisted of isolating the hydraulic permeation, this was done by setting the current of the fuel cell to 0 A, and by setting the same water content on both sides of the membrane to eliminate back diffusion. It is not known if this assumption is valid, the total water flow was not broken down into components. It is not known how much of the total flow is based on the pressure component. The total water flux across the membrane in the hydraulic permeation experiment is shown in Figure

2.3.4:

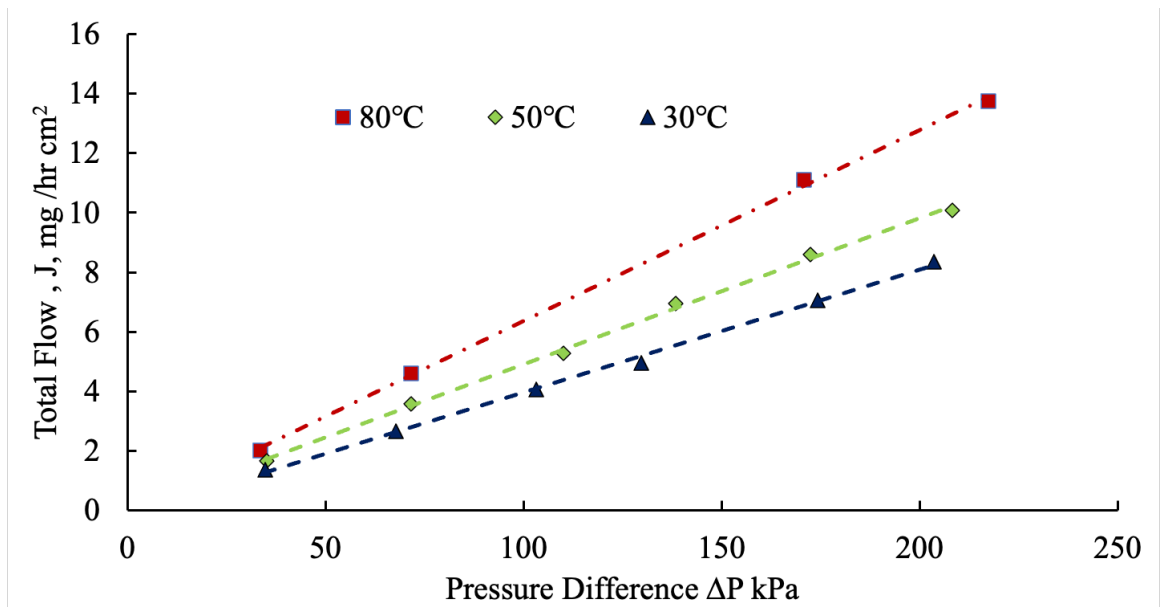


Figure 2.3.4 Total Water Flux from Hydraulic Permeation Experiment [65]

The total water flow was increasing linearly with the pressure difference. The total water flow was fit to linear trendline Husar et al [65] in the paper did not extrapolate the

trendline to the origin, it is not known if the flow was forced through the origin or if the data fit was not forced through the origin. It was assumed that all measured fluid flow originated from the pressure difference. Since the total water flow measured, the pressure component needs to be extracted from the total water flow. The strength of the other fluid drivers are unknown and need to be evaluated. Husar et al [65] noted as the temperature increases, the water flow through the membrane from hydraulic permeation increased. Husar et al [65] set up a separate water diffusion experiment where one side of the membrane was fed over saturated nitrogen and the cathode was fed dry air.

Lastly, Husar et al [65] ran an electro-osmotic drag experiment, where the pressure on the anode was the same as the pressure on the cathode to eliminate the effects of hydraulic permeation and to eliminate diffusion, the water content on both sides of the membrane is held the same. The anode was over saturated with water vapor, and the cathode is also over saturated with water vapor. The total water flow across the membrane from the electro-osmotic drag experiment is shown in Figure 2.3.5:

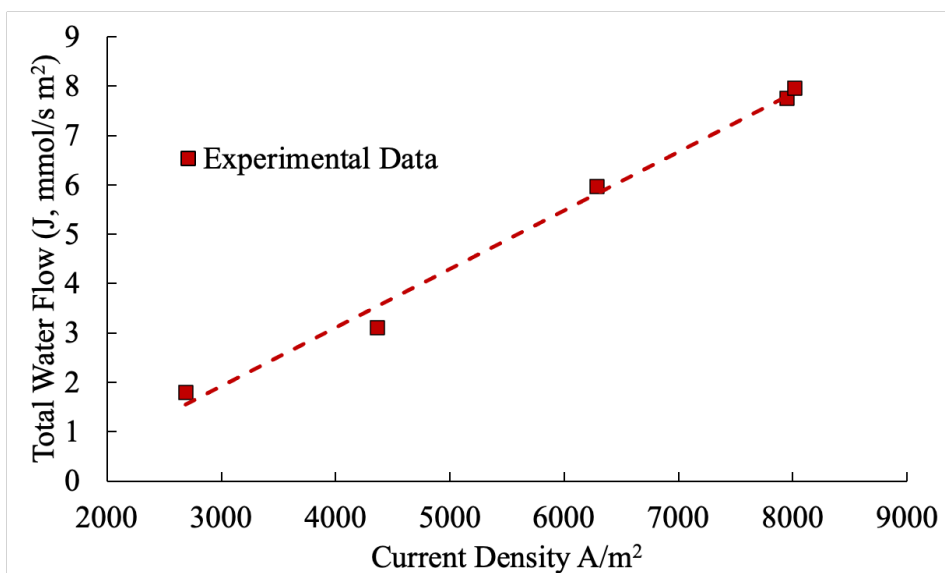


Figure 2.3.5 Total Water Flux from Electro-Osmotic Drag Experiment [65]

The total water flow does increase with current density. The total water flow was reported, and the total water flow did increase with current density. An assumption was made that all the total water flow is electro-osmotic drag, the total water flow was not broken down into its electro-osmotic drag and back diffusion components. The total water flow does increase with current density, since the total water flow was measured, the total water flow will contain electro-osmotic drag and back diffusion.

Husar et al [65] did not use the slope of the line to compute the electro-osmotic drag but did a calculation based on the mass balance. Husar et al [65] related the water transport across the membrane to the water generated by the fuel cell. The reported electro-osmotic drag coefficient is reported in Figure 2.3.6:

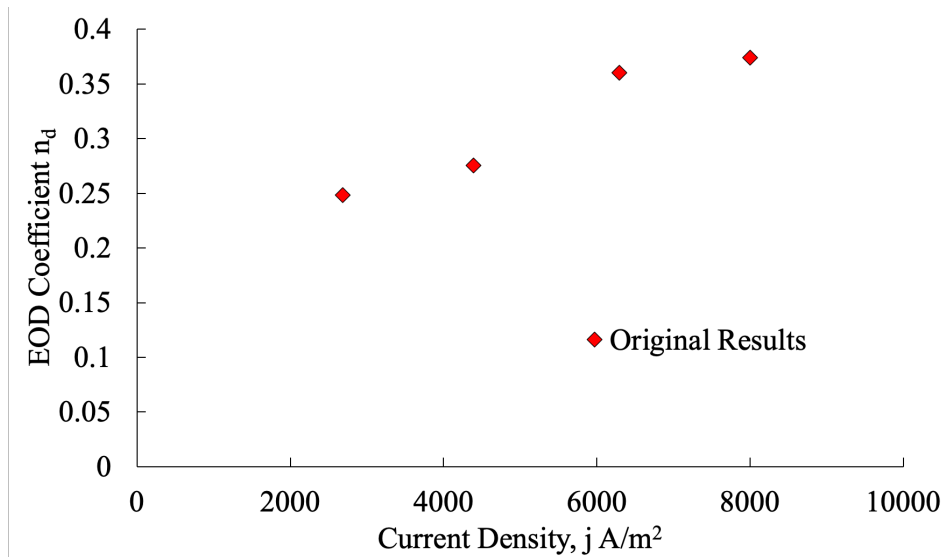


Figure 2.3.6 Reported Electro-Osmotic Drag Coefficient [65]

The reported electro-osmotic drag is increasing with current density, and this value is much lower than some of models, a further analysis is required. It is not known if the assumption of neglecting back diffusion is valid, the calculated electro-osmotic drag may have the back diffusion in it. The total water flow was not broken down into its electro-osmotic drag and back diffusion components. The total water flow must be reanalyzed with the total water flow broken down without assuming a transport coefficient.

Ye et al [46] had run a total water flow experiment with a hydrogen pump to determine the electro-osmotic drag coefficient for PEM fuel cells. Ye et al [46] had set up a 5 cm² PEM fuel cell Ye et al [46] had fit a trendline through all data points and the trendline went through the origin there was no consideration of how the hydration state of the membrane impacts the electro-osmotic drag coefficient. As shown in Figure 2.2.1, the electro-osmotic drag coefficient does change with the hydration state of the membrane.

Ye et al [46] assumes that the electro-osmotic drag is not changing at the different conditions and assumed that electro-osmotic drag is not a function of current density, it is not known if this assumption is valid also. The data trendline that was fit through all the data point was also forced through the origin. Ye et al [46] also noted that the membrane thick enough where back diffusion could be neglected, and this assumption was not validated. The plot of the data is shown in Figure 2.3.7, and the first membrane was a Gore membrane.

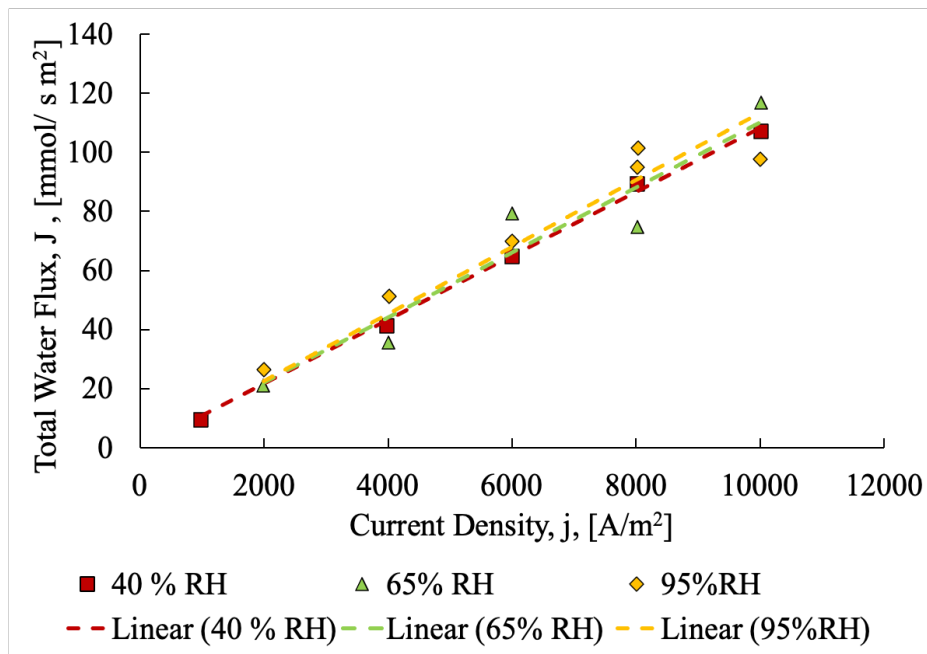


Figure 2.3.7 Total Water Flow via Hydrogen Pumping through Gore Membrane [46]

The total water flow was reported so there was no need to convert the total water transfer coefficient into the total water flow. The total water flow is changing with current density. The slope of trendline is positive, indicating the total water flow is increasing with current density. The slope of the trendline is constant is indicating that electro-

osmotic drag coefficient is not a function of current density. While the trendline is forced through the origin it will neglect other fluid drivers present. Based on the slope of the trendline through all data points and through the origin, Ye et al [46] had determined the electro-osmotic drag coefficient is 1.07. This is a contradiction between Nguyen and White's [32] data showing the electro-osmotic drag is decreasing with current density. The dependency of electro-osmotic drag on current density needs to be confirmed. By forcing the total water flow through the origin, it assumes there no back diffusion component. It is not known if this assumption is valid. The total water flow needs to be broken down into its electro-osmotic and back diffusion components to confirm if the assumptions made were valid. Also, the choice of the linear trendline needs to be further examined, it assumes that the electro-osmotic drag coefficient does not change, and it also assumes that the electro-osmotic drag coefficient is not a function of current density.

Adachi [37] conducted total water flow with variable membrane thickness and showed that the membrane thickness will impact the total water flow trendline. It was not established what membrane thickness is thick enough to prevent back diffusion because the total water flow was not broken down. The total water flow across the membrane needs to be broken down to determine how much back diffusion is present.

Ye et al [46] did run a second fuel cell which consisted of a Nafion membrane, and a third membrane Gore Select 25 μ m. As before the trendline was forced through the origin and the slope of the trendline was used to determine the electro-osmotic drag coefficient.

The slope obtained by Ye et al [46] was 1.10. Ye et al [46] repeated the same process for the second experiment. The total water flow is increasing with current density. The slope of the line indicates that electro-osmotic drag coefficient is constant. This is a contradiction between Nguyen and White's [32] data showing the electro-osmotic drag is decreasing with current density. Also, the total water flow was not broken down to determine how much of the total water flow is from electro-osmotic drag.

Ye et al [46] repeated the same test with a Gore-Select 25 μm membrane. As before the slope of the trendline through all the data was used to determine the electro-osmotic drag coefficient, which was 0.5, the trendline was also forced through the origin. As the membrane thickness decrease, the back diffusion portion of the total water flow will increase. The thinner membranes would promote more back diffusion than the previous cases. The total water flow was broken down into its electro-osmotic drag and back diffusion components to see if the assumptions made are valid and the data trendline needs to be examined to see if the linear trendline is the best fit.

Ge et al [48] set a up 25 cm^2 active area fuel cell and a hydrogen pump was used to simulate electro-osmotic drag. Ge et al [48] reported out the total water flow across the membrane as shown in Table 2-2. In this data, the total water flow was measured. The relative humidity across the membrane was varied and the current density fixed. In this experiment, an empirical model was selected back diffusion coefficient was selected and the electro-osmotic drag is determined as shown in equation 17. Ge et al [48] has chosen

their own back diffusion model from their own experimental data [60]. With the inconsistency of the back diffusion model, their electro-osmotic drag coefficient results will be depended on their back diffusion model. The goal is to independently determine both the electro-osmotic drag and back diffusion coefficient with the data provided.

Table 2.3-1 Total Water Flow Across the Membrane Ge et al [46]

Temperature	Current Density	RH1	RH2	Total Water Flow
T	j	α_i	α_r	Ny
K	A/m ²	%	%	mol/s m ²
303	500	60	40	0.001095
303	500	70	50	0.001647
303	500	75	55	0.001939
303	500	80	60	0.00222
303	500	85	65	0.00244
303	500	90	70	0.002548
303	500	95	75	0.002567
303	500	100	80	0.00257
303	500	100	85	0.002096
303	500	100	90	0.001627
323	1000	40	20	0.001495
323	1000	50	30	0.001677
323	1000	60	40	0.002221
323	1000	70	50	0.0326
323	1000	80	60	0.004843
323	1000	90	70	0.006511
323	1000	95	75	0.007221
323	1000	100	80	0.007831
323	1000	100	85	0.006874
323	1000	100	90	0.005858
353	2000	40	20	0.002878
353	2000	50	30	0.003708
353	2000	60	40	0.004793
353	2000	70	50	0.006538
353	2000	80	60	0.009121
353	2000	90	70	0.012914
353	2000	95	75	0.01505
353	2000	100	80	0.017407
353	2000	100	85	0.016377
353	2000	100	90	0.015131

The data in Ge et al [48] was not plotted to show how the trendline goes through the data.

Note the highlighted portion of the Ge et al [48] data reflects the two-phase flow and the

unhighlighted data points are single-phase region. Ge et al [48] reported electro-osmotic drag is shown Figure 2.3.8.

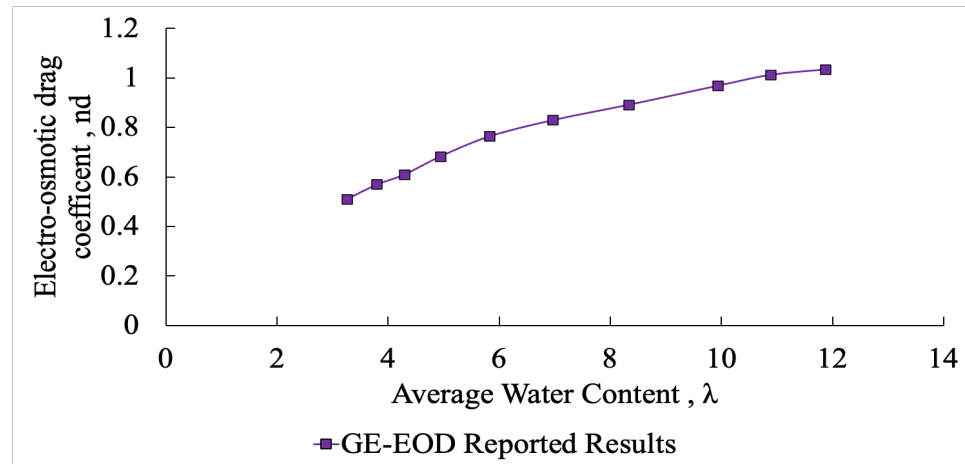


Figure 2.3.8 Computed Electro-osmotic drag coefficient from Experimental data [48]

Ge et al [48] is showing that the electro-osmotic drag coefficient is increasing with water content. Nugyen and White [32] have shown how electro-osmotic drag varies with current density, these are not comparable unless the hydration state of the membrane is known. The electro-osmotic drag was based on the back diffusion model selected; the back diffusion model was not validated with the experimental data. Since the data was performed at a fixed current density, it is not possible to see how the electro-osmotic drag changes with current density.

The total water across the membrane needs to be decomposed into its electro-osmotic drag and back diffusion components without assuming a back diffusion or electro-osmotic drag coefficient. The total water flow needs to be broken down without assuming a back diffusion coefficient model, a method is needed to determine electro-osmotic drag

and back diffusion assumption free. Kusoglu and Weber [5] also noted that the electro-osmotic drag coefficient does increase with temperature for liquid water. The temperature does not impact water vapor. The temperature impact on electro-osmotic drag is shown in Figure 2.3.9:

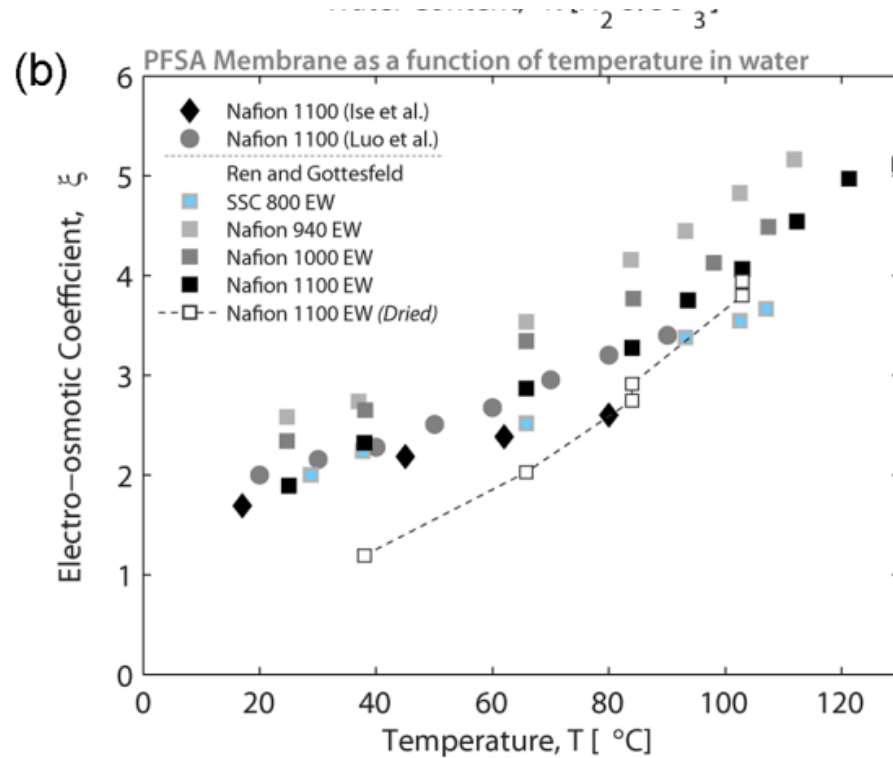


Figure 37. Electro-osmotic coefficient as a function of (a) water content (for Nafion at 25 °C unless otherwise noted) and (b) temperature in liquid-water (for Nafion and SSC PFSA).^{60,95,113,269,606,613–615,617}

Figure 2.3.9 Electro-osmotic drag in liquid water at different temperatures [5]

The electro-osmotic drag coefficient is increasing with temperature, this only occurs in the liquid water, it does not occur with water vapor. Temperature does impact electro-osmotic drag for liquids only. The same phenomenon was seen in Ren et al [63] This

phenomenon needs to be examined further; it seems that it coincides with Schroeder Paradox. The explanation of why the electro-osmotic drag is dependent on temperature for liquid has not fully understood.

Back Diffusion experiments were also examined, some of the experiments were already touched on in the electro-osmotic drag section with experiments by Yan et al [25] and Adachi [37] and in some back diffusion experiments have thermal osmosis or other effects mixed in with them. Chadha et al [73] ran a back diffusion experiment to obtain the back diffusion of Nafion. Chadha et al [73] had used the equation 26 to compute the back diffusion coefficient.

$$N_m = \frac{\rho}{EW} D_\lambda \Delta \lambda \quad (26)$$

This approach assumed that no other fluid drivers are present, Chadha et al [73] did not graph to show the functional fit the trendline data but did provide a table of values shown in Table 2.3.

Table 2.3-2 Determination of Back Diffusion Coefficient [73]

RH A	RHC	D (cm ² /s)	J (mmol/s m ²)
20	40	1.58E-07	0.6
20	80	2.35E-07	5.1
20	100	1.60E-07	8.1
40	60	4.31E-07	2.5
40	80	1.79E-07	3.1
40	100	1.26E-07	5.9
60	80	3.78E-07	4.4

The total water flux was measured, and the back diffusion coefficient was solved for back on knowing the concentration gradient. other fluid drivers could be present in the experimental results. The current process does not check to see if other fluid drivers are present, and the data must be further examined. The total water flux needs to be broken down into its fundamental fluid drivers. The back-diffusion portion of the total water flow must be determined, and the strength of the other fluid drivers needs to be confirmed because the current back diffusion coefficient could either be over or understated pending on the direction of the other fluid drivers.

2.4 Thermal Osmosis

There are several drivers for fluid flow, the fluid drivers are voltage gradient, concentration gradient, thermal gradient and pressure gradient as shown in Figure 2.4.1:

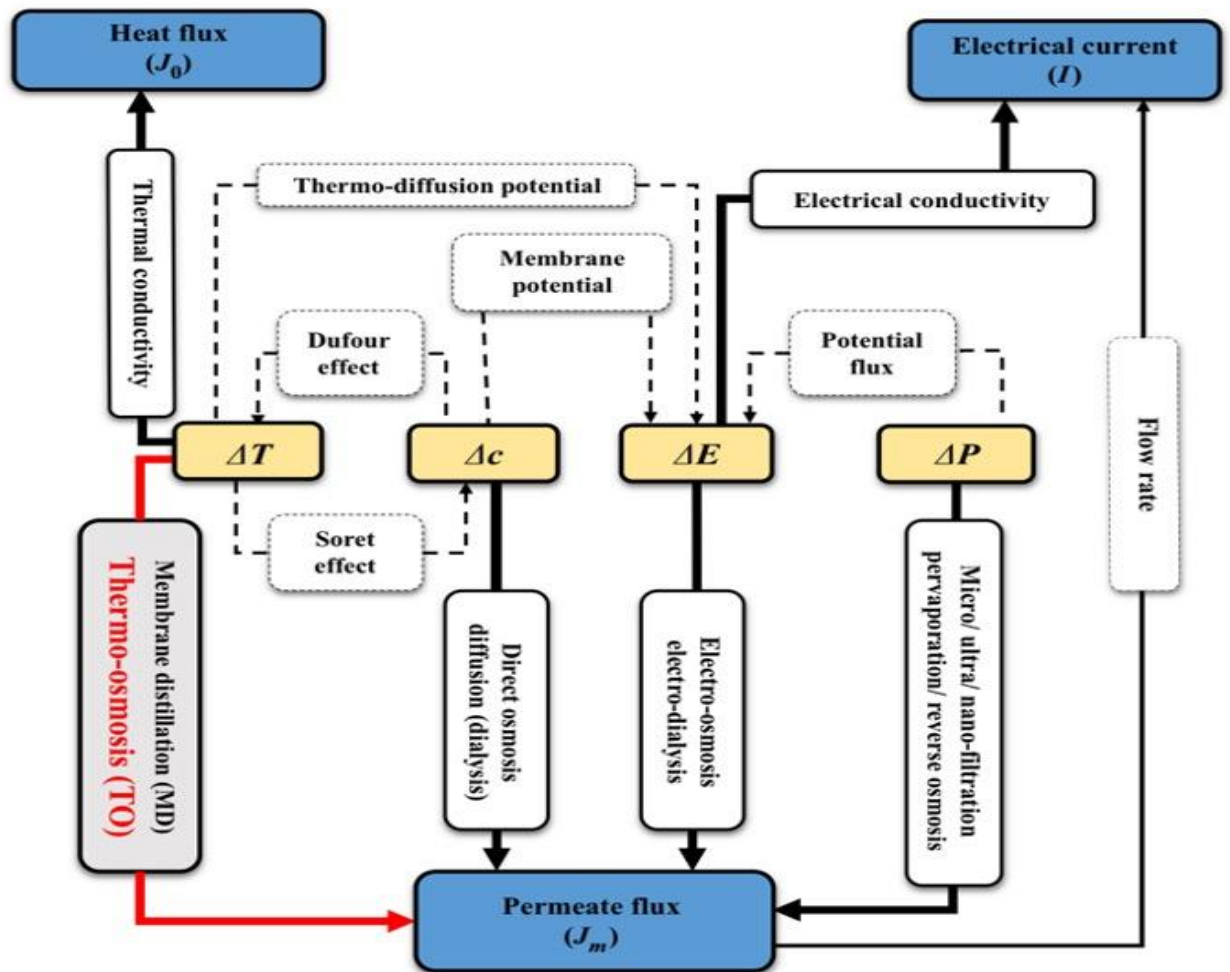


Figure 2.4.1 Energy, Charge and Fluid Driving Gradients [74]

The Nernst-Planck equation does not consider the thermal effects since it is an isothermal equation, to add thermal osmosis to the Nernst-Planck equation the magnitude and direction need to be considered. Thermal osmosis is fully understood with the magnitude, and the direction of the fluid flow is not fully understood. Kim and Mench [75] have stated that for a hydrophobic membrane the flow will be in the direction of hot to cold but for hydrophilic the direction is cold to hot. Kim and Mench [75] set up a fuel cell with 25 cm² active area.

Kim and Mench [75] focused on the temperature driven flow across the membrane. The thermal gradient across the membrane was varied and three different membranes were tested, the first one tested was Nafion 112, the second one was Gore-Select and the last was a Flemion membrane. The membranes tested have hydrophobic and hydrophilic regions and the experiments were conducted with liquid water. The Nafion membrane was run with different cell temperatures and the flow across the membrane was measured as shown in Figure 2.4.2:

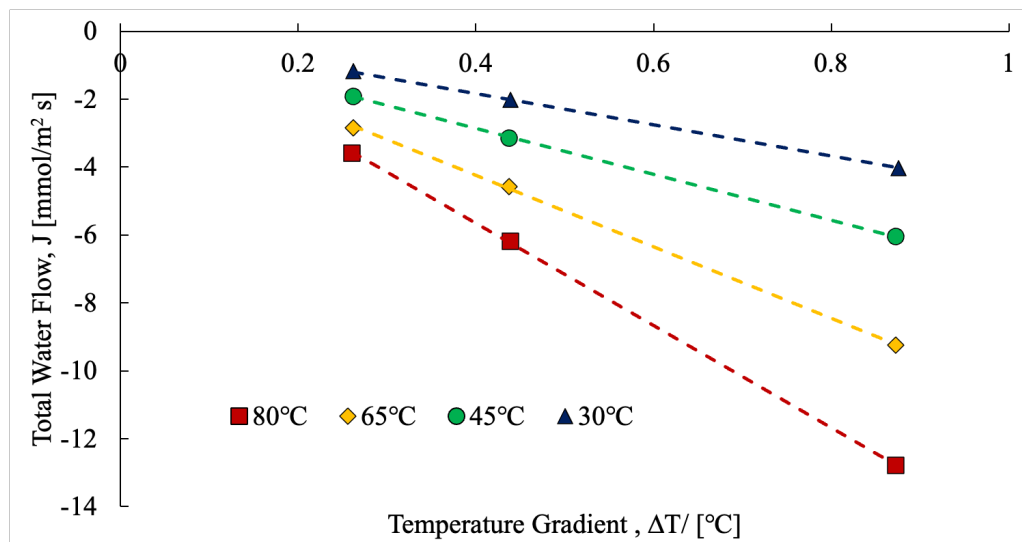


Figure 2.4.2 Temperature Driven Flow through Nafion [75]

The total water flow was reported, the slope of the trendline is negative indicating that the thermal osmosis is opposing the thermal gradient, this indicated that the thermal osmosis flow is in the direction of cold to hot. The trendline was forced through the origin which will assume that no other fluid drivers are present. Kim and Mench [75] had selected the Springer et al [33] back diffusion model that Nguyen and White [32] used in their

experiment and they had issues with the back diffusion model. In addition, there are several models for back diffusion, it is difficult to isolate thermal osmosis if the back diffusion is not known. The wrong back diffusion model would lead to an inaccurate thermal osmosis determination. Not all the fluid flow is from thermal osmosis that thermal osmosis portion of the total water flow needs to be obtained without assuming a back diffusion model.

Kim and Mench [75] stated that thermal osmosis is a function of temperature difference as shown in equation 27. The thermal osmosis should follow a linear trendline. The trendline should fit linear.

$$J_{TO} = -D_T \nabla T \quad (27)$$

The thermal osmosis coefficient is also a function of temperature; it follows an Arrhenius behavior as shown in equation 28. To obtain how the thermal osmosis transport coefficient changes with temperature multiple experiments are needed to compute the thermal osmosis coefficient at each temperature.

$$D_T = D_T^o e^{(-\frac{\Delta G}{RT})} \quad (28)$$

The thermal osmosis coefficient equation has two unknowns, the one thermal osmosis coefficient D_T^0 . The thermal osmosis coefficient and the Gibbs free energy. The two unknowns can be determined with equation 29.

$$\log_{10}(|D_T|) = \log_{10}(|D_T^0|) - .4343 \frac{\Delta G}{RT} \quad (29)$$

Kim and Mench [75] reported the Nafion thermal osmosis coefficient as a function of temperature, the value reported is shown in equation 30. The absolute value was used for the thermal osmosis transport coefficient, and it was not attempted without the absolute value. The Gibbs free energy is negative indicating that the process is spontaneous. The original data did not separate out the thermal osmosis portion of the total water flow.

$$D_T \left\{ \frac{kg}{m \ s \ K} \right\} = -1.04 * 10^{-5} e^{(-2362 \pm \frac{106}{T})} \quad (30)$$

There are other membranes that can be used for fuel cells, Nafion, Gore-Select and Flemon are other types of membrane. Each membrane will have a different amount of side changes which will make a membrane either more hydrophilic or less hydrophilic. The thermal osmosis coefficient was determined for Nafion, Gore-Select and Flemon, by plotting the total water flux vs the temperature gradient as shown in Figure 2.4.3.

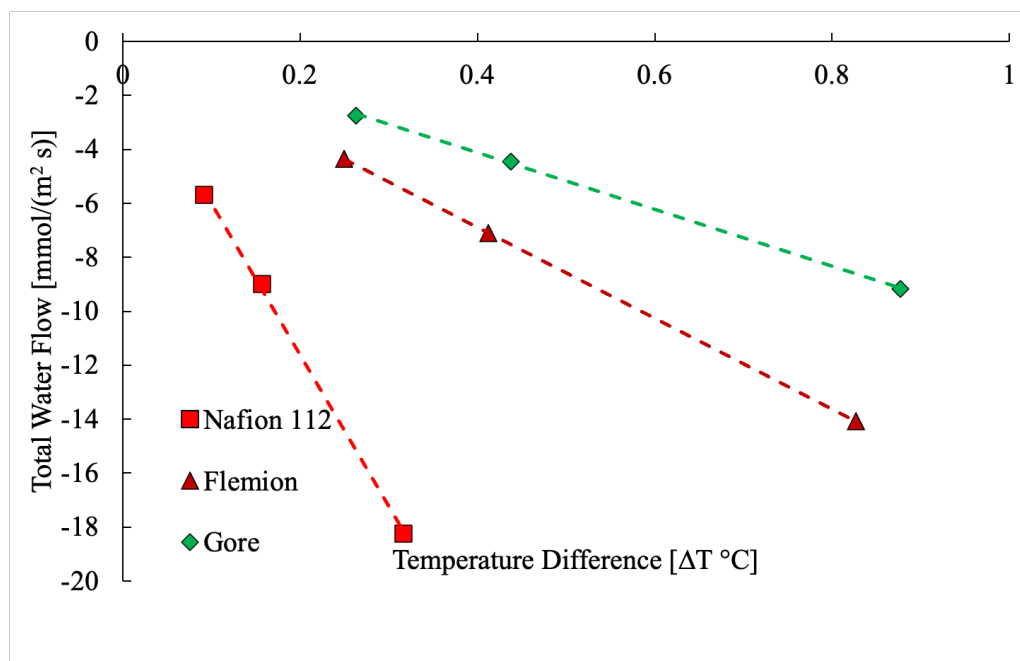


Figure 2.4.3 Temperature Driven Flow through Nafion, Gore and Flemion [75]

The total water flow is increasing with the thermal gradient. The membranes tested have hydrophobic and hydrophilic regions and it is not known if the membrane is more hydrophobic or hydrophilic in a liquid environment. The thermal osmosis experiment was performed with liquid water and not water vapor. The total water flow was reported, and the experimental data was fitted to a linear trendline that was forced through the origin. By forcing the trendline through the origin, it assumes that no other fluid drivers are present and all the fluid flow measured is from thermal osmosis. The slope of the line is negative, indicating that the thermal osmosis flow is opposing the thermal gradient. The data need to be refitting to a trendline that is not forced through the origin to determine how much of the total water flow is thermal osmosis.

Kim and Mench [75] stated that back diffusion is about 10 times larger than thermal osmosis with a temperature difference of 2°C, this comparison was done with the Springer et al [33] back diffusion model and must be examined further since there are several back diffusion models and the thermal osmosis will always be dependent on the model chosen. In addition, with the total water flow being so small, the assumption of forcing the total water flow through the origin needs to be examined further to make sure no other fluid driver is lumped in with thermal osmosis. There are several back diffusion models, and this conclusion was made to one of the models. The thermal osmosis portion of the total water flow needs to be obtained to understand its impact, and it needs to be compared to the back diffusion component to verify if Kim and Mench's [75] is valid.

Kim and Mench [75], [76] had started thermal osmosis in hydrophobic substances will go in the hot to cold direction and for hydrophilic substances the thermal osmosis flow is cold to hot. The objective of the experiments was to investigate a phenomenon known as phase change flow (PCI) in the PEM fuel cell. The study was aimed at quantifying water transport driven by thermal gradient. It is also aimed at distinguishing between thermal osmosis and phase change induced flow. A thermal osmosis experiment was not done with water vapor only and it is not known if the same logic for liquid will work with water vapor.

Kim and Mench [76] had noted that PCI will occur in catalysts layer (CL), microporous layer (MPL) or diffusional media when both water vapor and liquid water are present.

This process is sometimes called the heat pipe effect it involves the evaporation of water on the hot side and condenses on the cold side. Kim and Mench [76] had also noted that the driving force is driven by the vapor pressure difference, and the direction is always from the hot side to cold side regardless of the hydrophobic nature of the material. Experiments were not conducted with liquid on one side and vapor on the other. It was also noted that PCI exceeds thermal osmosis, thermal osmosis goes from cold to hot and PCI goes from hot to cold. Experiments were performed with liquid water. Kim and Mench [76] have plotted the total water flow through the membrane with hydrophilic material as shown in Figure 2.4.4. The total water flow was forced through the origin.

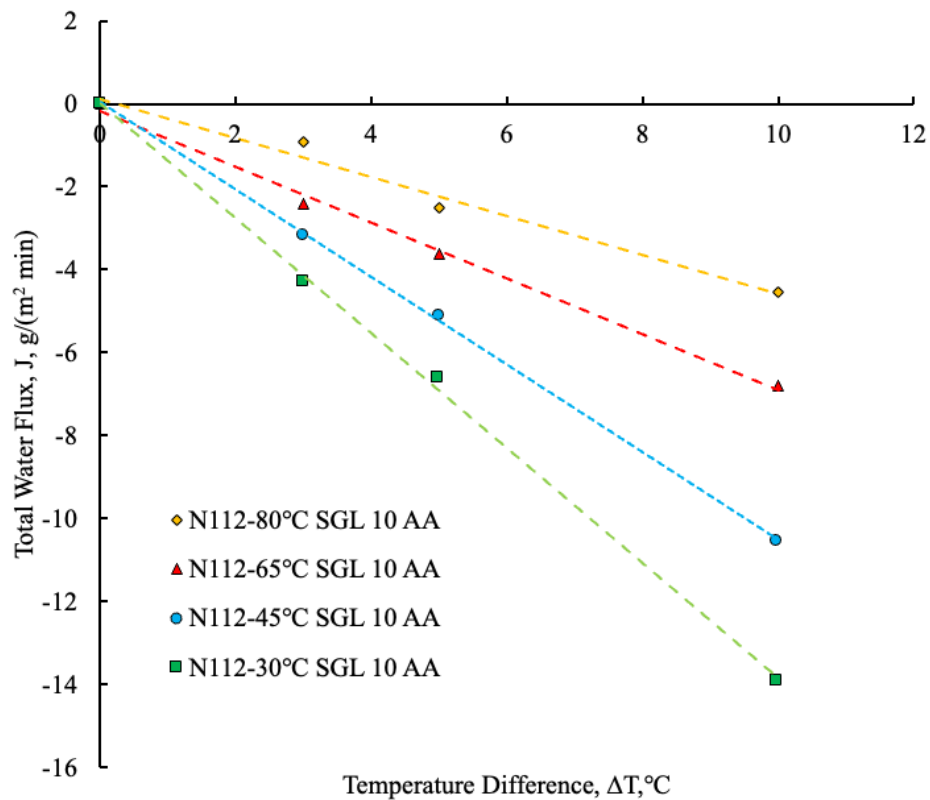


Figure 2.4.4 Temperature Driven Flow through Hydrophilic Material with liquid water [76]

The experimental data was also fitted to a linear trendline that is forced through the origin. In the hydrophilic scenario the total water flow was in the direction of cold to hot, the slope of the trendline is negative. By forcing the trendline through the origin it assumes that all the water flow across the membrane is thermal osmosis, and it assumes that no other fluid drivers are present. The data needs to be reexamined to extract the thermal osmosis portion of the total water flow and what are the contributions of the other fluid driver. The thermal osmosis was also run with hydrophobic material as shown in Figure 2.4.5:

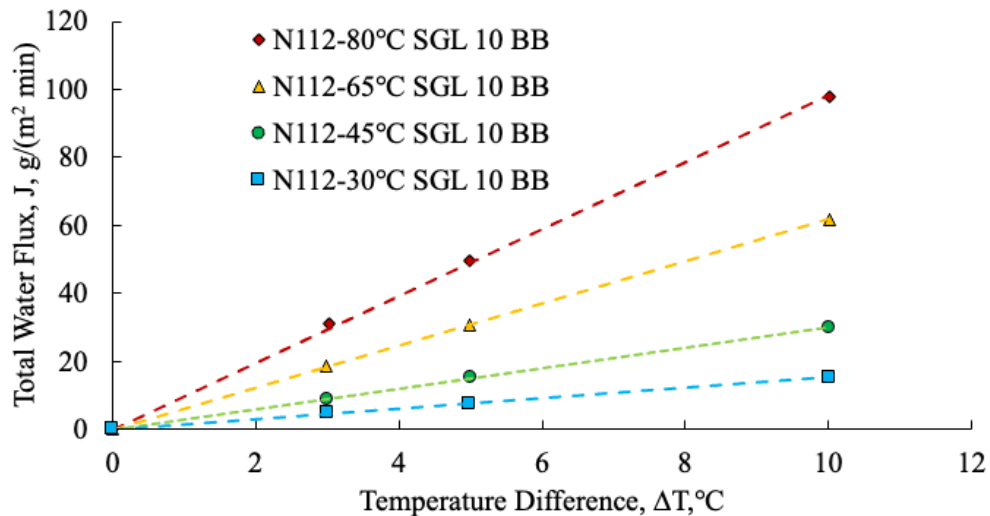


Figure 2.4.5 Temperature Driven Flow through Hydrophobic Material with liquid water [76]

The total water flow data was fit to a linear trendline that was forced through the origin. In the case with hydrophobic material, the total water flow was in the direction of hot to cold based on the slope of the trendline. The total water flow was increasing with the thermal gradient. The total water flow was fit to a linear trendline that was forced through the origin. By forcing the trendline through the origin, it assumes that all the total water

flow is thermal osmosis, and no other fluid drivers are present. The thermal osmosis portion of the total water flow needs to be extracted from the total water flow and the total water flow data needs to be reanalyzed.

The total water transfer for a hydrophobic case moves more water compared to the hydrophilic case. Kim and Mench [76] have also examined different membranes with different gas diffusion layers, one test set up had hydrophobic diffusion material and the second one had hydrophilic material. The hydrophobic case was also known as Phase Change Induced (PCI) flow where the liquid would evaporate and pass through the membrane then condenses when the water vapor passes through the membrane. There is also the Schroeder Paradox which states a membrane will pass more water when exposed to liquid water and moves less when exposed to water vapor.

When the hydrophobic material is added to the fuel cell, the total water flow was in the direction of hot to cold not cold to hot and the total water flow was forced through the origin. With other fluid drivers present in the experiment, the thermal osmosis portion of the total water flow needs to be extracted. The changes in the gas diffusion layer are causing the change in the direction of the fluid flow. More water flow is being moved across the membrane when the membrane is hydrophobic. The total water flow needs to be examined to determine how much of the total water flow is from thermal osmosis and the thermal osmosis must be extracted without assuming any transport coefficient. By separating the total water flow, the magnitude of thermal osmosis can be confirmed.

Villaluenga et al [77] ran thermal osmosis experiment with different mixtures of methanol and water ranging from 0% methanol to 100% methanol in a Nafion membrane with a finite temperature difference of the membrane. The area of the membrane was 25.2 cm². Villaluenga et al [77] theorized that the entropy difference between the fluid in the membrane and the free fluid will impact the direction of thermal osmosis flow. In the case where there is no pressure difference and concentration difference in the membrane, the thermal osmosis flow is expressed in terms of equation 31.

$$-J_i^o = D_i^o \Delta T \quad (31)$$

It is expected that thermal osmosis will follow a linear trendline like in the Kim and Mench cases. If J_i^o is in the direction of cold to hot as this experiment data will do, D_i^o and if the direction is hot to cold then D_i^o is negative. The thermal osmosis coefficient can also be expressed in terms of entropy as shown in equation 32.

$$D_i^o = D_i^* \Delta s \quad (32)$$

The entropy difference will influence the direction of thermal osmosis, if the direction of thermal osmosis. If the entropy change is positive then the direction will be cold to hot, if the entropy change is negative then the direction will be hot to cold. The total water flow across the membrane is shown in Figure 2.4.6:

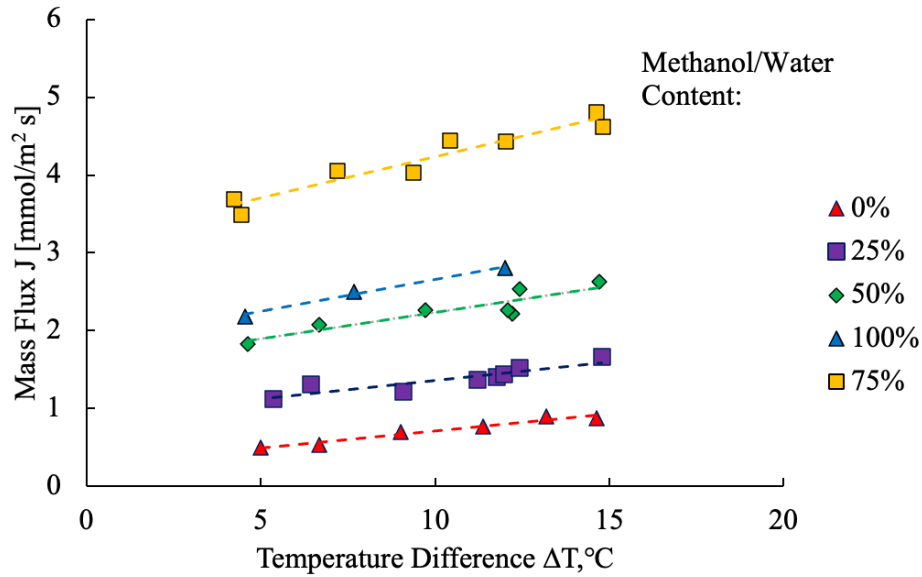


Figure 2.4.6 Temperature Driven Flow for Different Concentration of Methanol [77]

The total water flow across the membrane was fit to a linear trendline, the data trendlines appear not to go through the origin, and this indicates that other fluid drivers are present. Since the total water flow was measured, an unknown percentage of the total water flow is thermal osmosis.

Villaluenga et al [77] noted “**In the case of pure water or methanol, the thermal osmosis coefficient D_i^o can be estimated by fitting the data to equation 30, the fittings of the data was deemed good with correlation coefficients equal to 0.94.**” If the total water flow is forced through the origin, then other fluid drivers are present in experiment are lumped in the thermal osmosis data. The trendlines do not go through the origin which indicates that another fluid driver is present. The strength of the other fluid drivers is not known and it must be determined without assuming a thermal osmosis coefficient.

The positive slopes of the trendlines indicate that the temperature driven flow is in the direction of cold to hot like Kim and Mench [76]. The data must be reanalyzed in such a way where the trendline does not go through the origin and the thermal osmosis portion of the total water flow needs to be obtained. The true thermal osmosis needs to be obtained free of assumption and this can be done through analyzing the total water flow data.

Fu et al [78] has set up an experiment with Nafion membrane with an active area of 25 cm². Their goal was to determine if back diffusion is dominant over thermal osmosis. The catch is there are several back diffusion models, if a model is chosen then the thermal osmosis will be dependent on the back diffusion coefficient model chosen. The study concluded that in the context of a polymer electrolyte membrane fuel cell (PEFC) under thermal gradients, the dominant mechanism for water transport across the membrane is not thermal osmosis (thermo-osmosis), but rather diffusion driven by a water concentration (activity) gradient induced by the temperature difference. Specifically, although previous works have reported water flux due to thermo-osmosis (typically from the cold side to the hot side when both sides are in contact with liquid water), the experimental results in this study showed that when both inlet gases are fully humidified, the water flux is in the direction from the hot side to the cold side. The numerical model, which did not include thermo-osmosis but instead modeled diffusion due to concentration gradients, closely agreed with the experimental results. This suggests that thermo-osmosis is negligibly small under PEFC operating conditions, and the water transport is

dominated by diffusion driven by the concentration gradient resulting from the temperature difference. The experiment consisted of keeping the cold side of the membrane at constant temperature and at 100% RH, and the hot side RH is varied from 30% to 85 % The experimental total water flow is shown in Figure 2.4.7.

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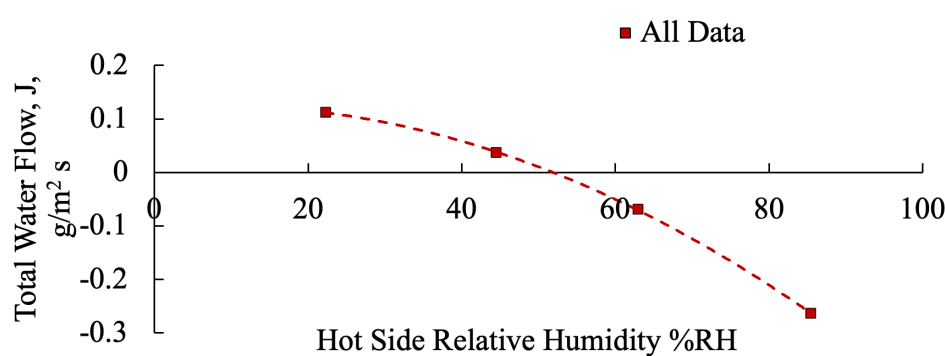


Figure 2.4.7 Temperature Driven Fluid Flow [78]

The total water flow does not vary linearly with the relative humidity, the total water flow changes direction when the hot side relative humidity is greater than 50%. The current data is not expressed in terms of the concentration gradient. The concentration gradient needs to be determined to obtain the back diffusion portion of the total water flow. Fu et al [78] had selected Motupally et al [79] back diffusion model, this is one of the many back diffusion models to calculate the back diffusion portion of the total water flow. their conclusions about thermal osmosis are coupled with the Motupally et al [79] back diffusion model. The thermal osmosis portion of the total water flow depends on the back diffusion model chosen. There is not agreement on the back diffusion models so it is not known if this is the best model to choose. A method is needed to independently determine back diffusion and thermal osmosis portion of the total water flow and once they are separated then the back diffusion and thermal osmosis can be compared to one another.

The experimental data does not break down the total water flow into its back diffusion and thermal osmosis components so any conclusion about thermal osmosis are not conclusive. The conclusions made were based on the selected back diffusion model, and different back diffusion models would yield different results. The back diffusion portion of the total water flow needs to be extracted from the total water flow without assuming a back diffusion model. The total water flow needs to be broken down to isolate the back diffusion and thermal osmosis portion of the total water flow to reach conclusions on thermal osmosis, also the actual back diffusion model was not compared to the back

diffusion model used. The back diffusion portion of the total water flow needs to be extracted from the total water flow without assuming a back diffusion model. The total water flow needs to be broken down to isolate the back diffusion and thermal osmosis portion of the total water flow to reach conclusions on thermal osmosis, also the actual back diffusion model was not compared to the back diffusion model used.

Zaffou et al [80] set a 25 cm² fuel cell with a water balance on the anode and cathode. The fuel cell was run at a constant current density, and the inlet gases were fully humidified. The total water flow across the membrane was recorded, and this total water flow will contain electro-osmotic drag, back diffusion and thermal osmosis. The experiment was designed to quantitatively investigate the effect of the through plane temperature difference effect on the water transport across the membrane. The experiment was also aimed at determining whether a temperature difference across the fuel cell could cause significant water transport. The test results were intended to consider the through plant temperature profile in the design and operation of the fuel cell. The test data is shown in Table 2.4-1

Table 2.4-1 Total Water Flow through the Fuel cell [80]

Temperature of liquid water in WTP _{cathode} (°C)	Temperature of liquid water in WTP _{anode} (°C)	Cell Voltage (V)	m^a_{mem} (g/min)	m^c_{mem} (g/min)	Error* (%)
60	60	0.688	-0.0323	-0.0388	12
			-0.0243	-0.0308	12
	57	0.688	-0.0599	-0.0575	-4
			-0.0502	-0.0598	17
	55	0.680	-0.0633	-0.0664	6
			-0.0626	-0.0696	13
65	50	0.686	-0.1090	-0.1101	2
			-0.1105	-0.1077	-5
	65	0.671	0.0042	0.0042	0
			-0.0061	-0.0075	2
	62	0.689	-0.0551	-0.0639	16
			-0.0546	-0.0639	17
70	60	0.690	-0.0714	-0.0808	17
			-0.0767	-0.0772	1
	55	0.690	-0.1322	-0.1397	13
			-0.1117	-0.1171	10
	70	0.675	0.0034	0.0064	-5
			0.0053	0.0053	0
75	67	0.684	-0.0680	-0.0659	-4
			n/a	n/a	n/a
	65	0.684	-0.0831	-0.0853	4
			-0.0788	-0.0747	-7
	60	0.692	-0.1369	-0.1422	9
			-0.1453	-0.1466	2
75	75	0.682	0.0575	0.0573	0
			n/a	n/a	n/a
	72	0.680	-0.0603	-0.0647	8
			n/a	n/a	n/a
	70	0.684	-0.1159	-0.1153	-1
			n/a	n/a	n/a
75	65	0.682	-0.1674	-0.1602	-13
			-0.1694	-0.1648	-8

Zaffou et al [80] noted that the thermal osmosis water flow on an active fuel cell at a fixed current density. The experiment consisted of fixing the cathode temperature and varying the anode temperature. The total water flow across the fuel cell membrane consisted of electro-osmotic drag, back diffusion and thermal osmosis. The composition of the total water flow is not known. The electro-osmotic drag, back diffusion and thermal osmosis portion of the total water flow need to be computed. The total water flow

was in the direction of hot to cold. Zaffou et al [80] also plotted the total water flow vs the temperature difference as shown in Figure 2.4.8:

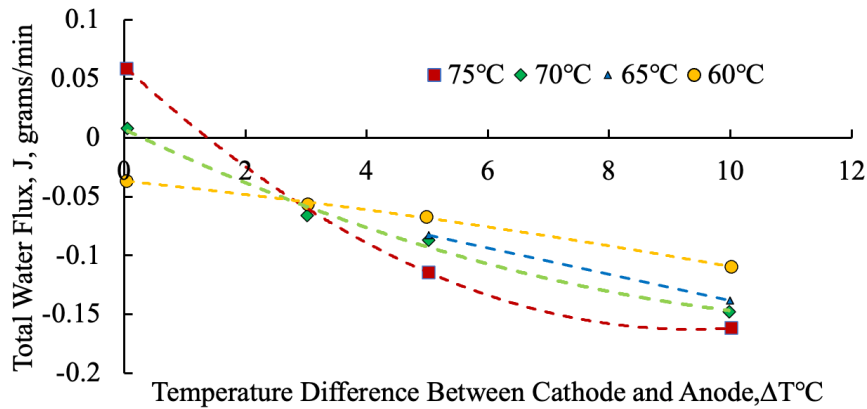


Figure 2.4.8 Total Water Flow through the Fuel cell [80]

The total water flow was fit to a polynomial for three of the four cases, the 65°C case was fit to a linear trendline. There is water flow at no temperature difference across the membrane, this is a result of other fluid drivers being present such as electro-osmotic drag and back diffusion, these fluids drivers need to be isolated from the total water flow. Zaffou et al [80] did not break down the total water flow into its fundamental fluid drivers and this needs to be completed to fully understand thermal osmosis. The variation in the electro-osmotic drag and back diffusion models make it difficult to assume a transport coefficient, the experimental data must be used to obtain the thermal osmosis portion of the total water flow, and the thermal osmosis must be compared to the other fluid drivers.

Thomas et al [81] set up 24 cm² PEM fuel cell to perform a quantitative study on the thermal effects on water transport. The temperature difference was fixed, and the current

density is varied, and both the anode and cathode relative humidity was set to 100 %.

There were three cases examined, the first one being an isothermal case, a case where the cathode is warmer than the anode, and the last case is where the anode is warmer than the cathode as shown in Figure 2.4.9. Thomas et al [81] noted that the water flow was in the direction of hot to cold, this is contradiction to what Kim and Mench [75] and Villalunga et al [77].

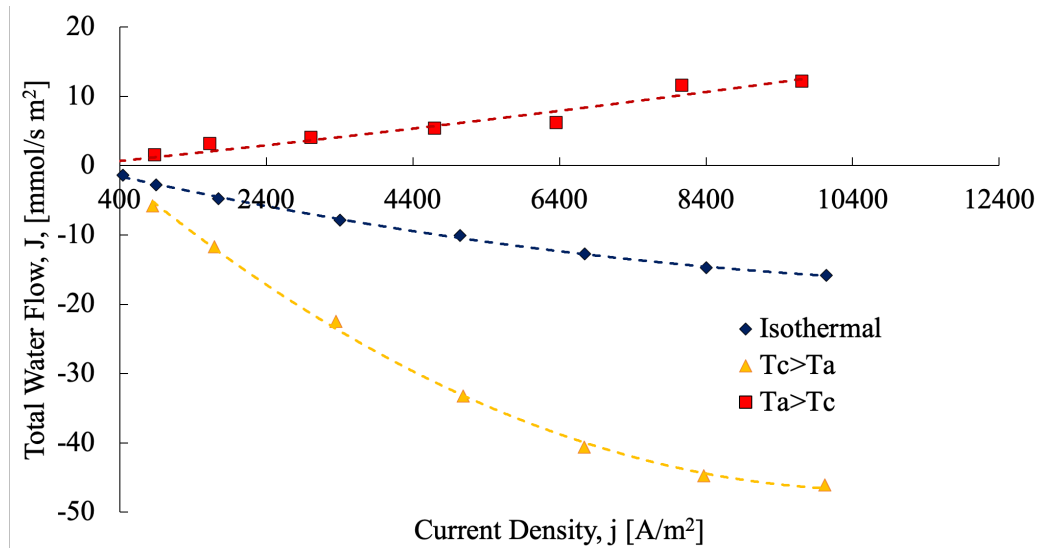


Figure 2.4.9 Total Water Flow with Fixed Temperature Difference [81]

The total water flow was reported and not the total transfer coefficient, and the total water flow does not vary linearly with current density. In the isothermal case the direction of the total water flow was in the hot to cold direction or cathode to anode, and this for all current densities. When the temperature of the cathode was increased, the total water flow across the membrane increased and the direction did not change but when the anode was warmer than the cathode the direction of water was in the hot to cold direction, and the direction of water flow was from anode to cathode. The thermal gradient did impact

the direction of the total water flow. The direction of the total water flow was influenced by the thermal gradient; the total water flow was flowing in the hot to cold direction.

Thomas et al [81] noted that vapor transport dominated over thermal osmosis. The total water flow was not broken down into its components. The fuel cell was generating current, and the fuel cell will have electro-osmotic drag, back diffusion and thermal osmosis. The total water flow was not broken down into its electro-osmotic drag, back diffusion and thermal osmosis components. The data needs to be reanalyzed to extract thermal osmosis from the total water flow and compare it to the other fluid drivers.

Kjelstrup [82] had duplicated Kim and Mench [76] thermal osmosis experiments as with hydrophobic and hydrophilic material to better understand thermal osmosis. Like Kim and Mench [76] the total water flow was fitted to a linear trendline which was forced through the origin as shown in Figure 2.4.10. The thermal osmosis experiments were performed with liquid water. The original trendline was forced through the origin, by forcing the data trendline through the origin this would assume that all the total water flow thermal osmosis which would neglect other fluids drivers present in the experiment.

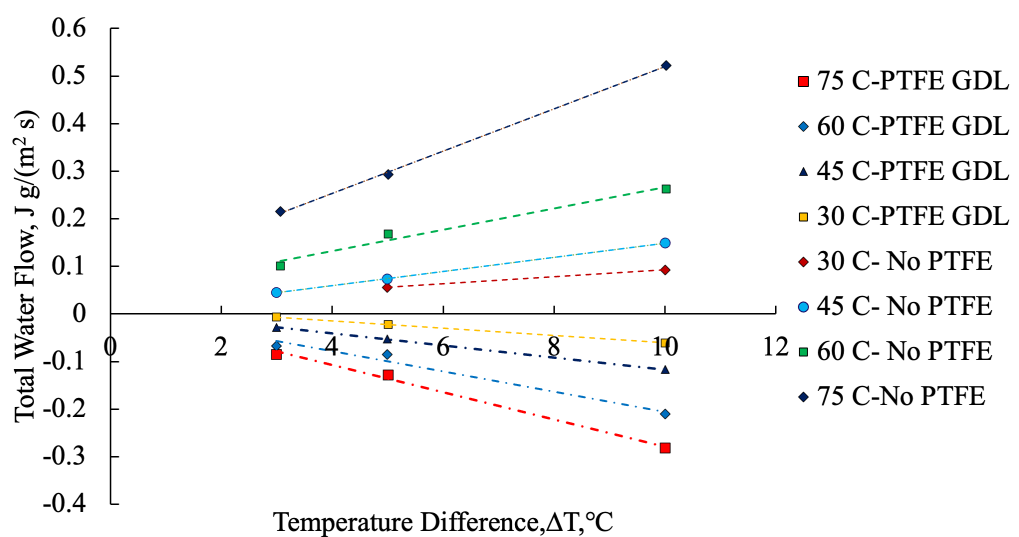


Figure 2.4.10 Total Water Flow with Fixed Temperature Difference [81]

Like in Kim and Mench [76], the total water flow was fitting to a linear trendline that was forced through the origin; this assumes that all the fluid flow is from thermal osmosis and no other fluid drivers are present. It is not known if this assumption is valid. As in Kim and Mench [76] thermal osmosis work, the direction for hydrophobic material was hot to cold and for hydrophilic cold to hot, this direction was confirmed by the slope of the trendline, if the slope is positive then the temperature driving flow is moving with the thermal gradient and if it is negative the temperature driven flow is moving against the thermal gradient. The data needs to be further analyzed to ensure that only the thermal osmosis portion of the total water flow was extracted. In addition, it is not known if the other fluid drivers are substantial drivers or neglectable. The thermal osmosis portion of the total water flow need to be extracted and its contribution to the total water flows needs to be determined. It is not known if the other fluid driver is negligible or a major factor this must be determined before any conclusion is made about thermal osmosis.

Bozkurt et al [83] have also run thermal osmosis experiments with hydrophobic and hydrophilic material. The experiments were performed with liquid water. Their experiment consisted of measuring the thermal osmosis diffusion coefficient for various fuel cell configuration with hydrophobic and hydrophilic material. Their objective is to combine effects of all the layers in the fuel cells, these layers consist of the gas diffusion layer, membrane and microporous layer. The first experiment was performed with a hydrophobic case where Nafion membrane is surrounded by hydrophobic material as shown in Figure 2.4.11:

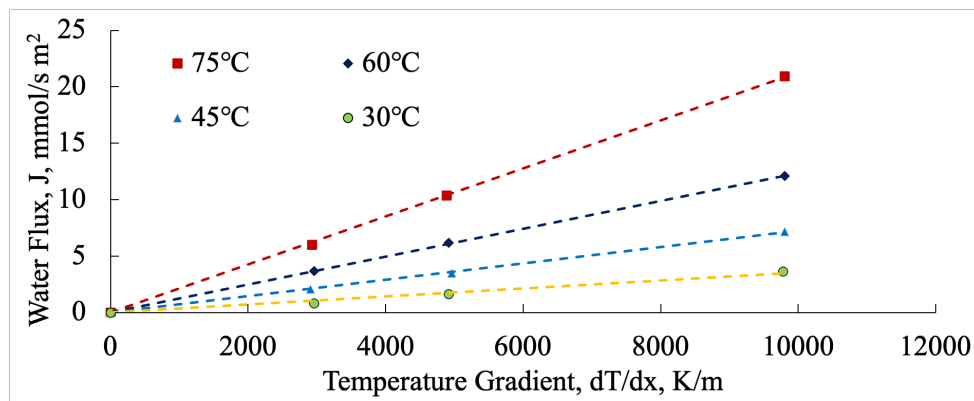


Figure 2.4.11 Total Water Flow with Fixed Temperature Difference [81]

The total water flow data trendline was forced to a linear trendline through the origin, which assumes no other fluid drivers are present. Forcing the trendline through the origin assumes all the fluid flow across the membrane is from thermal osmosis. The slope of the line was used to determine the thermal osmosis coefficient. The direction of the water flow was in the direction of hot to cold based on the positive slope. The thermal osmosis portion of the total water flow was not separated from the total water flow and

composition of the total water flow was not determined. It is not known if the other fluid drivers are substantial or neglectable. The thermal osmosis portion of the total water flow needs to be determined free of assumptions.

Bozkurt et al [83] ran the experiment at different temperatures and with the thermal osmosis coefficient at each temperature the activation energy can be determined as shown equation 33. To do so, multiple experiments are needed at different temperatures.

$$\ln D_T = \ln (|D_T^0|) + \frac{E_a}{RT} \quad (33)$$

The absolute value of the thermal osmosis coefficient was taken regardless of the material. The activation energy is determined by plotting the calculated thermal osmosis coefficient at each temperature. The activation energy is determined by taking the natural log thermal osmosis coefficients from Figure 2.4.11 and plotting them over the inverse of absolute temperature as shown in Figure 2.4.12. The hydrophobic and hydrophilic cases are treated the same way.

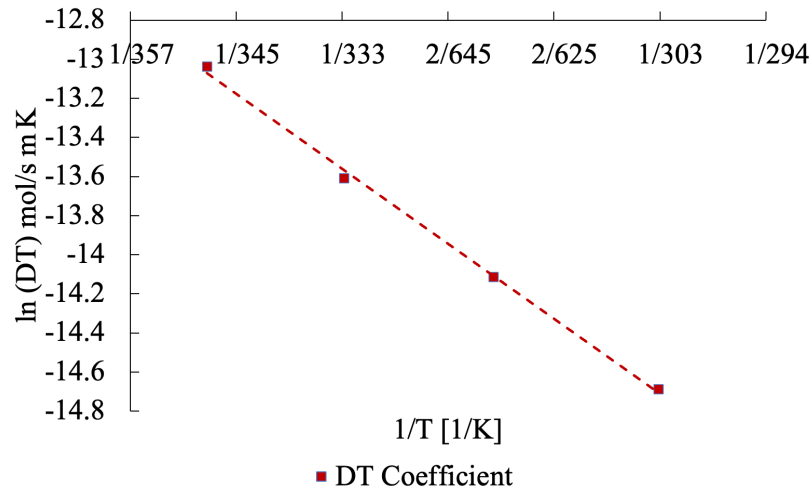


Figure 2.4.12 Activation Energy from Hydrophobic Case [81]

The linear trendline is obtained and the activation energy can be calculated, the thermal osmosis coefficient with only thermal osmosis water flow needs to be used. The results are based on the absolute value of the thermal osmosis coefficient. Since the thermal osmosis coefficient was used from original data it will have other fluid drivers lumped in with it and it must be determined with a thermal osmosis coefficient free of other fluid drivers. The activation energy will need to be redetermined with a new thermal osmosis transport coefficient.

Bozkurt et al [83] also examined a test set up with Nafion surrounded by hydrophilic material. The total water flow was plotted against the temperature gradient as shown in Figure 2.4.13:

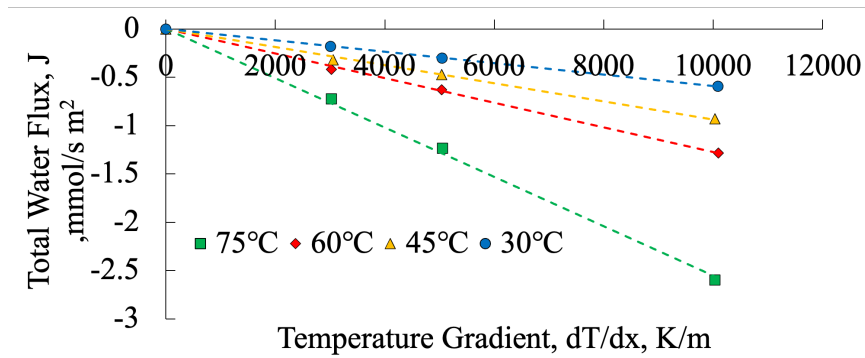


Figure 2.4.13 Water Flux for hydrophilic Case [81]

As before the total water flow was fitted to a linear trendline that is forced through the origin assuming no other fluid drivers are present, and assuming that the total water flow across the membrane is equal to thermal osmosis. The slope of the lines was used to determine the thermal osmosis coefficient. In this case slope is negative and the water flow was in the direction of cold to hot. The thermal osmosis coefficient was used on each case to determine the activation energy, equation 33 was used to determine the activation energy. The plot to determine the activation energy is shown in Figure 2.4.14:

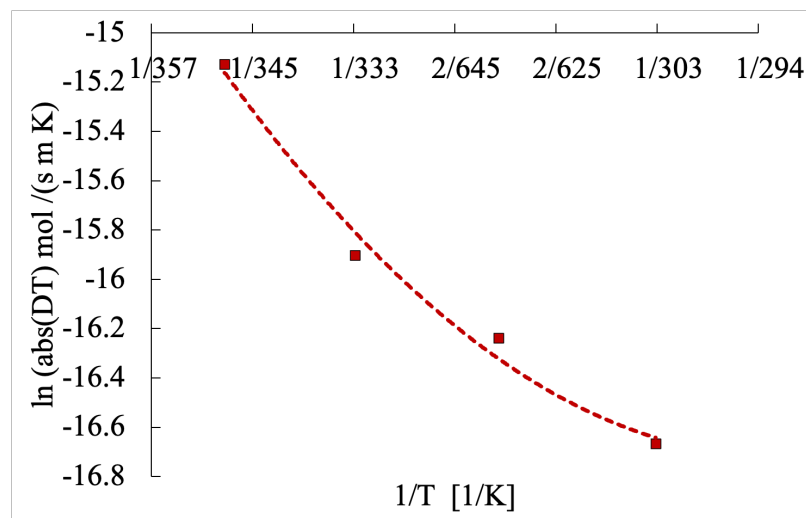


Figure 2.4.14 Activation Energy for Hydrophilic Case [81]

The absolute value of the thermal osmosis coefficient was used in both cases, there was no examination of the activation energy without the absolute value, it is possible that one processes is endothermic and the other is exothermic, the absolute value will treat both membranes the same but there is a difference between thermal osmosis and membrane distillation. The activation energy determination needs to be examined more for the hydrophobic and hydrophilic cases and with thermal osmosis coefficients free of other fluid drivers. Like Kim and Mench [75],[76] more fluid was transport via the hydrophobic membrane compared to the hydrophilic cases. Bozkurt et al [83] had seen similar results where the hydrophobic membrane transported more liquid water compared to the hydrophilic cases.

Tasaka et al [84] conducted thermal osmosis and osmotic pressure experiments. The purpose of the water flow experiments was to study solvent transport across cation-exchange membranes under two different conditions: a temperature difference and an osmotic-pressure difference. The aim was to better understand how these factors influence the movement of solvents through the membranes. Tasaka et al [84] also stated the total water flow across the membrane can be expressed in terms of thermal gradient and pressure gradient as shown in equation 34.

$$-J_v = D^*[\Delta s \Delta T - v_o \Delta \pi] \quad (34)$$

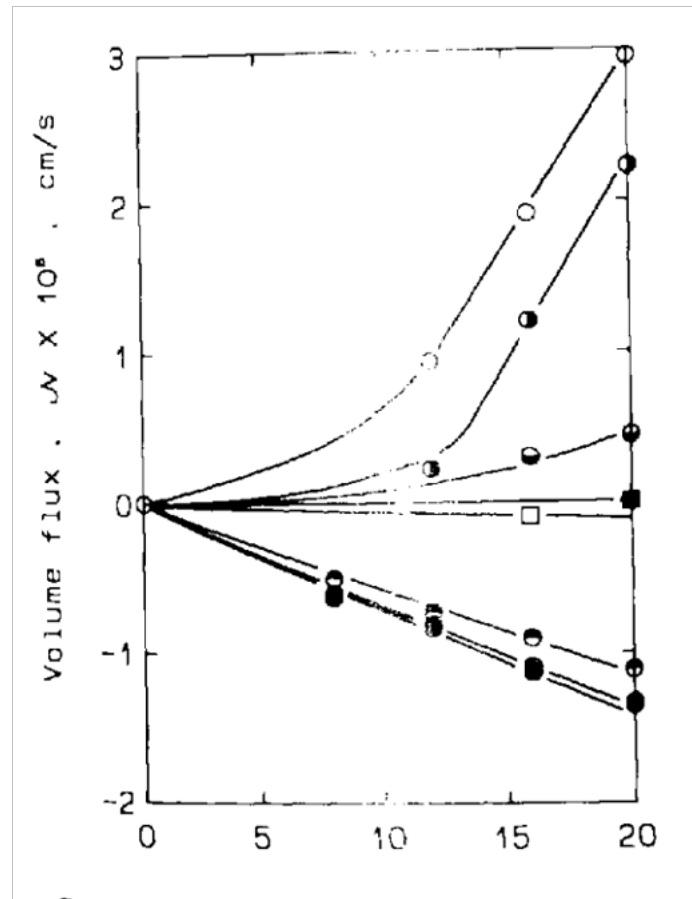
Tasaka et al [84] has stated that there are two fluid drivers a thermal gradient component and a pressure gradient component. In the case where there is no osmotic pressure the flow simplifies to equation 35.

$$-J_v = D^*[\Delta s \Delta T] \quad (35)$$

If there is no thermal gradient, then equation 34 simplifies to equation 36. There are two fluid drivers capable of moving water in thermal osmosis experiments, the first one is thermal osmosis, and the other one is osmotic pressure. Based on the equations, the trendline is expected to be linear.

$$-J_v = D^* \Delta \pi \quad (36)$$

Tasaka et al [84] has performed thermal osmosis experiments with Nafion membranes with hydrogen ions and other cation ions. The total water flux is plotted against the temperature gradient; in this case the total fluid flow is forced through the origin but in some of the cases the curve will not go through the origin as shown in Figure 2.4.15:



The total water flow data trendlines were forced through the origin, the reason for forcing the trendline through the origin was to account for no temperature driven flow with no thermal gradient. There are other fluid drivers that could be driving fluid flow when no thermal gradient is present. By assuming the data trendline through the origin, this also assumes that all the total water flow is equal to the thermal osmosis water flow. Tasaka et al [84] also noted that thermal osmosis in Nafion was not seen above a temperature difference of 12 K [84], it is not clear what is occurring in the temperature range below 12 K when Tasaka et al [84] had noted that there would be no thermal osmosis flow at no

temperature difference but when the plot is examined the trendline does not go through the origin as if there are other fluid drivers present.

The trendline that is forced through the origin, has a contradiction if thermal osmosis was only observed above certain temperature difference, then how can thermal osmosis be continuous and only seen about a certain temperature difference. The trendline forced through the origin contains a paradox. A solution to the paradox is there are other fluid drivers present, and they are masking thermal osmosis. The total water flow needs to be further examined to confirm the presence of other fluid drivers.

The slope of the trendline was used to obtain the thermal osmosis coefficient along with the direction of thermal osmosis. In the case with the hydrogen ions, the flow went in the cold to hot direction, and for the lithium-ion case the temperature driven flow was hot to cold. The negative sign in the thermal osmosis is the reason for the direction of the thermal osmosis water flow. The total water flow needs to be reexamined to understand if thermal osmosis is continuous and why thermal osmosis was only seen at certain temperature differences, it is most likely that other fluid drivers are present, and they could be masking thermal osmosis by moving in the opposite direction of thermal osmosis.

Pending on the cation, the direction of the water flow will either be hot to cold or cold to hot, it was found when hydrogen ions are in contact with liquid water the flow is in one

direction and when liquid water is in contact with other cation ions the water flow is in the opposite direction, one theory was the hydrogen bonding with the membrane.

Thermal osmosis is impacted by the membrane material, Tasaka et al [85] also performed experiments to fully understand thermal osmosis in a CM-3, CM-4 and CM-5 membrane as shown in the Figure 2.4.16:

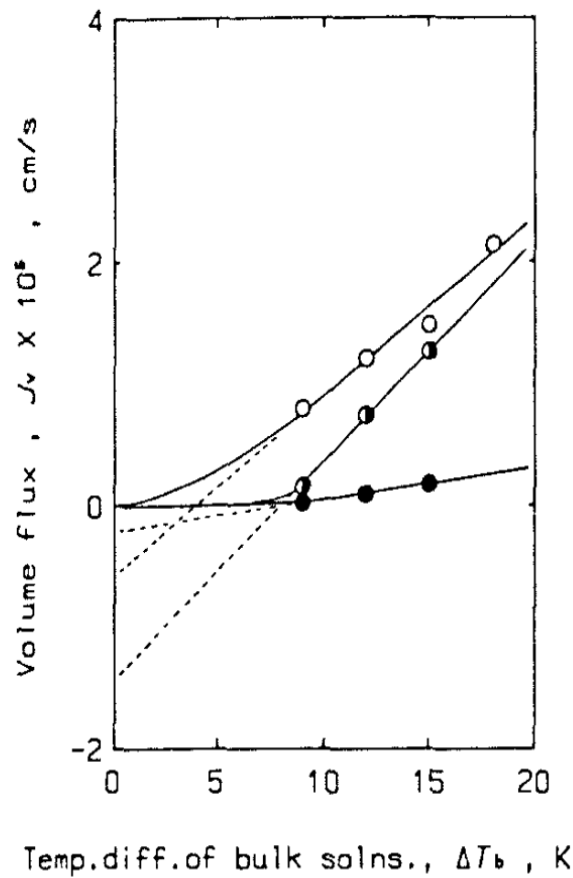


Figure 2.4.16 Total Water Flow Through CM-3, CM-4 & CM-5 Membrane [84]

Thermal osmosis is impacted by the membrane material, Tasaka et al [85] also performed experiments to fully understand thermal osmosis in a CM-3, CM-4 and CM-5 membrane

as shown in the Figure 2.4.16. The experimental data was processed with two trendlines, the first one which is forced through the origin and the second one **not** forced through the origin. The data trendline that is forced through the origin has a linear and non-linear region. The trendline forced through the origin assumes that the total water flow is all thermal osmosis and no other fluid driver are present. The second trendline assumes other fluid drivers are present and it is a linear trendline. It is not clear which trendline should be used for understanding thermal osmosis.

Based on the positive slope of the trendline, thermal osmosis was in the cold to hot direction. Tasaka et al [85] had noted the collodion membrane (CM) is hydrophilic. As in the other case with Nafion there are two distinct trendlines, only one trendline can be correct. In this case also there are two distinct lines, the first one where the data is forced through the origin to reflect the no thermal osmosis flow at zero temperature difference and the second case to where the data is not forced through the origin. The continuous trendline forced through the origin does not address the non-continuous thermal osmosis and the other trendline does account for other fluid drivers that may impact the total water flow.

It is unclear which line is correct, for Tasaka et al [84],[85] stated that no temperature difference, the thermal osmosis flow should be zero. A more detailed analysis of the data is needed. The total water flow needs to be broken down, and thermal osmosis portion of the total water flow needs to be obtained. Both trendlines cannot be correct, if the

trendline forced through the origin is correct it has the issue of explaining that the non-continuous thermal osmosis. The case where the trendline is not forced through the origin does allow for the non-continuous flow and it also assumes that other fluid drivers are present in the experiment. The total water flow needs to be further examined to determine the thermal osmosis portion of the total water flow and to see how the other fluid drivers impact thermal osmosis.

D'Ilario et al [86] also conducted thermal osmosis experiments with a composite membrane system consisting of two cellulose membranes and an aqueous solution of poly (ethylene oxide) and this composite membrane was used for thermal osmosis experiments. There were two scenarios examined the first with the absence of pressure the second with pressure as shown in Figure 2.4.17:

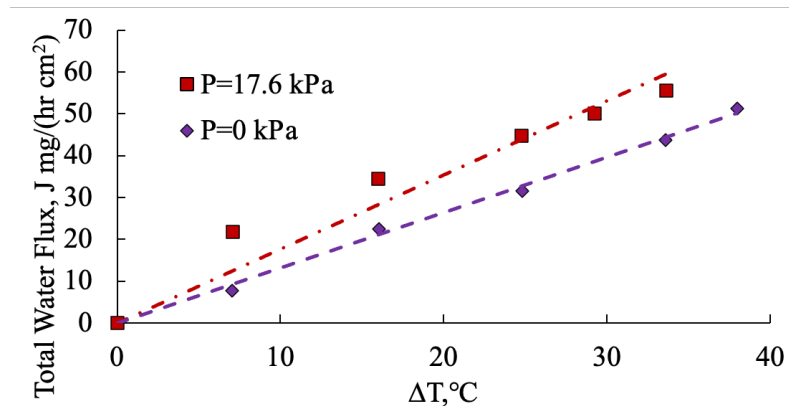


Figure 2.4.17 Thermal Osmosis with and without Pressure [86]

In both cases, the total water flow is increasing with the thermal gradient. The linear trendlines were forced through the origin assuming no other fluid drivers are present, but the pressure-based component will contribute to the total water flow. As in the other

researchers, the total water flow was forced through the origin, in the case where there is no pressure component this may be applicable but when the pressure component is applied this may not be true.

The data will be reexamined to determine how reprocessing the data will impact the transport coefficients. Forcing the trendline through the origin has a negative impact on the case with the pressure applied. For analyzing the data an approach should be universal and work on all cases not just one case. Since there is a pressure and thermal component of the total water flow, the thermal component needs to be extracted from the total water flow.

2.5 Summary

When an experiment measures the total water flow across the membrane, it is the summation of all the fluid drivers present in an experiment. An individual fluid driver cannot be measured by itself. The total water flow needs to be broken down into its component and determine the impact of the other fluid drivers. The total water flow coefficient does not tell how the total water flow changes with the gradient, it is expected that the total water flow varies linearly with the gradient, this is the main reason why the total water flow needs to be examined. There are inconsistencies with the electro-osmotic drag coefficient, back diffusion coefficients and thermal osmosis coefficient and the transport coefficients need to be determined, and there is not consistency with the magnitude and direction of thermal osmosis.

The empirical coefficient models for electro-osmotic drag, back diffusion and thermal osmosis cannot be used to subtract one of these drivers from the total water flow because there is inconsistency with these coefficient models. For this to occur there needs to be agreement on the electro-osmotic coefficient models and there needs to be way to extract the electro-osmotic drag portion from the total flow. If the coefficients are extracted from the experimental data, and they can be compared to the assumed transport coefficient and insight can be gained. The pressure gradient, concentration gradient, voltage gradient and thermal gradient can drive fluid flow. There are also secondary effects like the Soret and Dufour effect which will move water flow. The inconsistencies on the fluid drivers also make it difficult to assume a transport coefficient unless there is a way to validate the assumed coefficient.

In the experiments reviewed some researchers had forced the data trendline through the origin. By forcing the trendline through the origin it will neglect other fluids drivers that are present in the experiment, and it assumes that all the total fluid flow is from the measured fluid driver. This approach will lump in the other fluid drivers into the trendline which would misrepresent the relationship between the fluid flow and the measured gradient. A misrepresented transport coefficient could either lead to membrane dry out or fuel cell flooding. Since the PEM fuel cells had coupled heat and water management, accuracy and precision is required.

A method is needed to break down the total water flow into its fundamental fluid drivers without making assumption. A new method is proposed decompose the total water flow into its primary fluid drivers.

CHAPTER THREE

3 Theory

In any total water flow experiment the total water flow across the membrane is a summation of all the fluid drivers, as a result an individual fluid driver cannot be measured by itself. The desired fluid driver must be extracted with total water flow across the membrane otherwise the results will contain other fluid drivers. In cases of the fuel cells, there are two agreed modes of water transport from the Nernst-Planck equation they consist of electro-osmotic drag and back diffusion, there is not an agreement on the electro-osmotic drag coefficient nor is there agreement on the back diffusion coefficient, and these empirical models cannot be used extract the desired fluid driver. If an empirical coefficient model is chosen and the other driver is calculated, then the calculated driver will depend on the empirical model chosen, this process is viable if the empirical model can be validated by determining the transport coefficient experimentally.

The proposed method can be used to extract the electro-osmotic drag portion of the total water flow as well as extract the electro-osmotic drag coefficient. The calculated electro-osmotic drag coefficient can now be compared to the electro-osmotic drag coefficient model chosen for water management. The comparison of coefficients allows for validation of the empirical coefficient model or development of a new coefficient model. With the electro-osmotic drag portion of the total flow obtained, the back diffusion portion and thermal osmosis portion of the total fluid flow can be obtained.

The electro-osmotic drag coefficient can be calculated at each data point this is important because the membrane properties are dependent on hydration state of the membrane. This would allow for additional insight into electro-osmotic drag. For instance, it is not known if electro-osmotic drag is a function of current density or is it independent of current density. In the cases where electro-osmotic drag experiments were conducted, back diffusion and other fluid drivers are present, and the electro-osmotic drag portion of the total flow must be obtained. The calculated electro-osmotic coefficient portion can now be compared to theoretical model and validate the model. In addition, it is not known if the other fluid drivers are neglectable or substantial, and this needs to better understand electro-osmotic drag. The analysis of the electro-osmotic drag coefficient can also reduce the scatter in the current empirical models. The same process can be followed for back diffusion.

In the cases where electro-osmotic drag experiments were conducted, back diffusion and other fluid drivers are present, and the electro-osmotic drag portion of the total flow must be obtained. The calculated electro-osmotic coefficient portion can now be compared to theoretical model and validate the model. In addition, it is not known if the other fluid drivers are neglectable or substantial, and this needs to better understand electro-osmotic drag. The analysis of the electro-osmotic drag coefficient can also reduce the scatter in the current empirical models. The same process can be followed for back diffusion.

In the thermal osmosis experiments cases there are other fluid drivers present such as osmotic pressure or back diffusion, and as a result the thermal osmosis portion of the total water flow needs to be obtained. The thermal osmosis coefficient is not known, and the magnitude and direction are uncertain. There are also observations about thermal osmosis flowing in the hot to cold direction for hydrophobic material and cold to hot for hydrophilic materials, but this does not address hybrid membranes, and the thermal osmosis data must be further analyzed to confirm the magnitude and direction of pure thermal osmosis. Also in some thermal osmosis experiments, thermal osmosis was non-continuous, it was seen above finite temperature differences, and the researcher also forced the data trendline through the origin, and this implies that thermal osmosis is continuous and no other fluid drivers are present, this is further evidence that thermal osmosis needs to be better analyzed.

Also in some thermal osmosis experiments, thermal osmosis was non-continuous, it was seen above finite temperature differences, and the researcher also forced the data trendline through the origin, and this implies that thermal osmosis is continuous and no other fluid drivers are present, this is further evidence that thermal osmosis needs to be better analyzed.

One of the common errors made in some of the electro-osmotic drag, back diffusion and thermal osmosis experiments was that the data trendline were forced through the origin. By forcing the trendline through the origin it will neglect other fluid drivers present and

lump them in with the desired fluid driver, this will result in a transport coefficient is that will contain other fluid drivers. The other fluid drivers are not known to be substantial or neglectable, each case needs to be evaluated individually. Also, the fluid flow is so small any error would be substantial. The heat and water management of a fuel cells requires accuracy and precision this is the key reason why accurate in electro-osmotic drag, back diffusion and thermal osmosis coefficient is required.

In a case where only one fluid driver is present, the fluid flow trendline should go through the origin. In an electro-osmotic experimental setup, the total water flow should be measured at 0 A/cm², if the flow is 0 at this point there are no other drivers present, but if the values is not zero the other effects are present. The method proposed by the research will work on all cases. As shown in Figure 3.1.1, each driver requires other fluid drivers be zero.

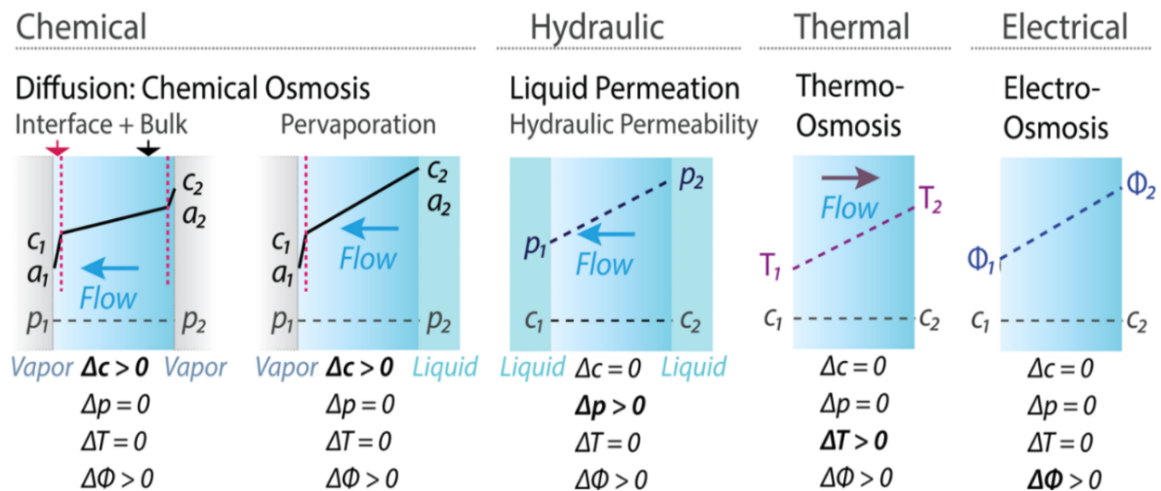


Figure 3.1.1 Different effects and how they are measured [5]

As shown in Figure 3.1 the desired fluid drivers need to be measured when the other drivers are zero, for instance for thermal osmosis, the concentration, pressure and voltage difference are zero. This is ideal because other fluid drivers will always be present for instance osmotic distillation could occur and this could also cause a thermal gradient. It may not be possible to zero out the other fluid effects.

The Nernst-Planck equation as shown in equation 17 and 18 is used to model water flow across the membrane of the fuel cell. The Nernst-Planck equation only considers two of the fundamental fluid drivers which are the voltage gradient and concentration gradient, the thermal gradient is neglected any net water experiment may have thermal osmosis in item based on the temperature profile across the fuel cell.

The heat generation in the fuel cell is non-uniform and is a function of discharge voltage. The thermal gradient is a result of the coolant temperature at the bi-polar plate along with the Ohmic heat generated in each layer. One of the biggest causes of the thermal gradient in the fuel cells is the reduction reaction at the cathode. A sample temperature profile of the fuel cell is shown in Figure 3.1.2.

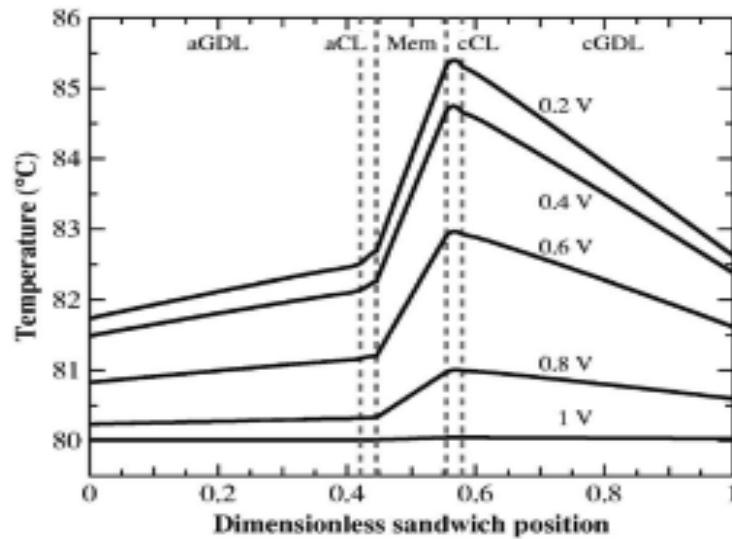


Figure 3.1.2 Temperature Profile of the Fuel Cell [103]

This thermal gradient could induce fluid flow across the membrane because of the higher temperatures in the cathode vs the anode. Based on the inconsistencies with thermal osmosis magnitude and direction this component cannot be quantified and since there are inconsistencies with the electro-osmotic drag coefficients and back diffusion coefficients it is not easy to decipher each driver. The discharge voltage will impact the fuel cell efficient and temperature profile. It is also possible that the thermal osmosis component could be lumped in with electro-osmotic drag or back diffusion pending on the direction of thermal osmosis.

It is not known if thermal osmosis is major driver of fluid flow, temperature difference is dependent on discharge voltage of the fuel cell, and the temperature gradient will influence the saturated pressure of the water on the anode side and cathode side.

The agreed water transport equation for water flow across the membrane is the Nernst-Planck equation, and it only contains electro-osmotic drag and back diffusion. It is also possible that the thermal effect will be further lumped into either the electro-osmotic drag or back diffusion and it is dependent on the discharge voltage.

The Nernst-Planck equation derived from the Stefan-Maxwell Equation, and an assumption in the derivation process is that the Nernst Planck equation is an isothermal equation and it must be in a dilute electrolyte. It is not known if this equation is applicable to fuel cells due to the thermal gradient across the membrane, it is applicable to batteries which are a closed thermodynamic system and batteries used a liquid electrolyte. The electrolytes in the fuel cells are different. Table 3-1 shows the different types of fuel cells and the electrolyte used.

Table 3.1-1 Types of Fuel Cells

Table 1. Fuel Cell Types and Characteristics

Type	AFC	PEMFC	DMFC	PAFC	MCFC	SOFC
Electrolyte	Aqueous Potassium Hydroxide (30-40%)	Sulphonated Organic Polymer (hydrated during operation)	Sulphonated Organic Polymer (hydrated during operation)	Phosphoric Acid	Molten Lithium / Sodium / Potassium Carbonate	Yttria-stabilised Zirconia
Operating Temp. °C	60-90	70-100	90	150-220	600-700	650-1000
Charge Carrier	OH ⁻	H ⁺	H ⁺	H ⁺	CO ₃ ²⁻	O ²⁻
Anode	Nickel (Ni) or precious metal	Platinum (Pt)	Platinum - Ruthenium (Pt, Ru)	Platinum (Pt)	Nickel / Chromium Oxide	Nickel / Yttria-stabilised Zirconia
Cathode	Platinum (Pt) or lithiated NiO	Platinum (Pt)	Platinum - Ruthenium (Pt, Ru)	Platinum (Pt)	Nickel Oxide (NiO)	Strontium (Sr) doped Lanthanum Manganite
C-generation Heat	None	Low Quality	None	Acceptable for many applications	High	High
Electrical Efficiency %	60	40-45	30-35	40-45	50-60	50-60
Fuel Sources	H ₂ Removal of CO ₂ from both gas streams necessary	H ₂ Reformate with less than 10ppm CO	Water / Methanol solution	H ₂ Reformate	H ₂ , CO, Natural gas	H ₂ , CO, Natural gas

The Alkaline Fuel Cell (AFC) was the predecessor to the PEM fuel cell. The Alkaline (AFC) does used a liquid electrolyte, it uses aqueous potassium hydroxide, and the Proton Exchange Membrane (PEM) fuel cell uses an organic polymer membrane with humidified hydrogen and air used for the fuel cell operation. The Direct Methanol (DM) fuel cell uses liquid methanol on the anode and humidified air on the cathode. The alkaline, direct methanol and proton exchange membrane use different electrolyte and will have different electro-osmotic drag and back diffusion coefficients. What is applicable for a direct methanol fuel cell or alkaline fuel cell may not be applicable to the proton exchange membrane because the membrane is the electrolyte.

3.1 Total Water Flow in the Fuel Cell

In the fuel cell, the total water transfer across the membrane is indirectly measured and thus it is a summation all the fluid drivers present in the experiment. The experiment results should not assume that only one fluid driver is present by forcing the experiment trendline through the origin. This assumption implies total water flow is from measured fluid driver, and it assumes all the fluid flow is from the measured fluid driver. The accepted equation for modeling fluid flow across the membrane is the Nernst-Planck equation.

The Nernst Planck considers two fluid drivers, the voltage gradient and chemical potential gradient, in the actual application the other drivers as shown in Figure 2.54 could be present, the temperature gradient, the concentration gradient, the voltage gradient and pressure gradient are the fundamental drivers. In addition to the primary drivers, there is coupling of the primary drivers to produce secondary effects like the Soret and Dufour effects, membrane potential, thermo-diffusion potential and potential flux.

The other fluid drivers must be considered when isolating electro-osmotic drag and back diffusion. The data needs to be examined and to isolate the desired effect from the total flow. The first step is to assume that the Nernst-Planck equation is an exact equation of state. If the partial derivative of the Nernst-Planck as shown in equation 17 is taken with

respect to current, only the coefficients in front of the current remain as shown in equation 37.

$$\frac{\partial J}{\partial j} = \frac{n_d(\lambda)}{F} \quad (37)$$

The partial derivative will mathematically eliminate the back diffusion coefficient from the total water flux. The same process can be repeated but, in this case, the partial derivative of the Nernst-Planck equation is taken with respect to the concentration gradient as shown in Equation 38.

$$\frac{\partial J}{\partial \left(\frac{d\lambda}{dx}\right)} = -D(\lambda) \quad (38)$$

The partial derivatives allow for the isolation of the other fluid drivers present. The back diffusion coefficient can also be put in terms of the membrane density and equivalent weight of the membrane as shown in equation 39.

$$D(\lambda) = -\frac{\rho_{Dry}}{EW} D_\lambda(\lambda) \quad (39)$$

It is noted that both electro-osmotic drag and back diffusion coefficient are dependent on the membrane hydration state of the membrane. It is expected that the coefficients are not going to be independent on the water membrane content.

The next step involves examination of the total fluid flow experimental data.

In the first scenario the current density is varied, and the concentration gradient is constant. If the total water flow is fit to a linear function that does not go through the origin as shown in equation 40. If the trendline does go through the origin a_0 would equal zero.

$$J = a_0 + a_1j \quad (40)$$

If the derivative of the water flow is taken with respect to current, then equation 41 is obtained.

$$\frac{dJ}{dj} = a_1 \quad (41)$$

The a_0 term will contain the other fluid drivers, no electro-osmotic drag is in this term. There is also insight gained with this technique, if a_0 and a_1 are the same sign then both drivers are in the same direction, if they are the opposite sign one driver is moving against another driver. If a_1 is positive the direction of electro-osmotic drag is in the direction of anode to cathode, if negative it is in the direction of cathode to anode. If the new method is compared with the older method the a_0 term will tell if the older method is overstating or understating. If a_0 is positive, then the results will be overstating the results and if a_0 is negative then the original method will be understating the results. The

linear trendline indicates the electro-osmotic drag coefficient is independent of current density.

Also, when a_0 and a_1 are the opposite sign there will be a point where no flow will occur this is obtained by setting J in equation 40 to zero and solving for the current, the results are shown in equation 42.

$$j = -\frac{a_0}{a_1} \quad (42)$$

The proposed method also can explain why there will be no water flow from electro-osmotic drag but there will be flow from other fluid drivers as shown in equation 43.

$$J = a_0 + a_1 * 0 \quad (43)$$

In cases where the trendline fit is not linear then the same process is applied to a polynomial. The first step is to fit the data to a polynomial as shown in equation 44.

In the case of the linear trendline fit, the electro-osmotic drag coefficient is not a function of current density because the derivative of the mass flux with respect to the current density is a constant.

$$J = a_0 + a_1 j + a_2 j^2 \quad (44)$$

The quadratic formula can also be used to determine if there are any points at which there will be no flow, this is done by setting the mass flux to zero and applying the quadratic formula and shown in equation. 45.

$$j_1, j_2 = \frac{-a_1 \pm \sqrt{a_1^2 - 4a_0a_2}}{2a_2} \quad (45)$$

The derivative equation 44 is taken to yield equation 46.

$$\frac{dJ}{dj} = a_1 + 2a_2j \quad (46)$$

As before the theoretical model in equation 37 is set equal to equation 46 to yield equation 47.

$$\frac{n_d(\lambda)}{F} = a_1 + 2a_2j \quad (47)$$

Equation 47 can be rearranged to obtain the electro-osmotic drag coefficient as shown in equation 48.

$$n_d(\lambda) = F(a_1 + 2a_2j) \quad (48)$$

In the case of the polynomial fit, the electro-osmotic drag coefficient will be a function of current density. The electro-osmotic drag coefficient will vary linearly with current density. With the electro-osmotic drag coefficient known, the electro-osmotic drag portion of the total water flow can be determined with equation 49.

$$J_{EOD} = n_d(\lambda) \frac{j}{F} \quad (49)$$

The back diffusion portion of the total water flow can now be extracted through equation 50.

$$J_{BD} = J_{Total} - J_{EOD} \quad (50)$$

The back diffusion can be expressed in terms of the concentration gradient as shown in equation 51.

$$J_{BD} = \frac{\rho}{EW} D_\lambda \left(\frac{d\lambda}{dx} \right) \quad (51)$$

If the concentration gradient is known the back diffusion can be obtained if it is not known, then only the back diffusion portion of the total water flow can be reported.

In the case where the current density is fixed and the concentration gradient is varied then the similar method can be employed as before. The first step involves fitting the total water flow to a linear trendline as shown in equation 52.

$$J = b_o + b_1 \left(\frac{d\lambda}{dx} \right) \quad (52)$$

The sign of b_o and b_1 provide insight, if b_o and b_1 are the same sign both fluid drivers are working in the same direction, if b_o and b_1 are opposite signs one of the fluid drivers is working against the other. If b_1 is negative the back diffusion portion is going in the opposite direction. If b_1 is positive the back diffusion flow is moving in the direction of the concentration gradient, and if b_1 is negative back diffusion is moving against the concentration gradient.

If the new method is compared to the original method, the sign of b_o will influence if the original results are overstating or understating the back diffusion. If b_o is positive, then the original method will be overstated and if b_o is negative then the original method will be understating. In cases where b_o and b_1 are opposite signs, there will be a point at which no flow takes place this point is found by setting the water flux of equation 52 to zero and solving for the concentration gradient as shown in equation 53.

$$\left(\frac{d\lambda}{dx} \right) = - \frac{b_o}{b_1} \quad (53)$$

As before the derivative of the total water flux is taken with respect to the concentration gradient as shown in equation 54.

$$\frac{dJ}{d\left(\frac{d\lambda}{dx}\right)} = b_1 \quad (54)$$

In the case where the total water flux is not linear it is fit to a polynomial as shown in equation 55.

$$J = b_o + b_1\left(\frac{d\lambda}{dx}\right) + b_2\left(\frac{d\lambda}{dx}\right)^2 \quad (55)$$

The quadratic formula can be applied to equation 55 to find where the zero flow points are in the water flow as shown in equation 56.

$$\left(\frac{d\lambda_1}{dx}, \frac{d\lambda_2}{dx}\right) = \frac{-b_1 \pm \sqrt{(b_1^2 - 4b_2b_o)}}{2b_2} \quad (56)$$

The derivative of the water flux from equation 55 is taken with respect to the concentration gradient as shown in equation 57.

$$\frac{dJ}{d\left(\frac{d\lambda}{dx}\right)} = b_1 + 2b_2\left(\frac{d\lambda}{dx}\right) \quad (57)$$

The theoretical model of back diffusion from equation 67 is needed, the derivative of equation 83 is taken with respect to the concentration gradient as shown in equation 58.

$$\frac{dJ}{d\left(\frac{d\lambda}{dx}\right)} = \frac{\rho}{EW} D_\lambda \quad (58)$$

The theoretical model of equation 39 is set equal to 58 to obtain the back diffusion coefficient as shown in 59.

$$\frac{\rho}{EW} D_{\lambda} = b_1 + 2b_2 \left(\frac{d\lambda}{dx} \right) \quad (59)$$

With the back diffusion coefficient known the back diffusion portion of the total water flow can be computed with equation 51. The electro-osmotic drag portion of the total water flow can be computed with equation 60. In this process no assumptions are made, the mathematics is used to determine the transport coefficients.

$$J_{EOD} = J_{Total} - J_{BD} \quad (60)$$

With the electro-osmotic drag portion known and the current density known the electro-osmotic drag coefficient can be determined as shown in equation 61. The results obtained from this process bypass the need to assume a transport coefficient.

$$n_d(\lambda) = \frac{J_{EOD}}{\left(\frac{J}{F} \right)} \quad (61)$$

With the electro-osmotic drag and back diffusion portion of the flow known the ratio of the total flow can be computed. The electro-osmotic drag portion of the total flow can be computed with equation 62 and the back diffusion portion of the total flow can be computed with equation 63.

$$R_{EOD} = \frac{|J_{EOD}|}{|J_{EOD}| + |J_{BD}|} \quad (62)$$

$$R_{BD} = \frac{|J_{BD}|}{|J_{EOD}| + |J_{BD}|} \quad (63)$$

This method can be used for the cases where the total water transfer across the membrane is reported. The proposed process calculates what percentage of the total water flow is electro-osmotic drag and which portion is back diffusion. This approach could be used for cases where the total water transfer coefficient was reported along with electro-osmotic drag and back diffusion experiments. Accuracy and precision are required heat and water management successful fuel cell operation, if too much water is present on the cathode the fuel cell will flood and if there is not enough water is present on the anode the Ohmic resistance will be higher, and heat generated will be larger. Additional insight is gained on the electro-osmotic drag and back diffusion transport coefficient, in cases where the data trendline is linear the transport coefficient will be constant but when the data is fit to a polynomial, the transport coefficient will vary linearly, this could be due to changing properties of the membrane.

3.2 Other Fluid Drivers are Present in experimental data

In Figure 2.54 there are primary fluid drives which are, pressure, voltage, concentration and thermal gradient. There are also secondary drivers which are a result of two primary effects, by pairing concentration gradient and thermal gradient will yield the Soret and

Dufour effect. By combining the thermal gradient and voltage gradient the thermos-diffusion effect is obtained, and the membrane potential is obtained with a voltage gradient and concentration gradient. Lastly when the voltage gradient and pressure gradient are combined then the potential flux is obtained.

In an operational fuel cell, there is a temperature gradient across the membrane because of the heat generation because of the reduction reaction at the cathode catalysts layer. A sample temperature profile is shown in Figure 3.2; the temperature profile is dependent on the cell voltage. The fuel cell efficiency is the discharge voltage divided by the theoretical voltage as shown in equation 64.

$$\eta = \frac{E_{Dis}}{E_{Theoretical}} \quad (64)$$

The heat generation of the fuel cell is also impacted by the current and the cell heat generation is shown in equation 65. The heat generation in this form is the overall heat generated it does not take into consideration of the temperature profile.

$$\dot{Q} = (E_{Theoretical} - E_{Dis})I \quad (65)$$

The lower the discharge voltage the higher the heat generation will be this is one of the key reasons why the mass transport losses can lead to higher heat generation and why the

membrane needs to be hydrated to lower its Ohmic resistance. According to Non-Equilibrium Thermodynamics (NET) there are three variables driving fluid flow, the fluid drivers are the thermal gradient, voltage gradient and concentration gradient as shown in equation 66.[105]

$$J_W = -\frac{\dot{q}}{T} \left(\frac{dT}{dx} \right) - D_w(\lambda) \frac{dc}{dx} - n_d(\lambda) \frac{j}{F} \quad (66)$$

The thermal osmosis coefficient is dependent on the heat of transport; this is the Nernst-Planck equation with thermal effects. The sign of heat of transport is also important to understand if the value is positive energy is required and if its negative thermal energy is released. The thermal osmosis heat of transport can be expressed in terms of the thermal osmosis coefficient and equation 67 can be rewritten. The thermal osmosis transport coefficient is dependent on the heat of transport.

$$J_W = -D_T \left(\frac{dT}{dx} \right) - D_w(\lambda) \frac{dc}{dx} - n_d(\lambda) \frac{j}{F} \quad (67)$$

There are two ways that the coefficients can be extracted, the first one is taking advantage of β from equation 16. And substitute equation 20 into 67, this will yield equation 68.

$$J_W = -D_T \left(\frac{dT}{dx} \right) + \beta \frac{j}{F} \quad (68)$$

This would separate the total water flow into two components, thermal osmosis and the overall transfer coefficient, this approach would require two steps, the first step involves taking derivative of the total water flow with respect to the temperature gradient as shown in equation 69.

$$\frac{\partial J_w}{\partial (\frac{dT}{dx})} = -D_T \quad (69)$$

The partial derivative of the total water flow can be taken with respect to current density as shown in equation 70.

$$\frac{\partial J_w}{\partial j} = \frac{\beta}{F} \quad (70)$$

The total water transfer coefficient β can then be broken down into electro-osmotic drag and back diffusion by using 37 to 63. The other way would be to work with directly with equation 68. The partial derivative of the total water flux can be taken with respect to the thermal gradient as shown in equation 71.

$$\frac{\partial J_w}{\partial (\frac{dT}{dx})} = -D_T \quad (71)$$

The partial derivative can be taken with respect to the concentration gradient as shown in equation 72.

$$\frac{\partial J_w}{\partial (\frac{dc}{dx})} = -D_w \quad (72)$$

The partial derivative of the total water flow can also be taken to the current density as shown in equation 73.

$$\frac{\partial J_w}{\partial j} = \frac{n_d}{F} \quad (73)$$

It should be noted that there are two fluid drivers under the thermal gradient, there is thermal osmosis and membrane distillation. Membrane distillation will only occur with hydrophobic material and liquid water. This form of thermal osmosis will have phase change of water. The other thermal osmosis case is single phase thermal osmosis this can occur with gases and with liquid, in the liquid case there is not phase change.

3.2.1 Examination of Total Water Flow

The total water flow of the fuel cell is currently broken down by assuming one fluid driver transport coefficient and using to it determine either the electro-osmotic drag or back diffusion portion of the total water flow and then subtracting this from the total water flow. By doing this there is a dependency on the fluid driver on the empirical coefficient model chosen. The proposed data mining relies on the theoretical model along with the experimental data to solve for the transport coefficient at each data point.

The proposed approach also allows for breaking down the total water flow into its fundamental fluid drivers. This is something new to understand the total water flow across the membrane. The proposed approach will also confirm if the transport coefficients are function of the gradient or if they are an independent of the gradient.

Some of the total water flow has been plotted with respect a relative humidity, and it has not been converted to a concentration gradient, the relative humidity on the anode and cathode need to be converted to a concentration difference. In the case where relative humidity is given, it is converted to hydration to the state of the membrane with the use of equation 74. By putting the relative humidity into the hydration state of the membrane, the concentration gradient across the membrane can be obtained.

$$\lambda = .0043 + 17.18p_a - 39.85p_a^2 + 36p_a^3 \quad (74)$$

Equation 74 is applied to the anode and cathode, and the concentration difference can be expressed in terms 75.

$$\lambda_{a/c} = (\lambda_a - \lambda_c) \quad (75)$$

The concentration gradient can be taken if equation 76 is divided by the membrane thickness as shown in equation 77. It should be noted that the thickness of the membrane will contribute to the back diffusion by changing the concentration gradient.

$$\frac{\lambda_{a/c}}{L} = \frac{(\lambda_a - \lambda_c)}{L} \quad (76)$$

Some of the researchers reported the total water transfer coefficient and this total water transfer coefficient needs to be converted to the total water; this is done by using equation 18. The determination of the electro-osmotic drag and back diffusion coefficient require the total water flow across the membrane.

Yan et al [25] total water transfer coefficient needs to be converted into total water flow as shown in Figure 3.2.1.1. The total water flow across the membrane was a polynomial fit. All the experiments were conducted with water vapor. It was expected that the total water flow data could be fit to the Nernst-Planck equation.

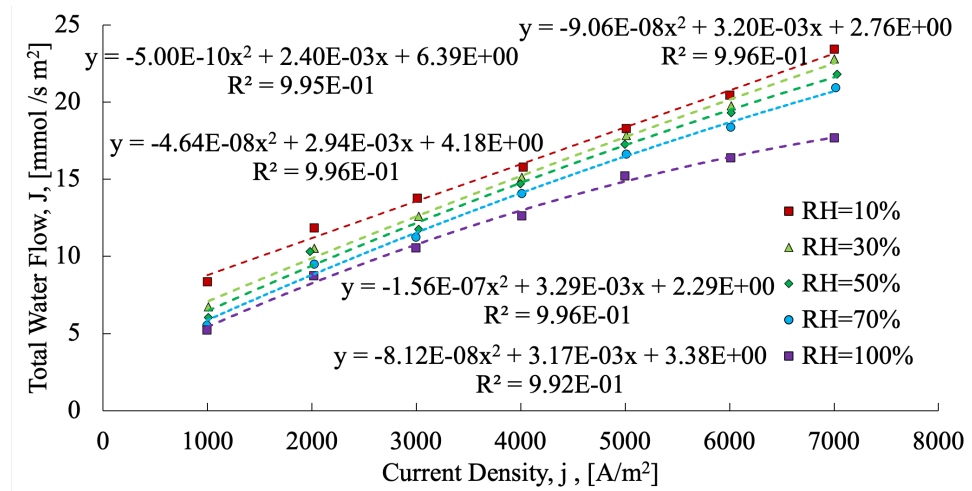


Figure 3.2.1.1 Total Water Flow with Anode Fully Humidified [25]

The total water flow was in the direction of anode to cathode, none of the trendlines were fit to a linear trendline, instead a polynomial fit was used to relate the total water flow to current density. The total water flow does appear to be linear, but the data is best fit to a polynomial. The most non-linear case is the 100% RH case; the total water flow starts to level off at 7000 A/m². As the inlet relative humidity increases the total water flow data starts to become more non-linear.

The non-linearity was not expected but it does indicate that the electro-osmotic drag and/or the back diffusion are changing because of current density. If the electro-osmotic drag and back diffusion were constant, then the total water flow trendline would be linear and follow the Nernst-Planck equation. The thermal gradient could also explain the non-linearity in the data because as the current increases, the discharge voltage decreases. The discharge voltage will impact the fuel cell efficiency and this have an impact the fuel cell thermal gradient. The temperatures across the membrane were not recorded so any separation of thermal osmosis cannot be computed.

The total water flow data in this form can be used to breakdown the total water flow into its electro-osmotic drag and back diffusion component. This insight is gained by examining the total water flow instead of the total water transfer coefficient. This approach allows for the dissection of the total water flow. According to the Nernst-Planck equation there are two fluid drivers, electro-osmotic drag and back diffusion and the data should be linear trendline but a polynomial fit work well for all cases. Based on the non-

linearity, there are other fluid drivers present in the experiment not accounted for or the electro-osmotic drag and back diffusion coefficient are changing at each data point. This experiment was also done with water vapor.

Yan et al [25] case at a fixed current density was also converted to a total water flux but in this case the relative humidity was expressed in terms of hydration state. The total water flow can now be expressed in terms of the concentration gradient as shown in Figure 3.2.1.2:

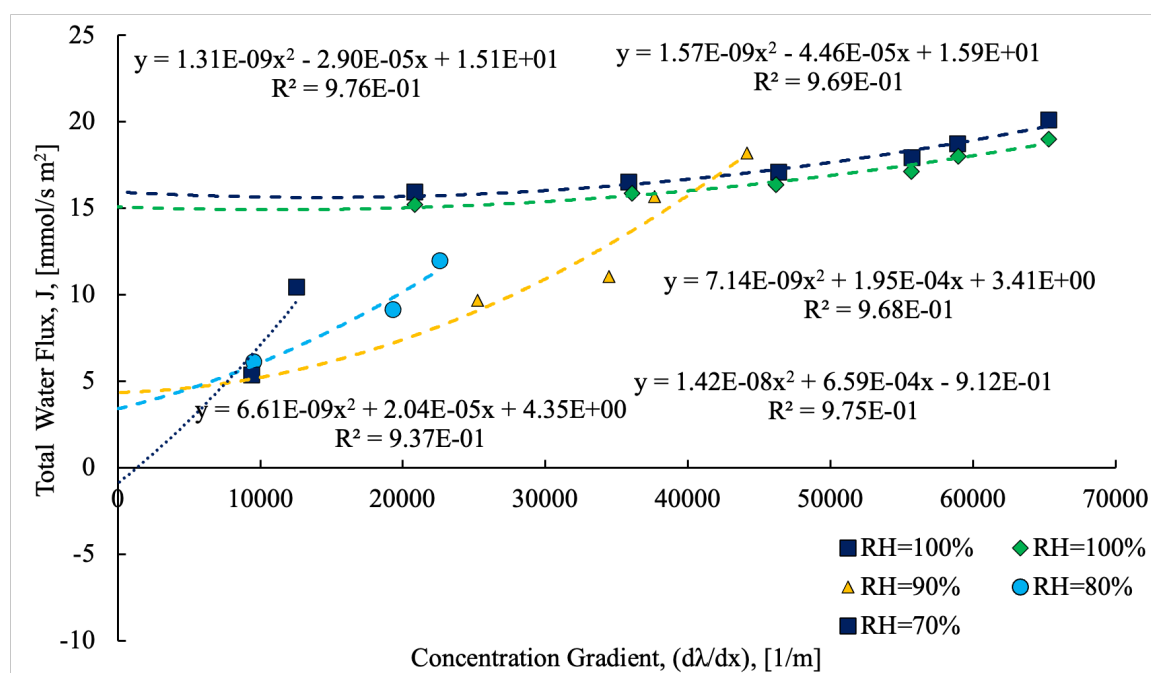


Figure 3.2.1.2 Total Water Flow with Variable Concentration Gradient [25]

To determine the back diffusion coefficient, the total water flow needed to be replotted in terms of the concentration gradient instead of the cathode inlet relative humidity. The initial attempt to fit the total water flow data to a linear trendline was unsuccessful, and

the total water flow was fit to a polynomial instead. A linear trendline was expected because of the Nernst-Planck.

The 70 %, 80% and 90% RH only had three data points, and the total water flow follows a polynomial, the 100% RH cases contained the most data points and the data appear linear, but it changes non-linearly with current density. In the 100% RH cases there is a high probability of liquid water being present and water vapor and liquid water will be moving across the membrane. The other possibility of the non-linearity could be due to the thermal gradient, as the current increases the discharge voltage will decrease and the thermal gradient across the membrane will increase. The electro-osmotic drag and back diffusions coefficients need to be obtained to gain insight into electro-osmotic drag and back diffusion

Yan et al [25] also performed experiments with different flowrate of hydrogen, as before the total water transfer coefficient needs to be converted to the total water flux, and the total water flux is shown in Figure 3.2.1.3:

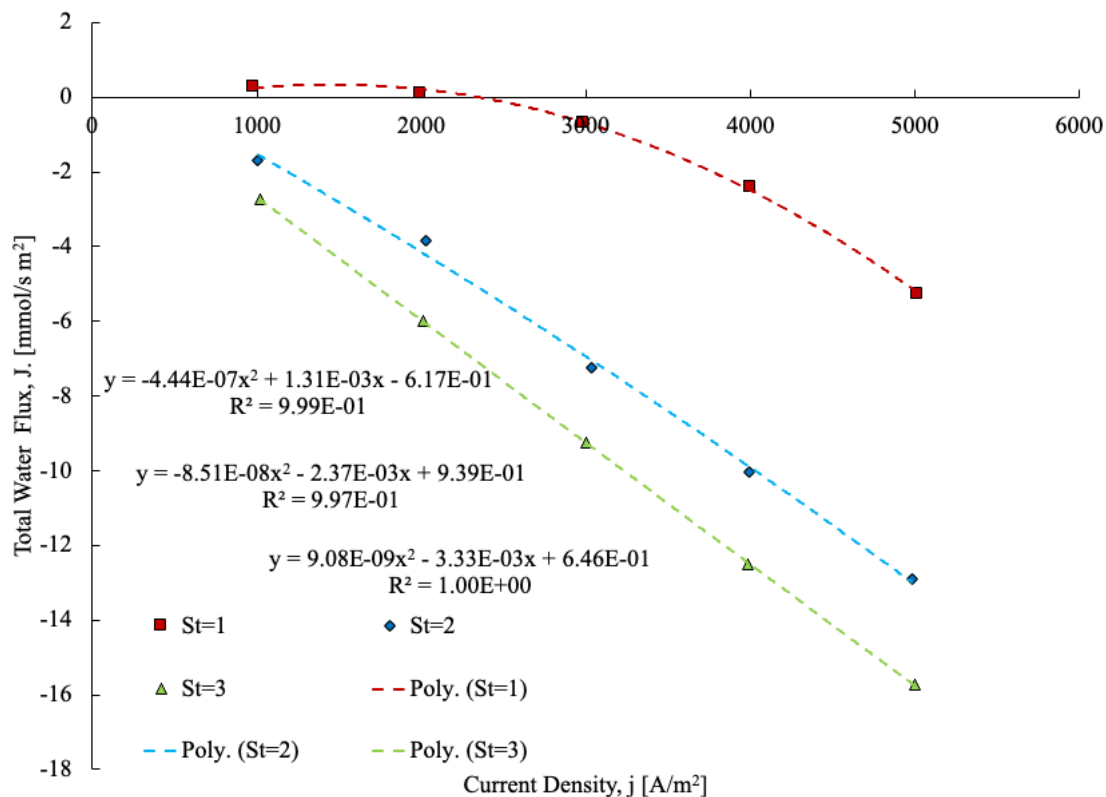


Figure 3.2.1.3 Total Water Flow vs Variable Stoich [25]

A linear fit was expected to relate the total water flow to current density because of the Nernst-Planck equation. The total water flow does not follow linear trend, the trendline does follow a polynomial trend. The stoichiometry of one was the most non-linear trendline, the stoichiometry of two are three look linear but were fit to a polynomial trendline. The polynomial fit indicates that the electro-osmotic drag coefficient is a function of current density. The discharge voltage of the fuel cell will impact the thermal gradient of the fuel cell, and the thermal gradient could also be impacting the total water flow across the membrane. This experiment was also done with water vapor. The

different mass flowrates of hydrogen do impact the total water flowrate across the membrane. The total water flow across the membrane must be broken down into its electro-osmotic drag and back diffusion components to better understand total water flow across the membrane.

Yan et al [25] also performed fuel cell experiments repeated some of the total water flow experiments with liquid water also. The first experiment was conducted with liquid water and a fixed current density. The total water transfer coefficient was used to obtain the total water flux across the membrane as the results are shown in Figure 3.2.1.4:

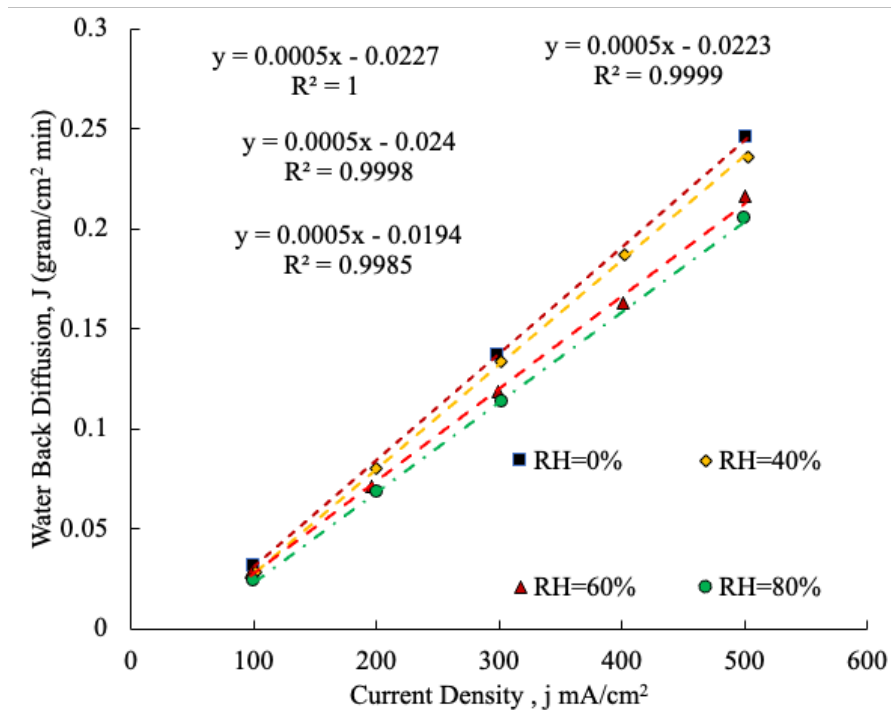


Figure 3.2.1.4 Total Water Flow at Fixed Current Density with liquid water [25]

The total water flow was originally reported and no transformation on the data is needed. The total water flow data was fit to a linear trendline, a polynomial fit was not needed. In this total water flow experiment, one side of the membrane was exposed to liquid water,

and the other side is exposed to water vapor. It is possible that the liquid on one side of the membrane can produce linear flow. The linear trendline does indicate that the electro-osmotic drag is not changing with current density. The Nernst-Planck equation is valid for liquid, and this experiment had liquid on one side. In all cases, the total water flux data was fit to a linear trendline, while cases with water vapor were fit to polynomial. The new data fits show that trendline does not go through the origin. This confirms that other fluid drivers are present, both electro-osmotic drag and back diffusion are present. To better understand electro-osmotic drag and back diffusion portions of the total water flow needs to be determined.

The next experiment that Yan et al [25] conducted was with humidified hydrogen and humidified air. As before, the total water transfer coefficient needs to be converted to the total water flux by using equation 17. The total water flux is shown in Figure 3.2.1.5:

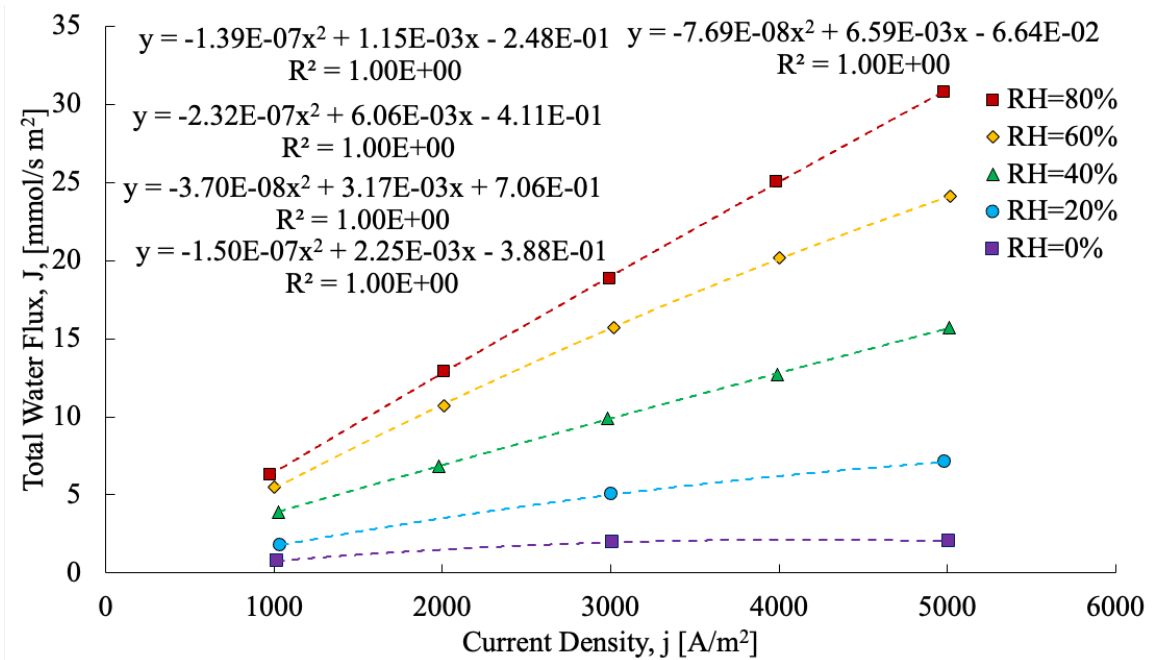


Figure 3.2.1.5 Total Water Flow with variable relative humidity [25]

The total water flows does not vary linearly with current density, it follows a polynomial trend. The total water flow was expected to follow a linear trendline, the polynomial trend indicates that the electro-osmotic drag coefficient and/or the back diffusion coefficient are changing with current density. The total water flow trendline was fit to a polynomial data for the best data fit. The non-linear behavior could be due to changing electro-osmotic drag coefficient with current density. To better understand electro-osmotic drag and back diffusion, the total water flow must be broken down into its electro-osmotic drag and back diffusion components to gain more insight.

Cai et al [31] had initially reported the total water transfer coefficient in their fuel cell experiments and the total water transfer coefficient needs to be converted to total mass flux across the membrane through equation 17 as shown in Figure 3.2.1.6:

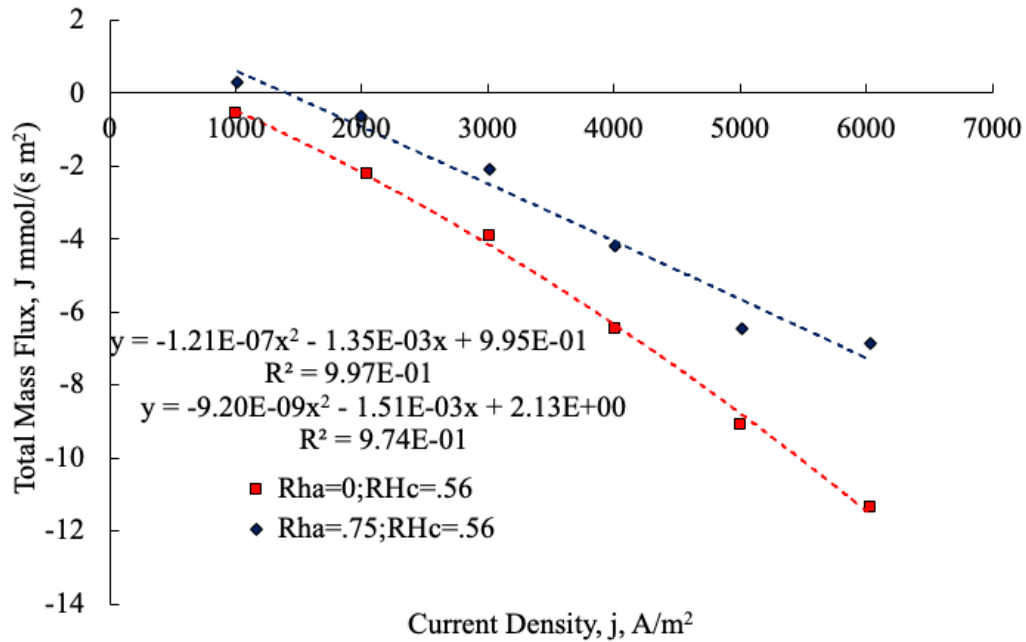


Figure 3.2.1.6 Total Water Flow Across the Membrane [31]

The total water flow data does show provide more insight compared to the total water transfer coefficient. It was not possible to fit the data to a linear trendline, instead it was fit to a polynomial, this could be due to the changing electro-osmotic drag coefficient and back diffusion coefficient changing with current density. The hydration state will be impacted by the total water flow moving across the membrane. The fuel cell experiment was conducted with water vapor. The electro-osmotic drag and back diffusion coefficient are a function of the hydration state of the membrane which if a factor on why the trendline is non-linear. The higher anode relative humidity has less negative total water flow this is due to the higher ionic conductivity at higher anode relative humidity. To further understand electro-osmotic drag and back diffusion, the total water flow needs to be decomposed into its electro-osmotic drag and back diffusion components.

In Nguyen and White's [32] fuel cell model, the total water transfer coefficient was reported, the total water flux across the membrane is needed and this done through equation 17. The total water flux for all three cases is shown in Figure 3.2.1.7:

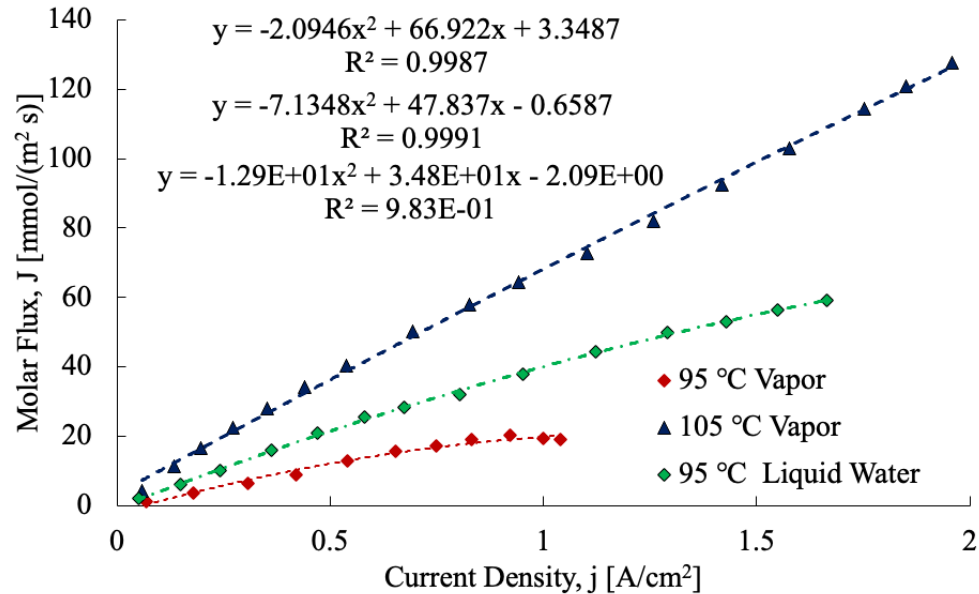


Figure 3.2.1.7 Total Water Flow Across the Membrane for liquid and vapor cases [32]

The total water flow across the membrane provides more insight compared to the total water transfer coefficient. The total water flow could not be fit to a linear trendline, it was fit to a polynomial. All the case the polynomial fit was a better fit compared to a linear trendline, this could be the results of the changing electro-osmotic drag and back diffusion coefficient. The electro-osmotic drag and back diffusion coefficient appear to be a function of current density. To better understand the electro-osmotic drag and back diffusion, the total water flow must be broken down into its electro-osmotic drag and back diffusion components.

Barragan et al [34] performed experiments with liquids, and Barragan et al [34] had reported the total water flux as shown in Figure 3.2.1.8. As can be seen, the total water flow is impacted by the voltage gradient, current and pressure gradient.

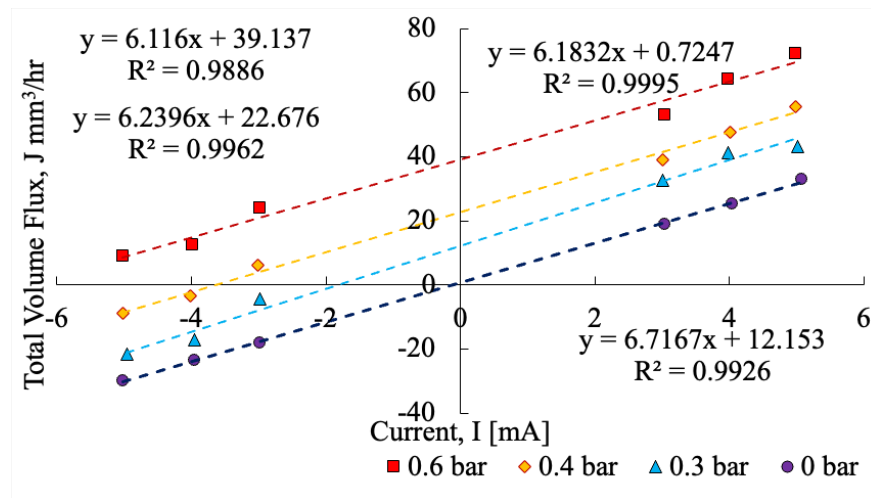


Figure 3.2.1.8 Total Water Flow Across the Membrane for liquids [34]

Barragan et al's [34] total water flow at each constant pressure was fitted to a linear trendline, there was no need to fit the experimental data to a polynomial fit. The linear fit indicates that the electro-osmotic drag coefficient and back diffusion coefficient are constant and independent of current density. As the system pressures increases, the linear trendline shifts, upwards and away from the origin. The slopes of the trendline are very close to one another ranging from 6.116 to 6.7167 mm³/(mA hr.) and the constant changed from 0.7247 mm³/hr. at 0 bar to 39.137 mm/hr. at 0.6 bar. The total water flow data was not broken down to determine how much of the total water flow is from each fluid driver. The total water flow needs to be analyzed to understand each fluid driver.

Choi et al's [35] total water flux coefficient was only reported in their experiments, and these value needs to be converted to total water flux through equation 17. The total water flux across the membrane is shown in Figure 3.2.1.9:

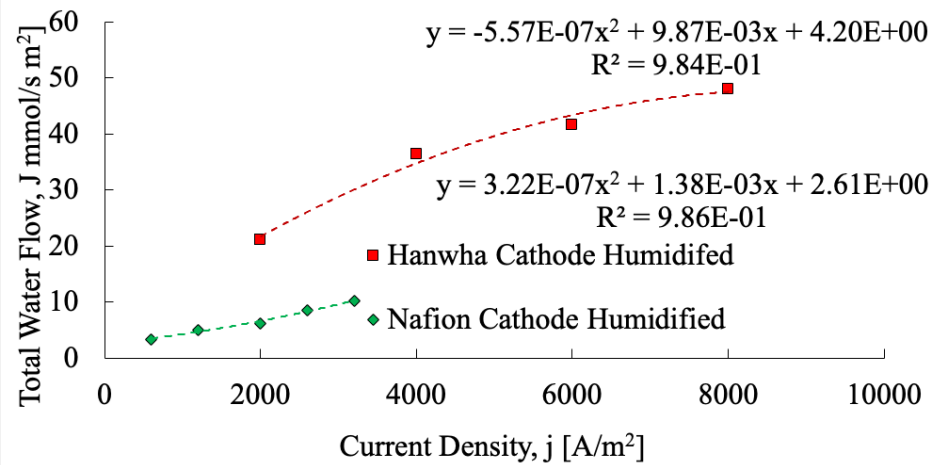


Figure 3.2.1.9 Total Water Flow Across the Membrane for Humidified Cathode [35]

The total water transfer coefficient does not tell how the total water flow varies with current density. It was also expected that total water flow would be linear based on the Nernst-Planck equation. It was not possible to achieve a linear fit of the data. In both cases the data was fit to a polynomial, the linear trendline did not provide a good correlation. The non-linear behavior could be due to changing electro-osmotic drag and back diffusion coefficient. The total water flow needs to be analyzed to determine the electro-osmotic drag and back diffusion component of the total water flow, to better understand how the transport coefficients depend on current density.

Colinart et al [36] had initially reported the total water transfer coefficient and the total water flux across the membrane needed to be obtained by using equation 17. The total

water flux data was fit to a polynomial data; the polynomial fit was better than the linear trendline. The total water flux across the membrane is shown in Figure 3.2.1.10:

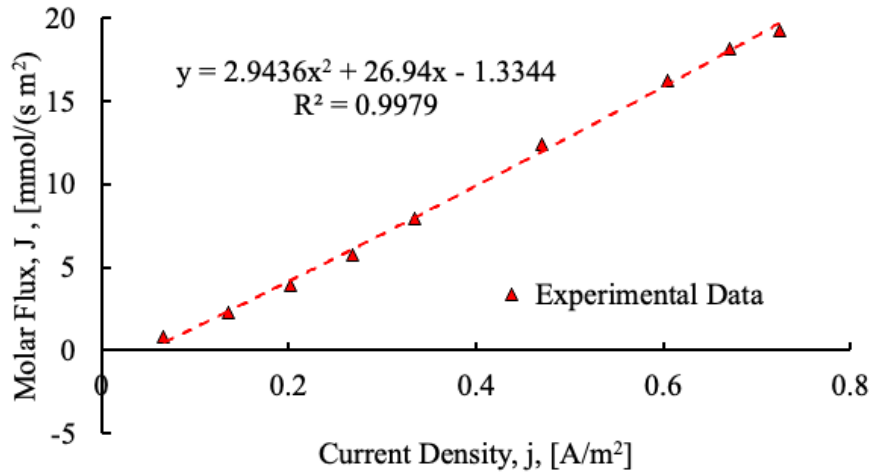


Figure 3.2.1.10 Total Water Flow Across the Membrane [36]

It was expected that the total water flow data follow a linear trendline, but the total water flow was fitting to a polynomial instead. The data fit was evaluated and the best trendline fit was a polynomial. The polynomial fit indicates the electro-osmotic drag and back diffusion coefficient are a function of current density. The transport coefficient will be changing because the membrane properties changing with hydration state of the membrane. The total water flow needs to be broken down into its electro-osmotic drag and back diffusion coefficients.

Adachi's [37] liquid and vapor along with the vapor/vapor experiments, in both experiments the relative humidity was converted to water content through equations 74-76. The total water flux with the concentration gradient and the trendline is showed in Figure 3.2.1.11:

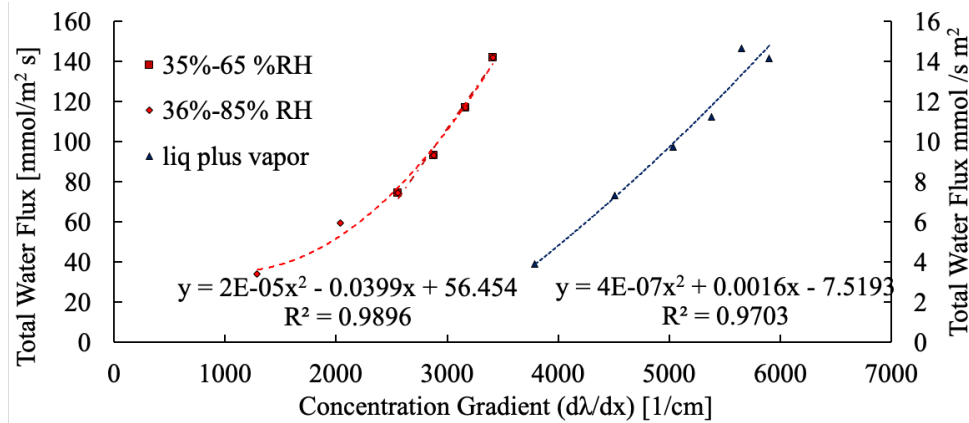


Figure 3.2.1.11 Total Water Flow Across the Membrane for vapor/vapor and liquid vapor [37]

In the vapor/vapor scenario, the total water flow did not vary linearly with the concentration gradient, it was expected that the total water flow varies linearly with the concentration gradient. There was a linear region in the trendline between the 35%-65% RH, the 85% RH data point made the trendline non-linearly. The total water flow in the liquid/vapor scenario, was not fit to a linear trendline, it was fit to a polynomial data. In both cases a polynomial fit was applied to liquid and vapor experimental data as well as the vapor and vapor data.

There is a difference on how much water is moved across the membrane for the when the membrane is exposed to liquid compared to water vapor. There is more water moved across the membrane when the membrane is exposed to liquid water compared to when the membrane is exposed to water vapor. This behavior is also seen in the Schroeder Paradox. The total water flow needs to be broken down to determine how much of the

total water flow is from the back diffusion and why there is a difference between the liquid/vapor scenario and the vapor/vapor scenario.

Adachi's [37] had initially provided the total water transfer coefficient this value needs to be converted to the total water flux with equation 18. The total water flow is expecting to be linear but none of the cases were fit to a linear trendline, all the data was fit to the polynomial. The total water flow plot is shown in Figure 3.2.1.12:

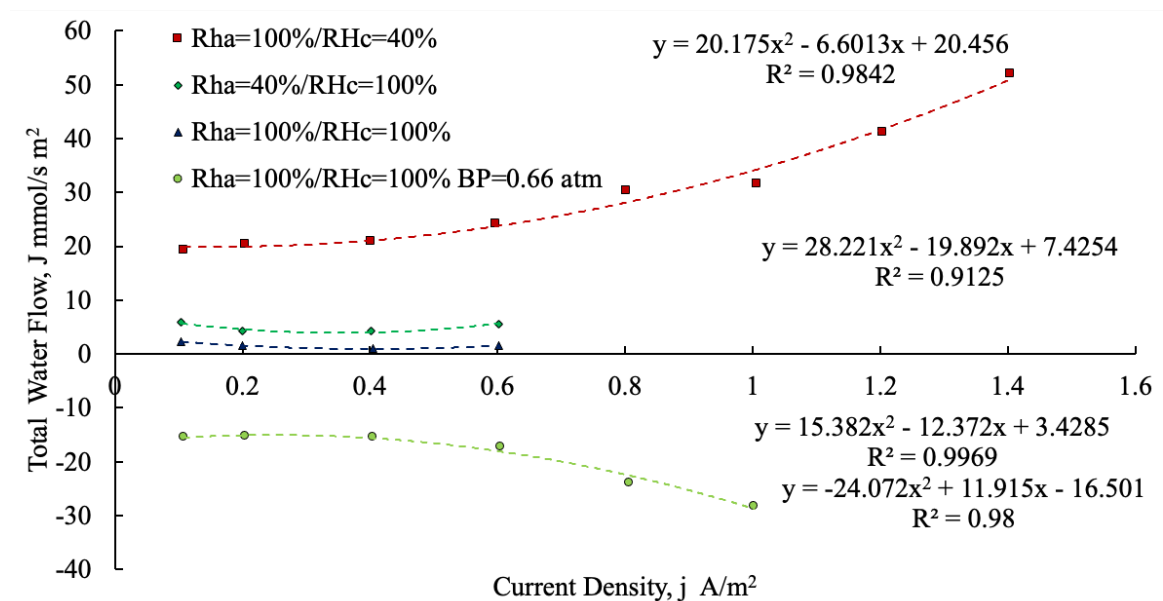


Figure 3.2.1.12 Total Water Flow Across the Membrane [37]

The initial thought was that the data would follow a linear trendline but that was not the case, the total water flow varied non-linearly. The total water flow does not follow a linear fit because the electro-osmotic drag coefficient and back diffusion coefficient are changing with current density and appear to be a function of current density. The inlet relative humidity does impact the total water flow. To better understand the total water

flow, the total water flow needs to be broken down into its electro-osmotic drag and back diffusion components to see how they are changing with current density.

One of the methods used to compare fuel cell configuration is to use the total water transfer coefficient, this way the electro-osmotic drag and back diffusion coefficient models do not come into play. The comparison does not provide the electro-osmotic drag and back diffusion coefficients. This was one of the cases that needed the data transformed to extract electro-osmotic drag and back diffusion portion of the water flow and extract the electro-osmotic drag and back diffusion coefficients.

Ito et al [39] had only reported the total water transfer coefficient and did not separate the total water flow into its fundamental components. The total water transfer coefficient along with the current density are used to obtain the total water flux as shown in Figure 3.2.1.13. In all the cases the total water flow is negative indicating it is in the direction of cathode to anode.

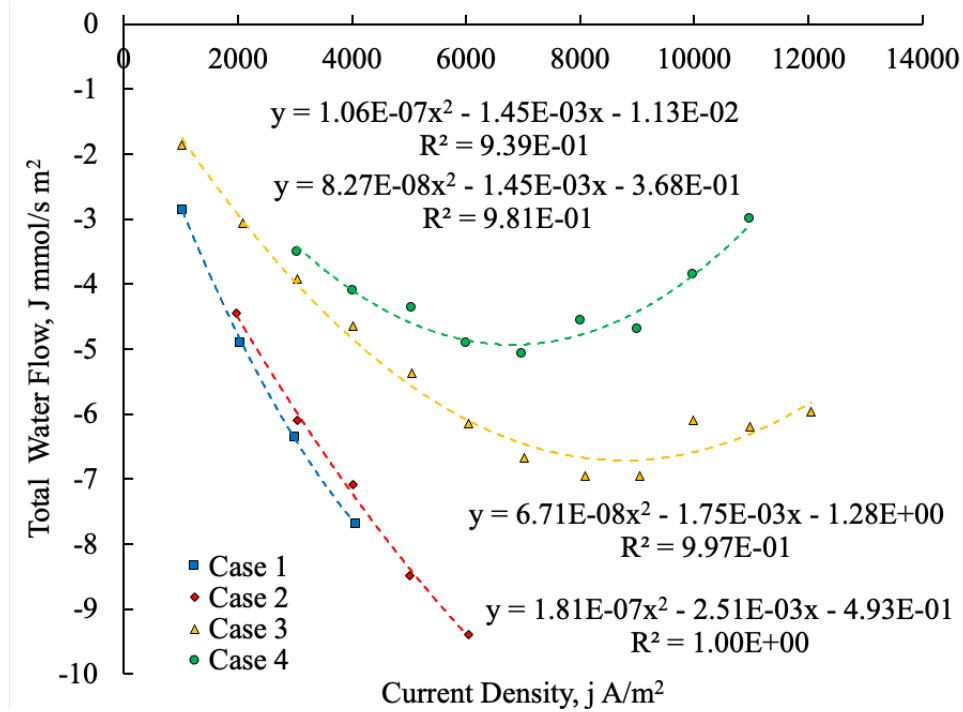


Figure 3.2.1.13 Total Water Flow Across the Membrane [39]

As before the total water flow was in the direction of cathode to anode in all cases, this would support humidification of the hydrogen, but it does not provide insight on electro-osmotic drag and back diffusion. The total water flow data did not follow a linear trendline, it instead exhibited a non-linear behavior. The non-linear behavior indicates that the electro-osmotic drag and back diffusion coefficients are a function of current density. To better understand how the electro-osmotic drag and back diffusion coefficients change with current density, the total water flow must be broken down into its electro-osmotic drag and back diffusion components without assuming any transport coefficient.

Ge et al [40], Bezamalinovic [41] and Anotani [43] reported results as total water flux across the membrane and no transformation of the data is needed. The data can be used to determine the electro-osmotic drag portion of the total water flow. Reid et al [42] kept the data as total water transfer coefficient and equation 17 was needed to obtain the total water flux as shown in Figure 3.2.1.14. The total water flow can be used to determine the electro-osmotic drag and its portion of the total water flow.

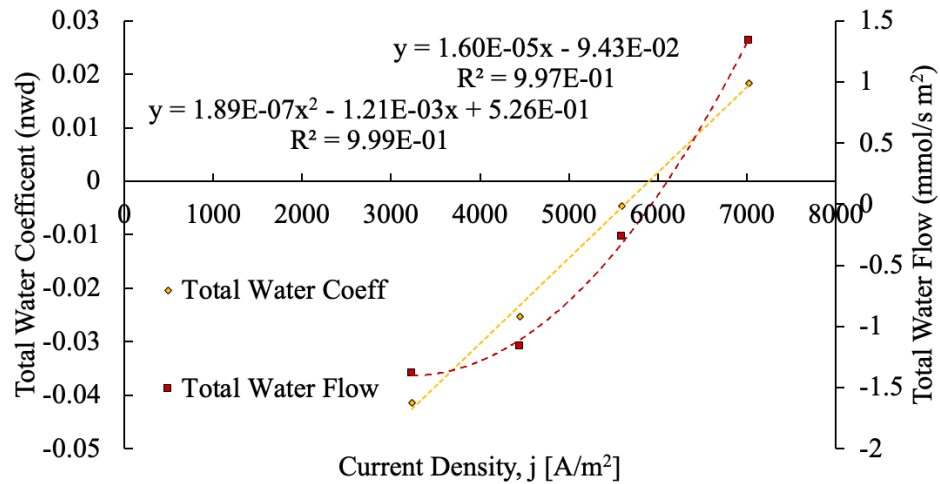


Figure 3.2.1.14 Total Water Flow Across the Membrane [42]

The total water flow across the membrane plotted against current density. The total water flow data trendline was fit to a polynomial fit, a linear fit was not used, this could be a result of the electro-osmotic drag and back diffusion are changing with respect to current density. To better understand the electro-osmotic drag and back diffusion, the total water flow must be broken down into its fundamental fluid drivers. The isolation of electro-osmotic drag and back diffusion must be done without assuming a fluid driver.

When the total water flow transfer coefficient was reported it did not provide the electro-osmotic drag coefficient and back diffusion coefficient, it only provided direction of the total water flow, with the proposed method the total water flow can be broken down into its electro-osmotic drag and back diffusion components analogous to breaking down a resultant vector into its x and y components.

3.3 Electro-Osmotic Drag and Back Diffusion

Individual fluid drivers cannot be measured by themselves, instead only the total water flow across the membrane can be measured indirectly and the desired fluid driver must be extracted from the total water flow. If the desired fluid drive is not extracted it will contain other fluid driver which can lead to over or under reporting the true results.

One of the issues that been observed in research is that the data trendline is assumed to be linear and it is forced through the origin. The assumption of linearity does come from the Nernst-Planck equation. When a linear trendline is assumed, it is assuming that the transport coefficient is independent of the measured variable. It is not known if this assumption is true as Nguyen and White [32] had shown in their fuel cell model that the electro-osmotic drag coefficient does change with current density. The only way to confirm this is to determine the electro-osmotic drag coefficient and plot it with respect to current density. The membrane hydration state will also impact the electro-osmotic drag and back diffusion coefficients.

By forcing the linear trendline through the origin, it assumes that all the total water flow is from the measured variable and no other fluid driver is present. If there are other fluid drivers present, then they are lumped in with the measured variable. The Nernst -Planck equation states there are two components the electro-osmotic drag and back diffusion components, and it also assumes that the transport coefficient is independent of the measured variable. The electro-osmotic drag coefficient needs to be obtained at each data point, and it must be plotted against current density. The plot of the electro-osmotic drag against current density will determine if electro-osmotic drag is a function of current density.

The same technique that was used for breaking down total water flow, can be used on the electro-osmotic drag experiments to extract only the electro-osmotic drag coefficient and its contribution to the total water flow. As mentioned before the total water flow is indirectly measured and it contains all fluid drivers present in the experiment. The total fluid flow is not all electro-osmotic drag. The electro-osmotic drag needs to be extracted from the total fluid flow.

The electro-osmotic drag models need to be further examined to see if other fluid drivers were present in the experiment. The original trendline is forced through the origin which neglects back diffusion and assumes the electro-osmotic drag coefficient is independent on current density. In addition, there is uncertainty how the electro-osmotic drag coefficient varies with current density. The first step is to refit the trendline data from

Ren et al [61] to see if the trendlines can go through the origin. When the trendline is refitted a constant is generated from the curve fitter. The first refit of Ren et al [61] is shown in Figure 3.3.1:

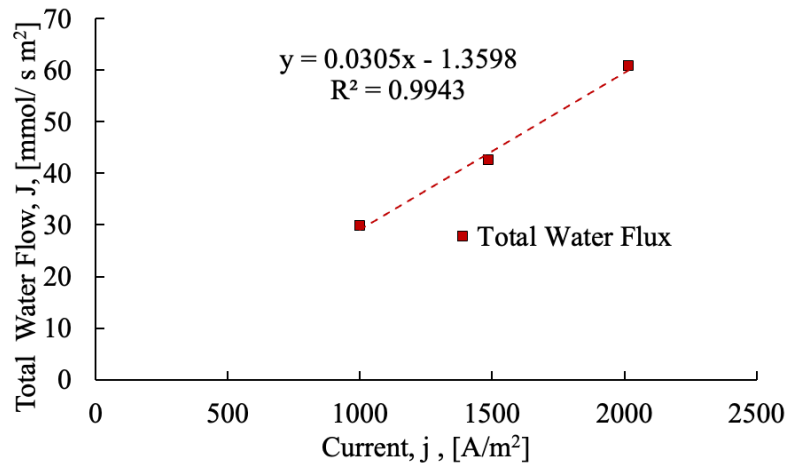


Figure 3.3.1 Total Water Flow Across the Membrane [61]

This is one of the few cases where the data was fit to a linear trendline. There is a constant that does appear and this constant is of the opposite sign of the slope of the line indicating that this driver is opposing electro-osmotic drag. This driver opposing electro-osmotic drag is back diffusion. The data will be further analyzed to compare results, it seems by forcing through the origin it is neglecting back diffusion. It is not known how strong the back diffusion component is and the total water flow data must be broken down to determine the electro-osmotic drag and back diffusion portion of the total water flow. The second case by Ren et al [61] was also refit and results of the refit are shown in Figure 3.3.2:

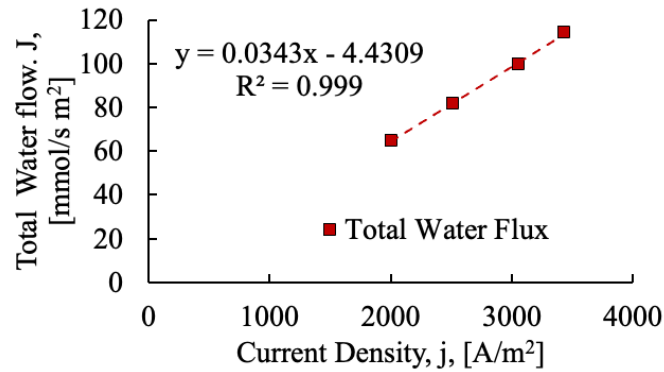


Figure 3.3.2 Total Water Flow Across the Membrane [61]

A new linear trendline was applied to the original data, in this case the data trendline was not forced through the origin, the new data fit does confirm the trendline does not go through the origin. The new data trendline does confirm that another fluid driver is present and the other fluid driver is back diffusion. The back diffusion is working against the electro-osmotic drag based on the sign difference of the two terms. The strength of the back diffusion is unknown, and it must be determined by breaking down the total water flow into its electro-osmotic drag and back diffusion component. Once the back diffusion and electro-osmotic drag terms are determined, the assumption of neglecting other fluid drivers can be further evaluated.

Lee et al [64] data was reexamined in this case all three relative humidity conditions were separated, the original data plot was not forced through the origin and to keep consistency the flow was not forced through the origin as shown in Figure 3.3.3. All the data was fit to a linear trendline and the trendline did not go through the origin indicating that back diffusion does have an impact on the total water flow.

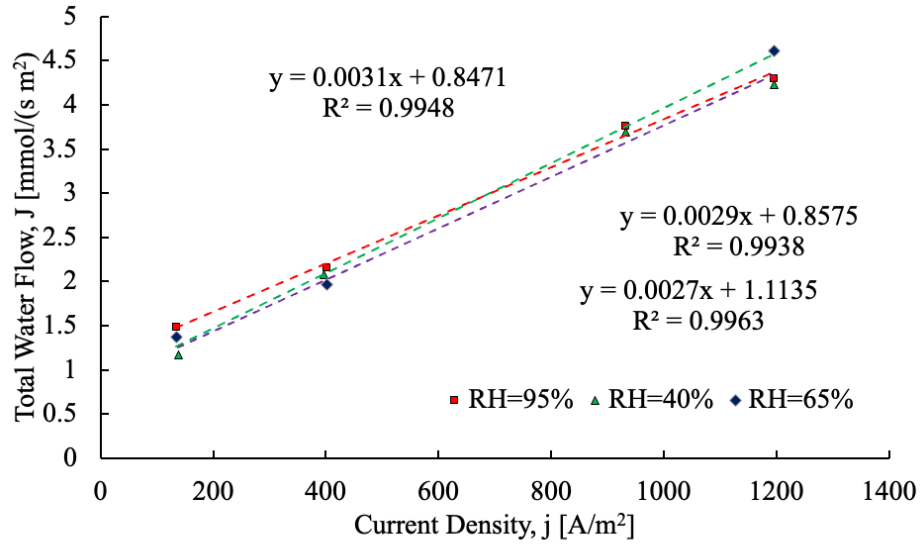


Figure 3.3.3 Total Water Flow Across the Membrane [64]

The refitted linear trendlines confirms that the data trendlines do not go through the origin, in fact that another fluid driver is present and it is back diffusion. This is one of the few cases where the total water flow was not forced through the origin which acknowledges the presence of back diffusion. Each relative humidity condition had its own trendline and based on the initial inspections, each trendline has its own different slope, and this indicates that each case has a different electro-osmotic drag coefficient. In this case the data fits to a linear trendline. The slope of each trendline is different and this indicates that the relative humidity does impact the electro-osmotic drag coefficient. Since the total water flow contains electro-osmotic drag and back diffusion, the total water flow needs to be broken down into electro-osmotic drag and back diffusion component without assuming a fluid transport coefficient, once this is done electro-osmotic drag and back diffusion can be examined further.

Husar et al [65] pressure driven flow data was examined with the assumption that other fluid drivers may be present, the data was not forced through the origin. The fuel cell is very sensitive on its hydration state, so accuracy is required to make sure the cathode does not flood. The replot of the data is shown in Figure 3.3.4.

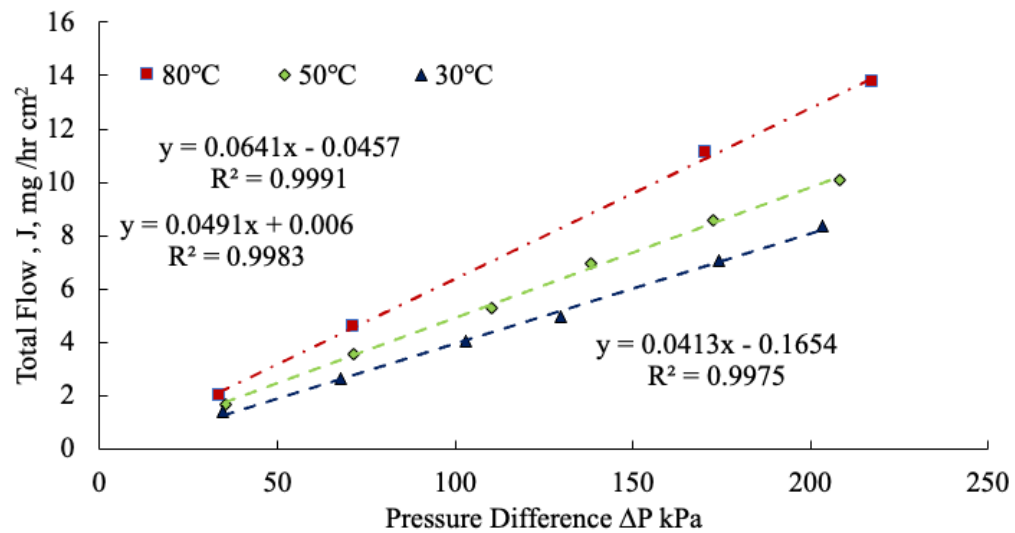


Figure 3.3.4 Total Water Flow Across the Membrane [65]

The total water flow was refitted to a new trendline that does not go through the origin, when the refitted occurred another the presence of another fluid driver was confirmed. In two of the three cases, the other fluid driver is working against the pressure gradient, and in the other case it is working with the pressure gradient. The strength of the unknown fluid driver and it must be determined, and this is done by breaking the total water flow down into is fundamental fluid drivers. Once the fluid drivers are determined the initial assumptions made can be evaluated.

The second experiment performed by Husar et al [65] was with total water flow and variable current density, this data was replotted where the trendline was not forced through the origin to account for other fluids drivers present. The total water flow is shown in Figure 3.3.5:

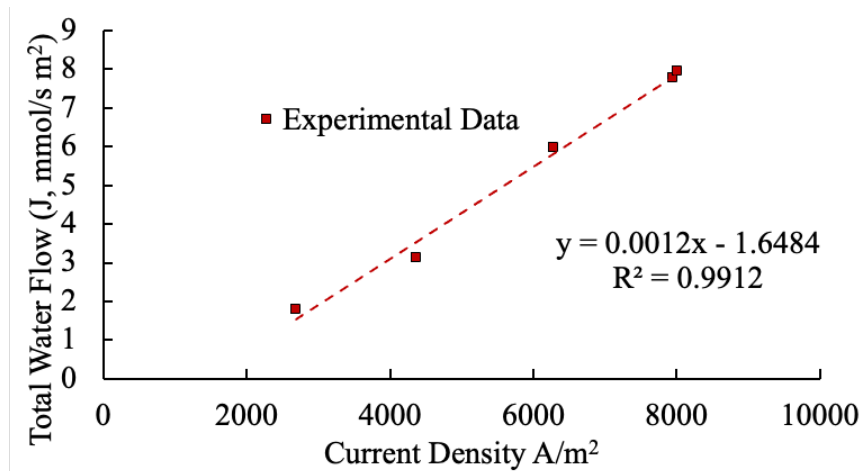


Figure 3.3.5 Total Water Flow Across the Membrane [65]

The total water flux was fitting to a linear trendline that does not go through the origin, and it was found that another fluid driver was present and the other fluid driver is back diffusion it is working against electro-osmotic drag. The total water flow must be broken down to determine how much of the total water flow is electro-osmotic drag and how much is back diffusion. When the electro-osmotic drag and back diffusion components are determined electro-osmotic drag and back diffusion can be further determined.

Ye et al [38] had used the slope of the trendline to compute the electro-osmotic drag coefficient, the total water flow trendline and had initially forced through the origin which also implies no other fluid driver is present, the slope of the original trendline give

an electro-osmotic drag coefficient that is not a function of current density. Ye et al [38] total water flow data was replotted and not forced through the origin to see if the assumption made about back diffusion being neglectable was correct. The first step involves refitting the data such that the trendline does not go through the origin. The first refit is shown in Figure 3.3.6:

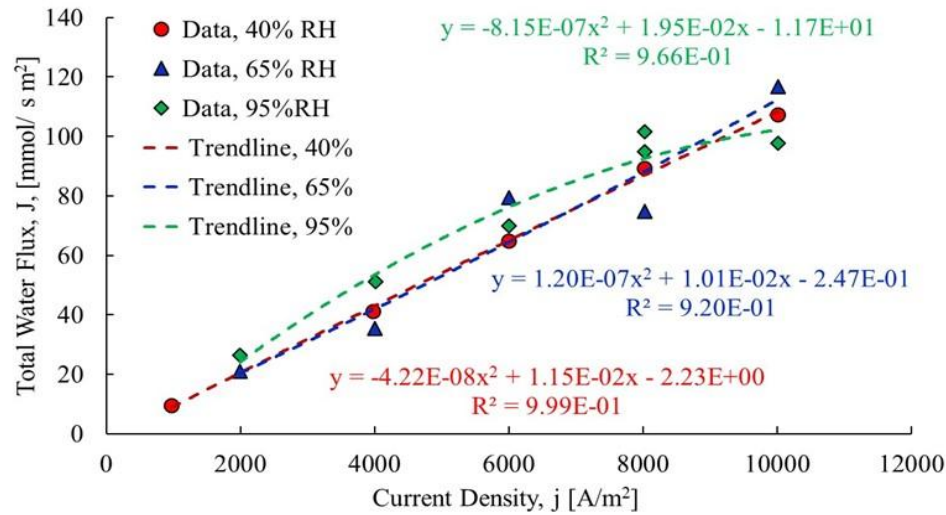


Figure 3.3.6 Total Water Flow Across the Membrane [38]

A linear fit in the trendline data was not obtained and a polynomial fit in data was used. It is clear the total water flow trendline does not go through the origin which indicates that other fluid drivers are present besides electro-osmotic drag. As the relative humidity of the fuel cell increases, the trendline becomes less linear, the 95% RH case deviates the most. The non-linear trendlines indicates that other fluid drivers are present and the linear trendline should not have been fit through all the data points as a result the electro-osmotic drag portion of the total water flow needs to be extracted from the total water flow. At high relative humidity such as 95% could have liquid water present. If liquid water is present, then the Schroeder Paradox could come into play. The impact of liquid

water needs to be understood. The total water flow needs to be broken down into its electro-osmotic drag and back diffusion components to determine if the initial assumption of neglecting back diffusion is valid.

Another reason that could influence the non-linearity is the presence of liquid water. The next electro-osmotic drag data that was further examined was Ge et al [48], and this data was run at three fixed temperatures and fixed current densities and variable concentration gradients. When the first set of data mining was occurring, it was noticed that a trendline through all data was not achievable. The data for the at 303 K is shown in Figure 3.3.7:

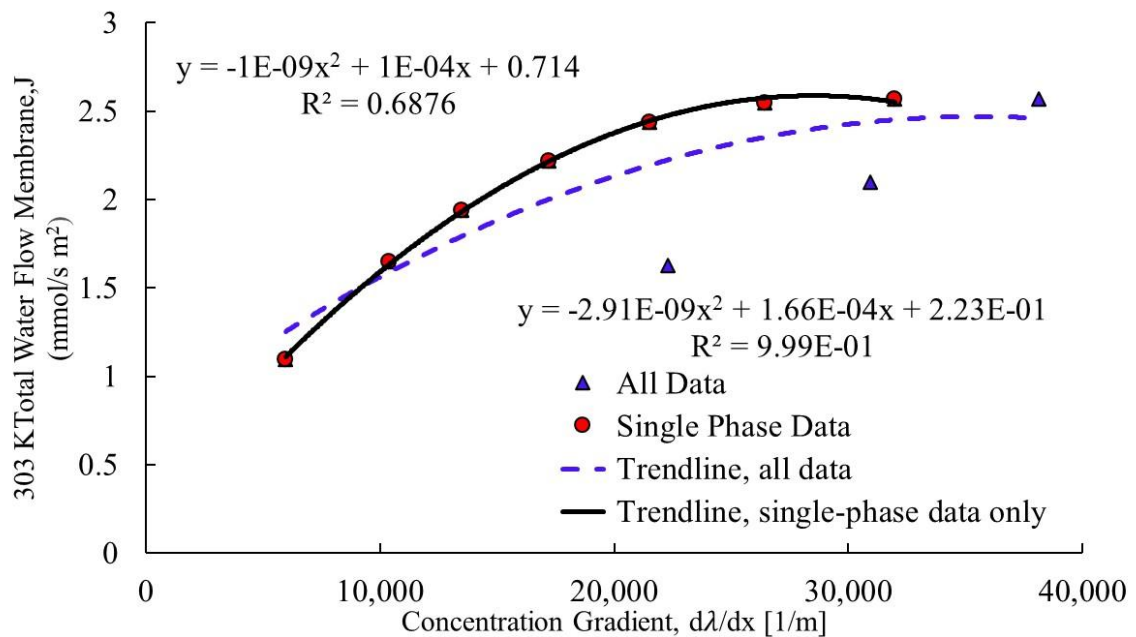


Figure 3.3.7 Total Water Flow Single-Phase and All data -303 K [48]

A trendline was fit through all data points and a good correlation could not be achieved, the data was then separated into a single-phase region, and a good fit was achieved. The data was then the two-phase data was plotted also. It was possible to achieve a trendline

through the single-phase water data, but it was not possible to achieve this for all the data.

The data was further replotted with the single-phase and phase data as shown in Figure

3.3.8:

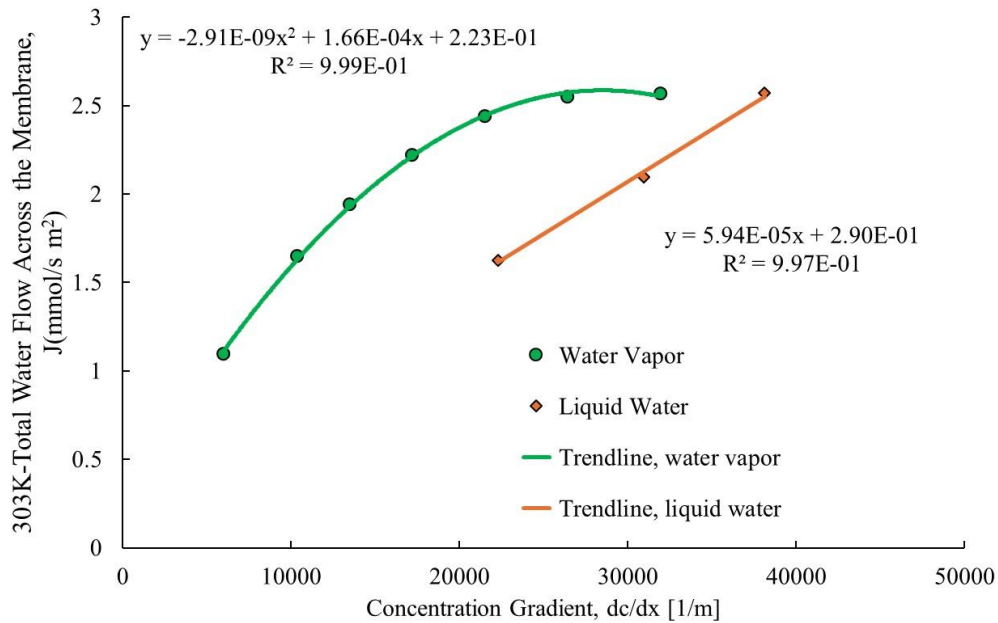


Figure 3.3.8 Total Water Flow Single-Phase and Two-Phase -303 K [48]

A trendline is achievable in both the single-phase and two-phase regions. The total water flow will be further analyzed between the single and two-phase regions. The liquid water scenario could be a result of the Schroeder Paradox. The single-phase region was non-linear, but the two-phase region was fit to a linear trendline. The different data fit indicates that there are different transport mechanisms in play with liquid water is present. The total water flow needs to be broken down to determine how the electro-osmotic drag and back diffusion are influenced by the single-phase and two-phase region and this down by breaking down the total water flow across the membrane.

Ge et al [48] electro-osmotic drag experiment at 323 K, was examined also, the first step involves obtaining a trendline for the experimental data. The plots of the data are shown in Figure 3.3.9:

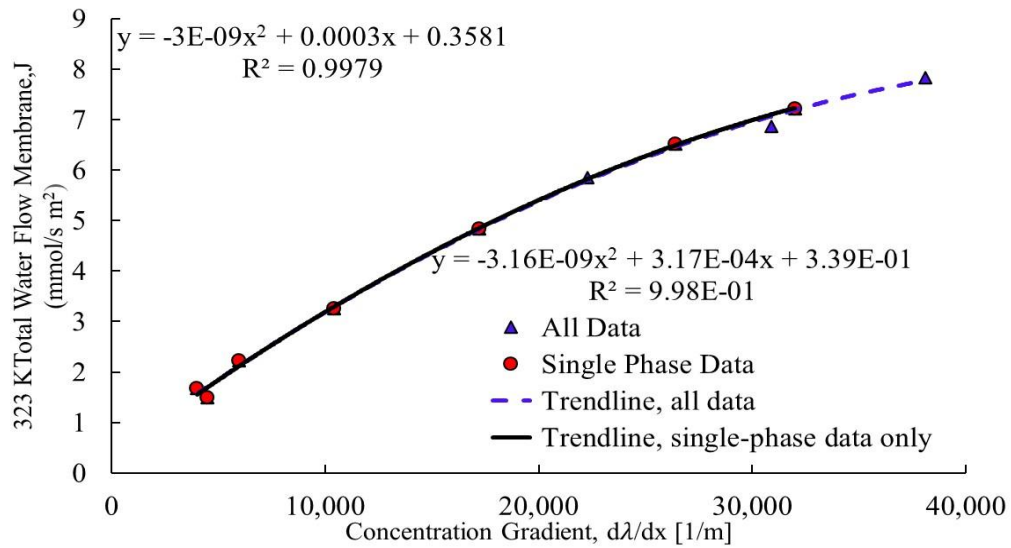


Figure 3.3.9 Total Water Flow Single-Phase and All data 323K [48]

A good trendline was achieved for the single-phase and all data, but the single-phase data does provide good correlation. The data is further separated into single-phase and two-phase was further plotted as shown in Figure 3.3.10:

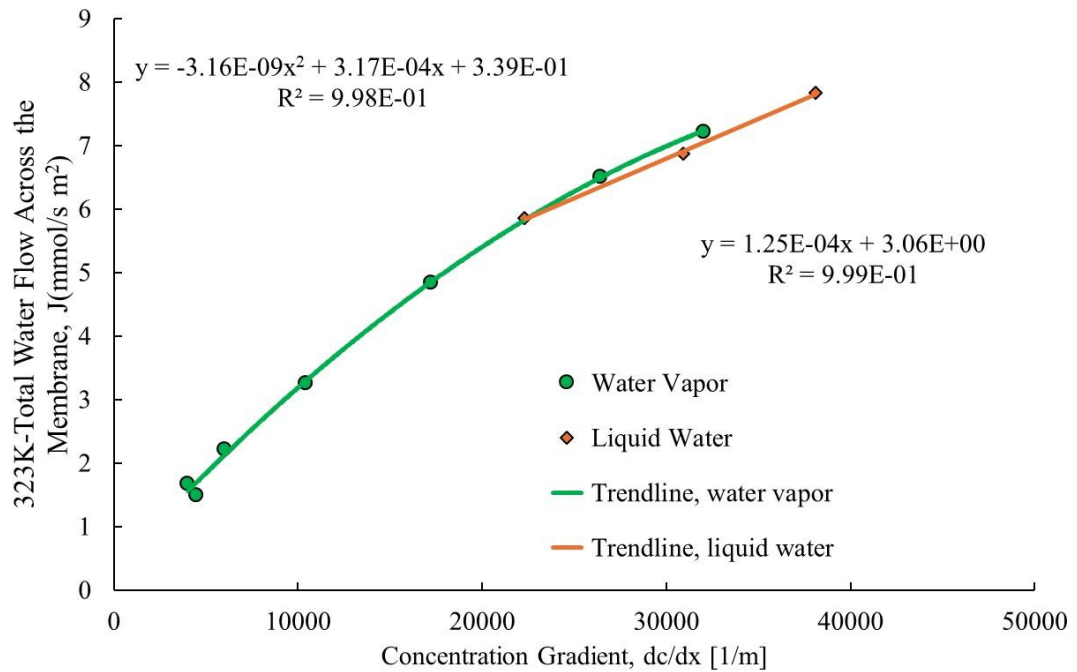


Figure 3.3.10 Total Water Flow Single-Phase and Two-Phase 323K [48]

To keep the consistency with the 303 K, the 323 K data will be answered the same way.

The last case Ge et al [48] performed was 353 K and the total water flow and single-phase data was plotted to obtain a trendline. The trendline for the total water flow and single-phase data is shown in Figure 3.3.11:

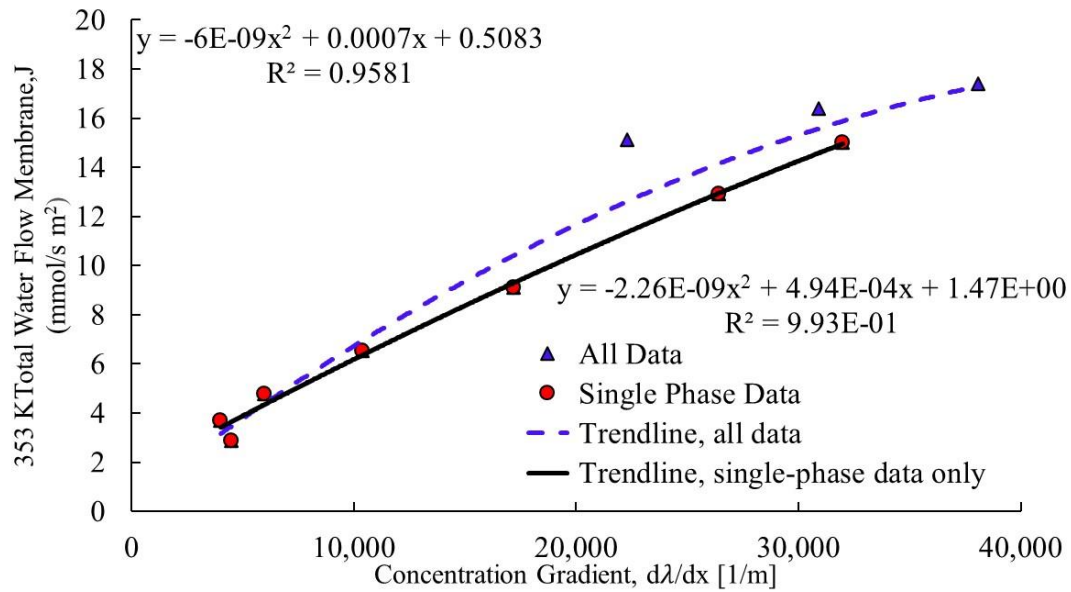


Figure 3.3.11 Total Water Flow Single-Phase and All Data 353K [48]

The all-data case did not have a good data fit compared to the single-phase only. As in the previous cases the total data is broken up into the single and two-phase data as shown in Figure 3.3.12:

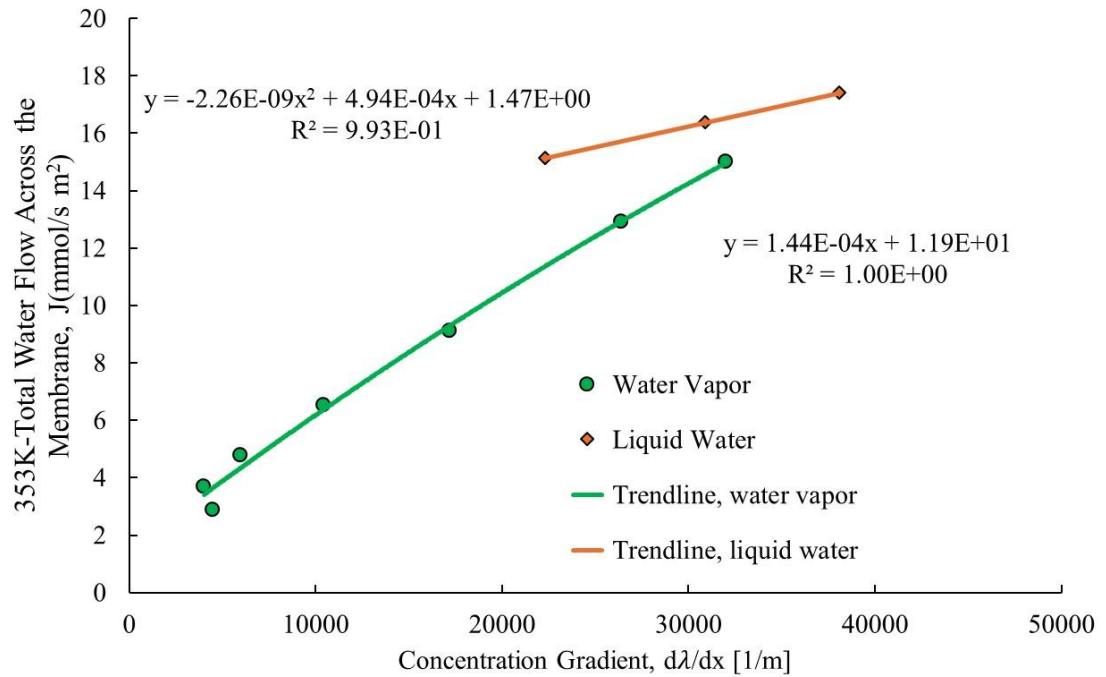


Figure 3.3.12 Total Water Flow Single-Phase and Two-Phase 353K [48]

Good data fit is achieved in the single and two-phase data is achieved. It seems that there are different trends in the single phase and two-phase data. To better understand the electro-osmotic drag and back diffusion, the total water flow should be broken down into its electro-osmotic drag and back diffusion components.

Ingarra et al [106] noted that water flow through a membrane will be different for water vapor compared to liquid water. The total water flow data trendlines change based on single phase and two-phase water flow, the key is to find when the transition is from single phase and two-phase flow. In summary there are differences in the single and two-phase data, this could come from the different fluid driver that come into play when liquid water is present.

Another mode of transport obtained from the Nernst-Planck equation is the back diffusion which is Fickian diffusion. Yan et al [25] examined back diffusion with variable current density as shown in 3.2.1.4 and Adachi [37] has examined diffusion in Figure 3.2.1.11 Chadha et al [73] performed experiments with total water flow to determine back diffusion. The total water flow data does contain single and two-phase data. The first step involved relating the relative humidity different to hydration state and plotting the data as shown in 3.3.13:

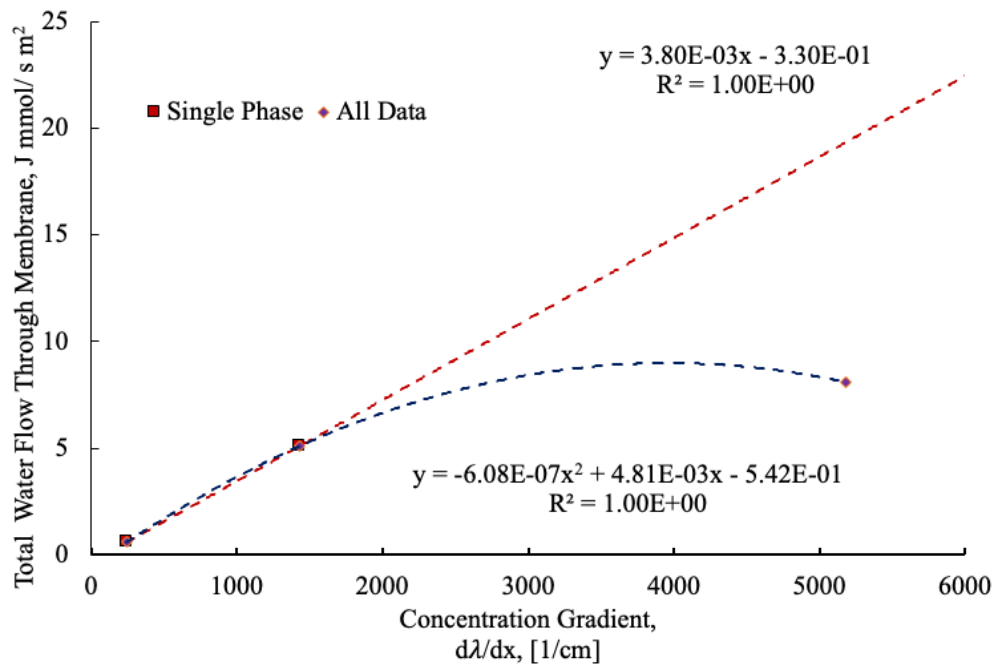


Figure 3.3.13 Total Water Data for Back Diffusion [73]

The original total water data was refitted. An anomaly was found in the data, the total water flux did not increase with concentration gradient, as a result the data was replotted

the single and two-phase data will be further isolated. The total water flow needs to be broken down to isolate the back diffusion component of the total water flow.

In summary when the total water flow is indirectly measured, it is the summation of all fluid drivers present in the experiment and as a result the total water flow needs to be broken down into its fundamental fluid drivers. An individual fluid drivers cannot be measured by itself. There appears to be another fluid driver in the experiments besides back diffusion.

3.4 No Consistent Thermal Osmosis Results

Ge et al [48] noted that temperature will play have an impact on electro-osmotic drag more so with liquid water compared to water vapor it is currently not known if this is another fluid driver. The temperature and phase of water will impact electro-osmotic drag. Huang et al [107] had noted that electro-osmotic drag dominates when the anode is humidified whereas back diffusion dominates when the cathode is humidified. The total water was not clearly broken down it is primary fluid driver components. Data analysis is important for isolating electro-osmotic drag and back diffusion from the total water flow.

Water transport through the membrane is driven by the hot to cold side of the cell. If the cathode is hotter than the anode, then electro-osmotic drag is suppressed even if the cathode relative humidity is lower than the anode. It is noted that the suppression increases with temperature difference. Back diffusion is also suppressed by thermal

gradients but to a lesser extent compared to electro-osmotic drag. Back diffusion is influenced by temperature and concentration gradients.

Humidity is not the main factor influencing water flow, inlet gas temperatures do play a factor. Also heating up the cathode does reduce the flooding in the fuel cell. To add further complications there is inconsistencies with thermal osmosis magnitude and directions. Researchers have attempted to understand thermal osmosis; they have either done it through modeling and/or experimentation. Kim and Mench [75],[76], Villaluenga et al [77], Tasaka et al [84][85][87], Zaffou et al [80], Bradaen et al [108], Fu et al [78], Thomas et al [81], and Perry and Patterson [109] have performed thermal osmosis experiments. These researchers have obtained conflicting results, however. Villaluenga et al [77], Fu et al [78] and Tasaka et al [84],[85] have observed thermal osmosis water flow in the direction of cold to hot, while Zaffou et al [80], Braden et al [10], and Perry and Patterson [109] have observed thermal osmosis flow in the direction of hot to cold. The thermal osmosis coefficient ranges from $7.5 \times 10^{-6} \text{ kg/ (m}^2\text{s } ^\circ\text{C)}$ through $4.1 \times 10^{-6} \text{ kg/ (m}^2\text{s } ^\circ\text{C)}$.

Bradaen et al [108] performed transient thermal osmosis experiments and Perry and Patterson [109] had performed experiments under sub-freezing conditions. Because of the variety of testing methodology, there were several possible inconsistencies with each type of experiment conducted. Villaluenga et al [77] performed experiments with methanol (CH_3OH) and water, Kim and Mench [75],[76], Tasaka et al [87][88] performed their

experiments with liquid water, while Zaffou et al [80] and Thomas et al [81] performed theirs with 100% humidified reactant gas. There have been inconsistencies with predicting the magnitude and direction of thermal osmosis.

Empirical thermal osmosis models were developed and some of these have been used in PEM fuel cell models. Fu et al [78], and Dickenson and Smith [110] have concluded that thermal osmosis could be neglected. Goshtasbi [111] has mentioned that there is uncertainty with thermal osmosis data. Fu et al [78] performed an experiment to determine to measure thermal osmosis, the experiment consisting of running with a fixed temperature gradient and a variable concentration gradient. They suggest that thermal osmosis can be neglected.

Dai et al [112] suggested that thermoosmotic transport of water in the membrane is not well understood but could contribute appreciably due to the internal temperature gradient, even in the presence of good thermal balance between the bi-polar plate”. Huang et al [107] had noted “Many researchers have studied the water transport phenomena in MEA, and most of the related works include experimental results and modeling predictions/comparisons. However, there is no consensus in the literature on a broad range of issues. Thermal osmosis needs to be further analyzed to reach conclusion about it.

Barragan and Kjelstrup [113] had noted that for hydrophobic membrane the fluid flow is in the direction as hot to cold and in the case of the hydrophilic membrane the fluid flow is in the direction of cold to hot as shown in Figure 3.41:

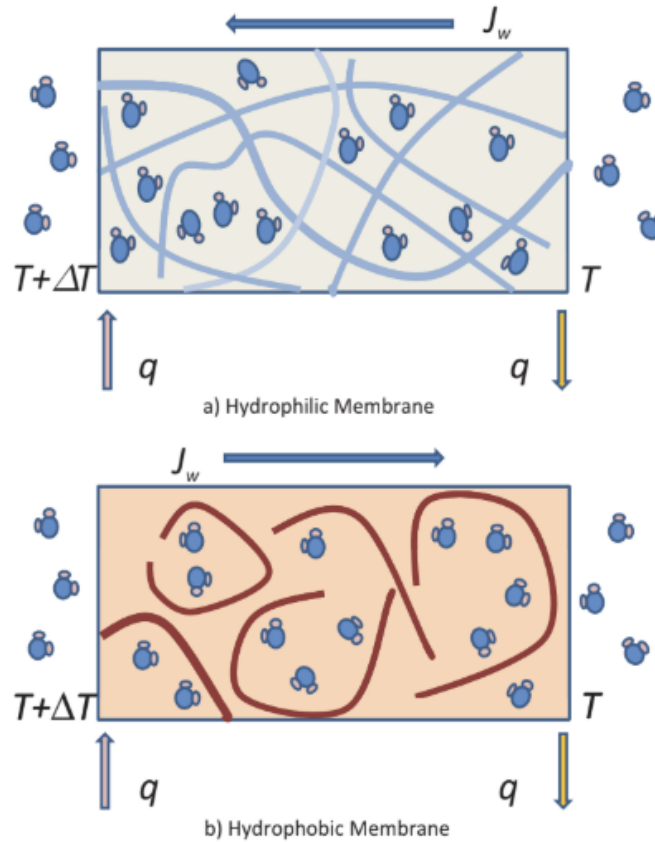


Figure 3.4.1 Thermal Osmosis for Hydrophobic and Hydrophilic Membrane [113]

The entropy difference between the free fluid and the fluid in the membrane will determine the direction of thermal osmosis. In the case of membranes used for fuel cells the direction of the water flow was in the cold to hot direction as shown in Table 3.4-1

Table 3.4-1 Thermal Osmosis for Fuel Cell Membranes [113]

Membrane [Reference]	$d_m/10^{-3}$ m	Liquid	$t/^{\circ}\text{C}$	$D_T/\text{kg.m}^{-1}.\text{s}^{-1}.\text{K}^{-1}$	Thermo-osmotic flux direction
Nafion 417 Tasaka et al. [45]	0.43	water	35	-1.5×10^{-9}	from cold to hot
Neosepta CM-2 Tasaka et al. [45]	0.12			-1.6×10^{-8}	
Nafion 117 Villaluenga et al. [4]	0.183	water methanol	26	-1.4×10^{-10} -2.7×10^{-10}	from cold to hot
Nafion 112 Kim and Mench [1]	0.050	water	65	-2.0×10^{-13}	from cold to hot
Flemion SH50 Kim and Mench [1]	0.050			-3.0×10^{-13}	
Gore-Select Kim and Mench [1]	0.018			-1.3×10^{-13}	

In all the thermal osmosis cases shown in Table 3.4-1 all the cases were tested with liquids, and it was not tested with vapors, it is not known if the same logic will occur for vapor. There are also two temperature driven flow, thermal osmosis and membrane distillation. The phase of the fluid needs to be examined when looking at thermal osmosis. It is possible that the phase of the fluid as well as the membrane will provide insight on thermal osmosis. The first examination involves comparing Kim and Mench thermal osmosis comparison with others with the phase of the fluid added as shown in Table 3.4-2:

Table 3.4-2 Thermal Osmosis for Fuel Cell Membranes [75]

Membrane	Researcher	Phase	Direction
Nafion 112	Kim and Mench[75]	Liquid	Cold to Hot
Nafion 117	Villaluenga et al [77]	Liquid	Cold to Hot
Nafion 417	Tasaka et al [85]	Liquid	Cold to Hot
PTFE Reinforced Nafion Membrane/Catalysts Coated Nafion	Zaffou et al [80]	100% Humidified	Hot to Cold
Gore Select 5510	Zaffou et al [80]	100 Humidified	Hot to Cold

It is possible that the thermal osmosis was not fully isolated from the total water flow, and this could be why there is deviations in thermal osmosis results. The thermal osmosis needs to be examined to confirm the magnitude and direction of thermal osmosis. The thermal osmosis portion of the total water flow needs to be extracted from the total water flow.

3.5 Analysis of Thermal Osmosis

In general, there is uncertainty with thermal osmosis, it is not known if it is truly neglectable. It is not possible to make these conclusions because there is inconsistency with the magnitude and direction of thermal osmosis. The same approach for thermal osmosis is taken for thermal osmosis in liquid and vapors. In the case of thermal osmosis there were two fluid drivers present the thermal osmosis component and the pressure component. The thermal component must be separated from the pressure-based component. The first step is to take the equation of state as shown in equation 77.

$$J = C\Delta T + B\Delta P \quad (77)$$

If the derivative is taken with respect to temperature equation 78 is obtained.

$$\frac{dJ}{d\Delta T} = C \quad (78)$$

If the derivative is taken with respect to the pressure gradient equation 79 is obtained:

$$\frac{dJ}{d\Delta P} = B \quad (79)$$

The next step is to fit the total water flow data to a linear trendline as shown in equation 80.

$$J = c_o + c_1\Delta T \quad (80)$$

The derivative of the data fit is taken with respect to the temperature difference and equation 81 is obtained.

$$\frac{dJ}{d\Delta T} = c_1 \quad (81)$$

The thermal osmosis coefficient can be obtained by setting equation 78 into equation 81 to yield equation 82. The thermal osmosis coefficient is solved by setting the theoretical model to the experimental data. The thermal osmosis coefficient is obtained without any assumption.

$$C = c_1 \quad (82)$$

In the linear fit case not all the fluid flow is from thermal osmosis, if temperature difference in equation 80 is set to zero then this explains fluid flow at this case as shown in equation 83.

$$J = c_o + c_1 * 0 \quad (83)$$

If the slope of the trendline is positive the thermal osmosis fluid flow is moving in the direction of the thermal gradient, and if the slope is negative the thermal osmosis is moving against the thermal gradient. The sign of c_o and c_1 also provide insight, if c_o and c_1 are the same sign, both fluid drivers are in the same direction, and if c_o and c_1 are opposite signs one of the fluid drivers is working against the other which would yield a point where no flow would occur and this point can be found by setting the water flux of equation 80 to zero and solving for the temperature difference as shown in equation 84. The true direction of thermal osmosis can also be determined based on the sign of c_1 if

the sign is positive thermal osmosis is in the predicted direction and if the sign is negative, it is the opposite direction.

$$\Delta T = \frac{-c_1}{c_0} \quad (84)$$

When a linear fit is used, the thermal osmosis transport coefficient is independent of the temperature difference. If the case where the trendline cannot be fit to a linear function is fit to polynomial as shown in equation 85.

$$J = c_o + c_1\Delta T + c_2(\Delta T)^2 \quad (85)$$

The derivative of the water flux is taken with respect to the temperature gradient as shown in equation 86.

$$\frac{dJ}{d\Delta T} = c_1 + 2c_2\Delta T \quad (86)$$

If the derivative of the total water flow with respect to the thermal gradient as shown in equation 86 is set equal to the derivative of the theoretical model as shown in equation 81 the thermal osmosis coefficient can be solved for as shown in equation 87.

$$C = c_1 + 2c_2\Delta T \quad (87)$$

With the thermal osmosis coefficient obtained the thermal osmosis portion of the total water flow can be obtained with equation 88. In the case where a polynomial fit is used for the total water flow, the thermal osmosis coefficient will be a function of the temperature difference.

$$J = C\Delta T \quad (88)$$

With the thermal osmosis portion of the water flow known, the pressure component can be computed as shown in equation 89. With the pressure component and temperature component known the portion of the total flow can be computed. Composition of the total water flow can be obtained.

$$J_{Pressure} = J_{Total} - J_{Thermal\ Osmosis} \quad (89)$$

The ratio of thermal osmosis flow and pressure-based flow is shown in equation 90 and 91 respectively. With the ratio of thermal osmosis flow to total flow known, it can now be evaluated to see how strong each driver is.

$$R_{TO} = \frac{|J_{TO}|}{|J_{TO}| + |J_{Pressure}|} \quad (90)$$

$$R_{Pressure} = \frac{|J_{Pressure}|}{|J_{TO}| + |J_{Pressure}|} \quad (91)$$

The approach allows for the pressure and temperature component to be separated from the total water flow. Now the fluid drivers can be compared to one another, and the other fluid drivers can be evaluated as neglectable, minor and major driver. In the PEM fuel cell material like Nafion, the properties of the membrane properties are a function of its hydration state this behavior would be expected when a membrane is in contact water vapor but when a membrane is in contact with liquid water the properties are not expected to change.

The proposed approach will allow for the separation of thermal osmosis from the total water flow. The magnitude and the direction of thermal osmosis can be determined. The proposed. The presence of other fluid drivers will influence and explain why certain phenomena are seen in experimental data. The presence of other fluid drivers will explain why non-continuous thermal osmosis is seen. The process assumes an equation of state for the fluid flow and the measured fluid flow is a summation of all the fluid drivers present. An individual fluid driver cannot be measured on its own.

3.5.1 Hydrophilic Membranes

There are two classifications of materials, there is hydrophobic and hydrophilic, in the case of hydrophilic the membrane has an affinity for water, liking water and the other type of material is hydrophobic which do not have an affinity for water and repel water. For instance, in the Nafion membrane shown in PEM fuel cells contains a hydrophobic and hydrophilic region as shown in Figure 1.6.1

Water is considered a polar molecule with a slightly positive end and a slightly negative end; the water would be attracted to the sulfonic acid (SO_3^-) group of the Nafion membrane. The Nafion membrane has both a hydrophobic and hydrophilic regions and when liquid water is present the membrane becomes more hydrophilic. It is not known how a hybrid membrane behaves, does it behave more like a hydrophobic membrane or more like a hydrophilic membrane.

3.5.2 Hydrophobic Membranes

A sample hydrophobic membrane is PTFE; this material is hydrophobic and repels water. In chemistry the analogy of like dissolving likes means that a polar/ionic can dissolve another polar/ionic like salt and water or sugar and water, but a non-polar can oil dissolve a non-polar is why oil and water do not mix. The same is true with hydrophobic and water, in the Nafion membrane there is a hydrophobic region, and this region is the fluorocarbon chains which are the backbone of the Nafion membrane these areas do not want to be exposed to liquid water. The contact angle of water will tell if something is hydrophobic or hydrophilic, if the contact angle is greater than 90 degrees it is considered hydrophobic and if the angle is less than 90 degrees it is hydrophilic.

3.5.3 Hybrid Membranes

A hybrid membrane is a membrane that contains hydrophobic and hydrophilic regions, it is analogous to inelastic and elastic collisions, those are the two extremes, and any

collision will fall somewhere between an elastic and a inelastic collision. For instance, the contact angle of the water changes as the membrane hydrates as shown in Table 1.6-1. As the membrane is hydrating or wetting the contact angle is decreasing making the membrane more hydrophilic and less hydrophobic. As shown in Figure 1.6.1, the sulfonic acid groups grab water and start to cluster and eventually form a chain connecting both sides of the membrane. A hydration state ($\lambda=22$) denotes a membrane exposed to liquid water, and a hydration state ($\lambda=14$) denotes a membrane exposed to fully humidified air. The structure of the membrane changes as the membrane hydrates and dehydrates.

With the changes in the membrane structure the ionic conductivity, electro-osmotic drag and back diffusion coefficient show also change also one would not expect them to remain constant. In the total water flow testing a Nafion membrane was used, in these cases how hydrophobic the membrane will be determined by the state of water at the membrane. In the hybrid membranes it is not known if the hydrophobic portion of the membrane will dominate or if the hydrophilic will be dominate.

3.6 Thermal Osmosis

The next step is to reprocess the thermal osmosis data to see if there are other fluid drivers present in the data. Kim and Mench [75] thermal osmosis data with liquid water the data replotted where it was not forced through origin as shown in Figure 3.6.1:

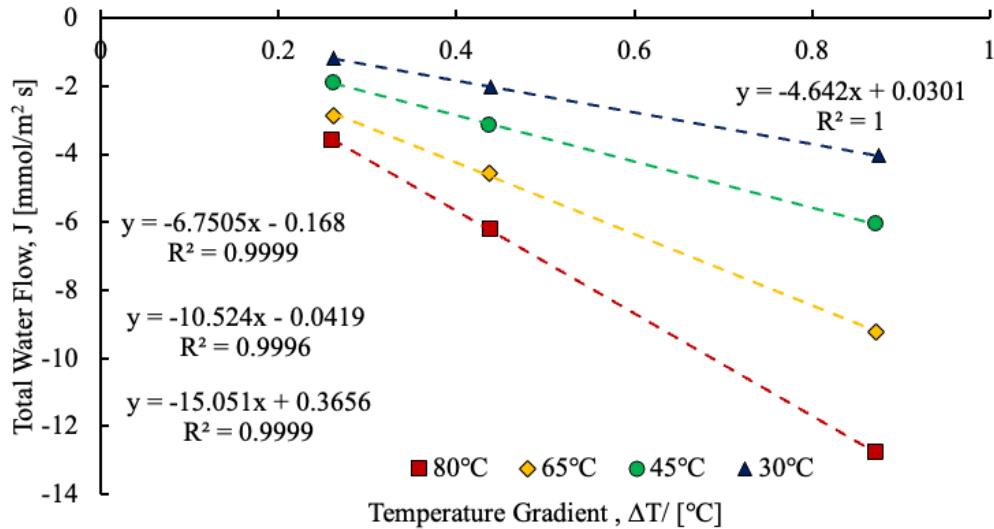


Figure 3.6.1 Total Liquid Water Flow Across the Nafion Membrane [75]

The total water flow data was fitted to a linear trendline that is not forced through the origin. The constant from the trendline indicates that other fluid drivers are present in the experiment and thermal osmosis is a portion of the total water flow. The initial trendline fit neglected other fluid drivers present. The slope of the line is negative confirming that the thermal osmosis portion of the total water flow is going in the direction of cold to hot.

There is also a constant present in the trendline fit, in some of the cases the constant is positive in this case the water flow from the other effect will oppose thermal osmosis, in the case where the constant is negative the water flow from the other fluid driver is in the same direction of thermal osmosis. This confirms that other fluid drivers are present and the thermal osmosis portion of the total water flow needs to be calculated, and the other fluid driver needs to be evaluated to see how strong the other fluid driver is and if the initial assumptions were valid. Kim and Mench [75] had also examined performed

thermal osmosis experiments with different fuel cell membrane material, the thermal osmosis data was replotted, and the total water flow was not forced through the origin as shown in Figure 3.6.2:

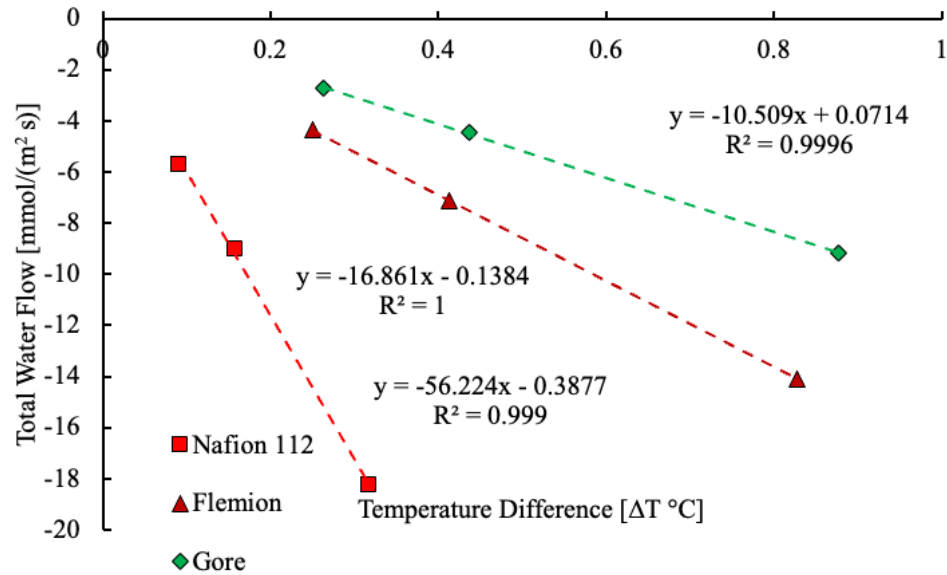


Figure 3.6.2 Total Liquid Water Flow Across the Other Fuel Cell Membrane [75]

The experimental data is fit to a linear trendline and the trendline is not forced through the origin. The slope of the trendline is negative, indicating that thermal osmosis is opposing the temperature gradient. The constant from the linear trendlines indicate that other fluid drivers are present in the experiments. Since the total water flow has thermal osmosis and other fluid drivers the thermal osmosis portion of the total water flow needs to be obtained. Like the other cases the thermal osmosis portion of the water flows in the cold to hot direction. In some cases, the constant from the trendline is positive and this is opposing thermal osmosis and, in cases where the constant is negative the other fluid driver is in the direction of thermal osmosis. Kim and Mench [76] performed experiments

with hydrophobic and hydrophilic material to understand thermal osmosis, the first step was to refit the data where it is not forced through the origin as shown in Figure 3.6.3:

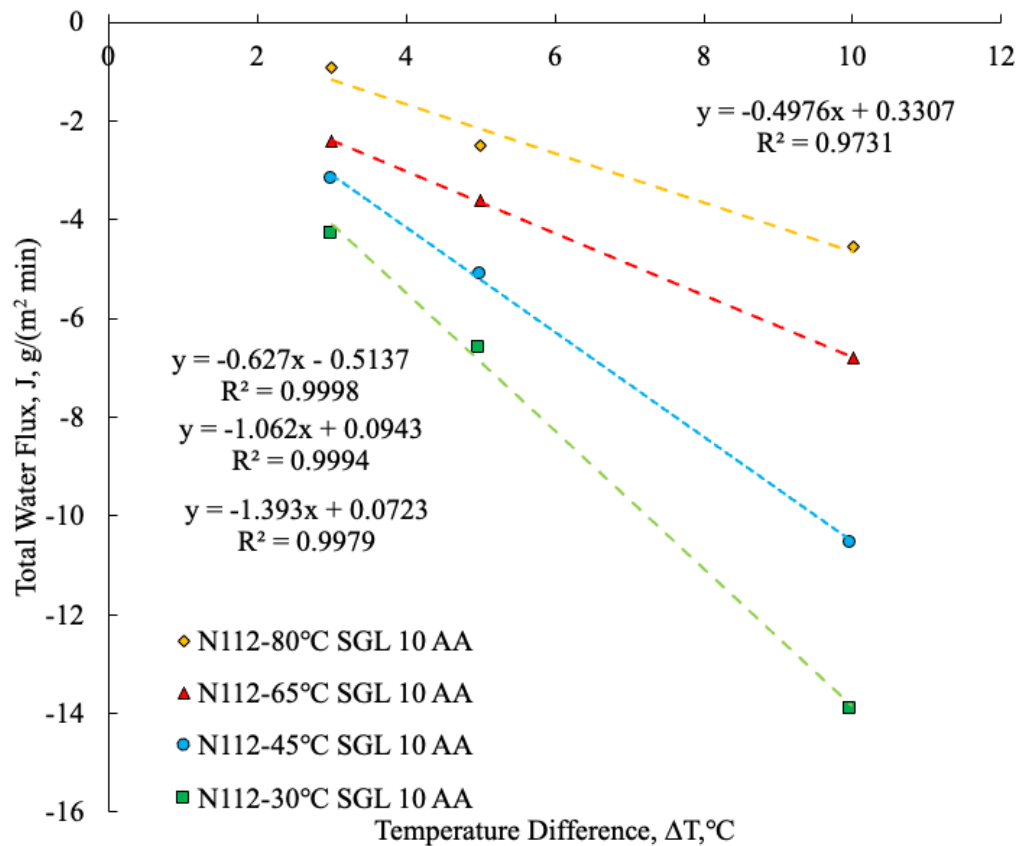


Figure 3.6.3 Total Liquid Water Flow with Hydrophilic Material [76]

The total water flow data is fit to a linear trendline, a polynomial fit was not needed, the constant from the linear trendline indicates that other fluid drivers are present and thermal osmosis is an unknown portion of the total water flow. The slope of the trendline is negative indicating that thermal osmosis is in the direction of cold to hot. The thermal osmosis portion of the total water flow needs to be computed, and the other fluid driver needs to be evaluated to see how the other fluid driver contributes to the total water flow.

With the hydrophilic case with liquid water, the thermal osmosis portion of the total water flow was in the direction of cold to hot, there was one instance where the constant from the trendline was the same sign as the thermal osmosis slope, in the case the fluid driver will be the same direction of thermal osmosis. In the other cases the other fluid driver is opposing thermal osmosis. There is a constant from the linear trendline fit, which indicates that there is another fluid driver present, and the total water flow is not all thermal osmosis.

The total water flow needs to be broken down to determine how much of the total water flow is thermal osmosis. It is not known if the other fluid driver is neglectable or if it is a major fluid driver. Once the total water flow is broken down, the total water flow can be examined, and conclusion can be made. Kim and Mench also ran thermal osmosis experiments with hydrophobic material, this data was also refit to a linear trendline where the data is not forced through of the origin as shown in Figure 3.6.4:

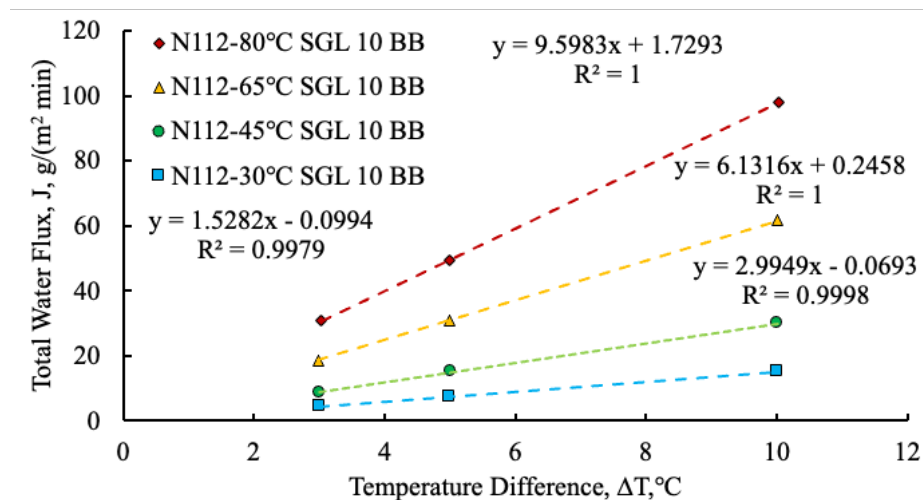


Figure 3.6.4 Total Liquid Water Flow with Hydrophobic Material [76]

The data was fit to a linear trendline where the trendline was not forced through the origin. A polynomial fit was not needed for the data fit. There is a constant in all the trendlines, indicating that not all the fluid flow is from thermal osmosis, in two of the cases the other fluid driver is opposed to thermal osmosis and in the other two cases the other fluid drive is in the same direction. The slope of the trendline is positive indicating that thermal osmosis is moving in the same direction of the thermal gradient. In all cases the thermal osmosis water flow was in the direction of hot to cold. The thermal osmosis portion of the total water flow needs to be obtained along with the other fluid drive to see how they contribute to the total water flow.

In the hydrophilic case, Kim and Mench [76] noted that there was a phase change, water would evaporate on the hot side, pass through the membrane and condense on the cold side. Kim and Mench [76] noted the water flow in the hot to cold direction is Phase Changing Flow (PCI). Kim and Mench [76] provided a schematic of how PCI occurs as shown in Figure 3.6.5. It was stated that water will evaporate on the hot side and pass through the membrane and condense on the cold side, but this does not cover cases when liquid is on the cold side and water vapor is on the hot side, this only examines liquid on both sides on the membrane.

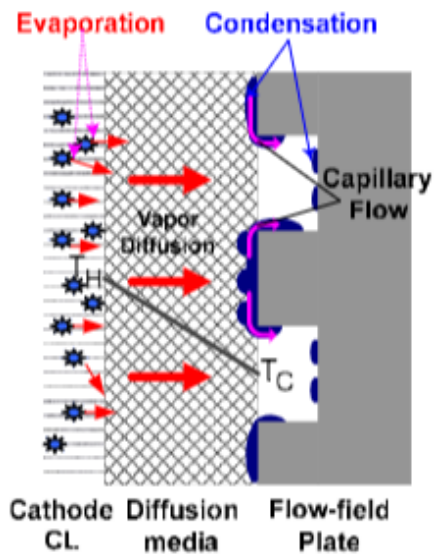


Figure 3.6.5 Schematic of Phase Change Induced Flow [76]

When comparing the hydrophobic and hydrophilic thermal osmosis experiments, the hydrophobic cases do more water across the membrane compared to the hydrophilic case. The mechanism of thermal osmosis for hydrophobic and hydrophilic are different but are governed by the thermal gradient. The hydrophobic cases do transport more liquid water compared to the hydrophilic cases.

Adachi [37] had noted that the water flow in their isothermal experiments water flow was in the direction of liquid to vapor when the membrane had liquid on one side and vapor on the other side. The Phase Change Induced (PCI) flow seems to be applicable when both sides of the membrane are exposed to liquids, there are possibilities where liquid could be on one side and vapor on the other as in Adachi [37] back diffusion experiments

Villaluenga et al [77] performed thermal osmosis experiment with methanol and water, the slope of their trendline was used to compute the thermal osmosis but equation 30 was used which assumes no other fluid drivers are present. The total water flow data was reexamined and plotted where the trendline was not forced through the origin as shown in Figure 3.6.6:

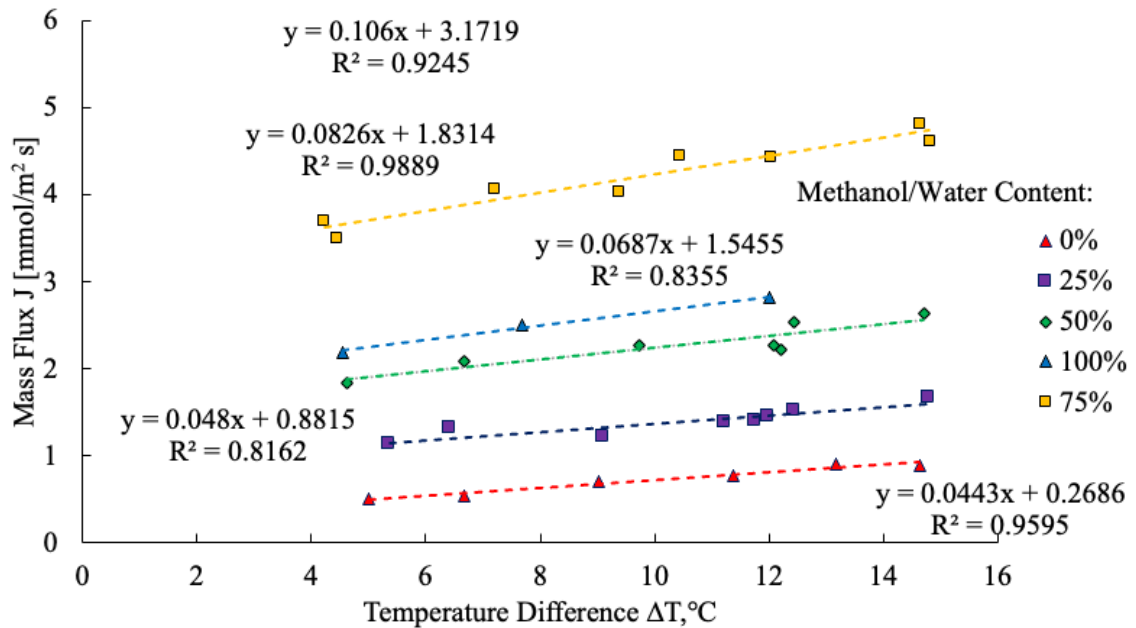


Figure 3.6.6 Total Water Flow Data Not Forced Through the Origin [77]

The total water flow was refitted to a line trendline that is not forced through the origin as shown in Figure 3.6.6 and a constant term was present. The constant indicates that other fluid drivers are present, this indicates thermal osmosis is not the only fluid driver present. The slope remains positive indicating that thermal osmosis is in the direction of cold to hot. The constant from the linear trendline fit indicates that the other fluid driver is moving in the same direction as thermal osmosis. The current process assumes that thermal osmosis is a percentage of the total water flow. The thermal osmosis transport

and thermal osmosis portion of the total water flow can now be computed, and the total water flow can be broken down into its fundamental fluid drivers. The data must be examined to obtain the thermal osmosis free of other fluid drivers.

Fu et al [78] thermal osmosis experiment was done with the cold side of the membrane fully humidified and the hot side partially humidified. The data needs to be reformatted into the terms of the concentration gradient for the back diffusion portion of the total water flow to be extracted. Initially a back diffusion model was selected, and this model was used to compute the back diffusion portion of the total water flow. This is one of the experiments that examined thermal osmosis with water vapor.

Fu et al [78] thermal osmosis data was reformatted in such a way that the concentration gradient was expressed in terms of $\frac{d\lambda}{dx}$, this was done through the use of equation 13 and for the anode and cathode side and equation 118 for the concentration difference , then equation 76 with the membrane thickness to obtain the concentration gradient.

The replot of the thermal osmosis data is shown in 3.6.7:

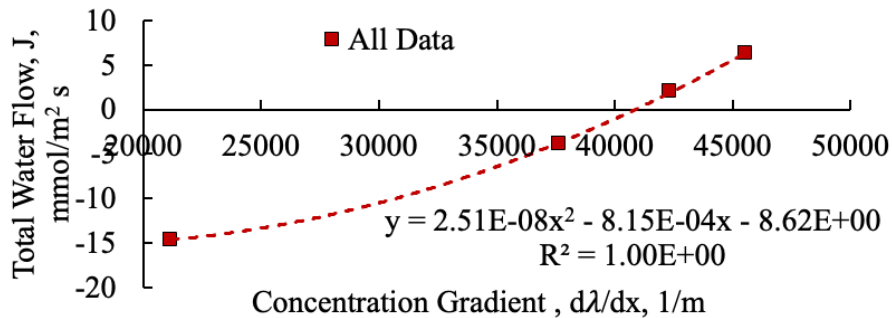


Figure 3.6.7 Total Water Flow Data Not Forced Through the Origin [79]

The experimental data was fit to a polynomial instead of a linear trendline, although there are a few points where the data is linear. The data contains back diffusion and thermal osmosis. The direction does change based on the concentration gradient. There seems to be a difference in fluid flow when liquid water is introduced to the system. Three of the data points appear to fit a linear trend but one other point does not permit the linear trendline. The data is further analyzed where the single-phase data and all data as shown in Figure 3.6.8. The direction of the water flow was in the direction of the hot side to cold side.

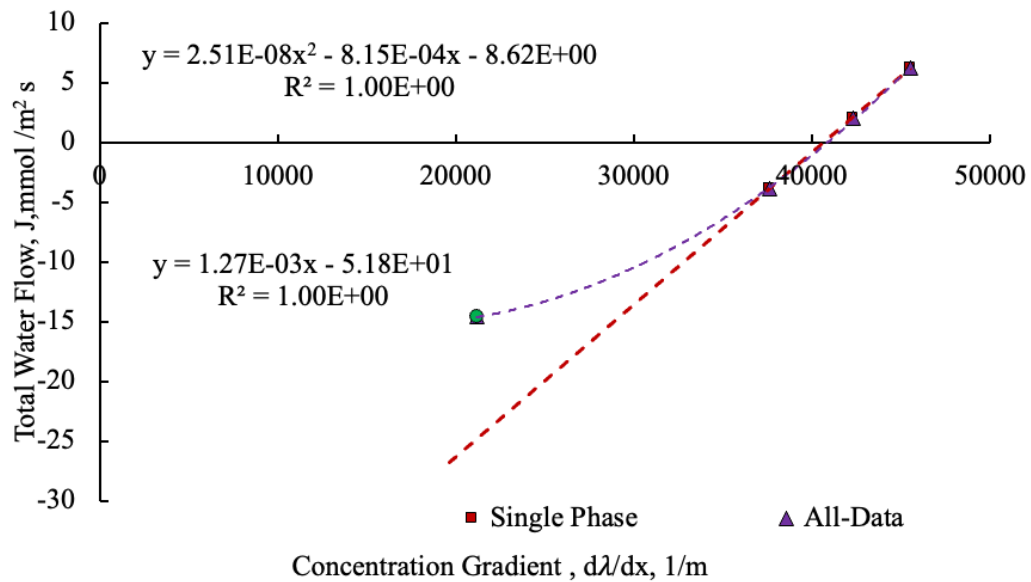


Figure 3.6.8 Total Water Flow Data Single Phase and All Data [79]

The total water flow data show different behavior in the single-phase region is different when it is isolated from all the data. The back diffusion coefficient along with back diffusion portion of the total water flow will be computed, then the back diffusion portion will be subtracted off the total water flow to compute the thermal osmosis portion of the

total water flow. This process is a new process to understand back diffusion and thermal osmosis.

The single-phase data can be fit to a linear trendline, the transition into the two-phase is analogous to the transition for laminar to turbulent flow. At higher relative humidity there is high probability that liquid water will be present. The direction of water flow was in the direction of cathode to anode, and the water flow was in the direction of hot to cold. The thermal osmosis and back diffusion need to be extracted from the total water flow without assuming a transport coefficient.

Zaffou et al [80] performed thermal osmosis experiments on an active fuel cell, at a constant current density and a variable temperature profile when the cathode was either at the same temperature than the anode or the cathode was warmer than the anode. Since the fuel cell was active, electro-osmotic drag, back diffusion and thermal osmosis would be present. The next step is to re-plot the data and obtain a trendline fit. The refitted data is shown in Figure 3.6.9:

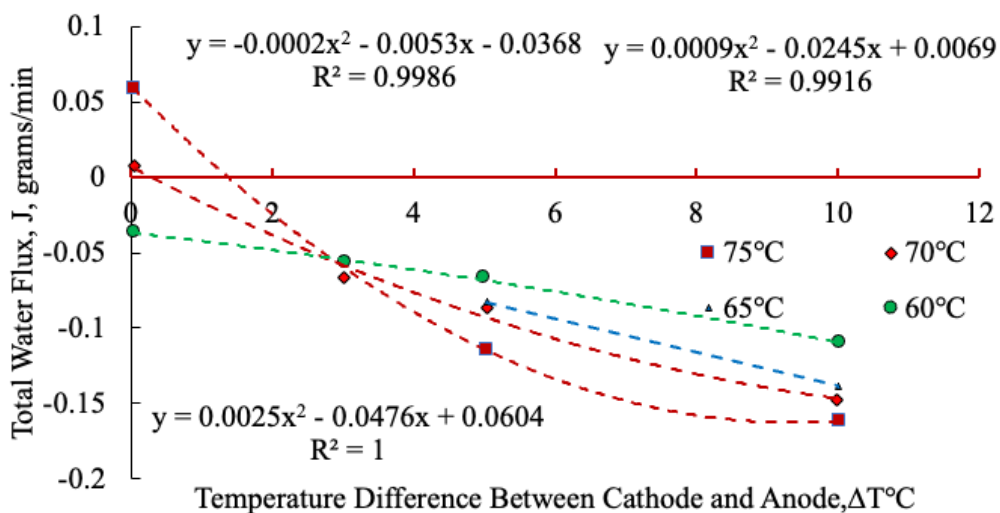


Figure 3.6.9 Total Water Flow Data used to get Thermal Osmosis [80]

The total water flow data is fit to a polynomial and not a linear trendline. There is water flow across the membrane when there is no temperature difference across the membrane. The total water data from table 2.4-1 have been plotted to see if the total water flow data goes through the origin and to extract thermal osmosis portion from the total water flow. The 60°C cathode is shown Figure 3.6.10:

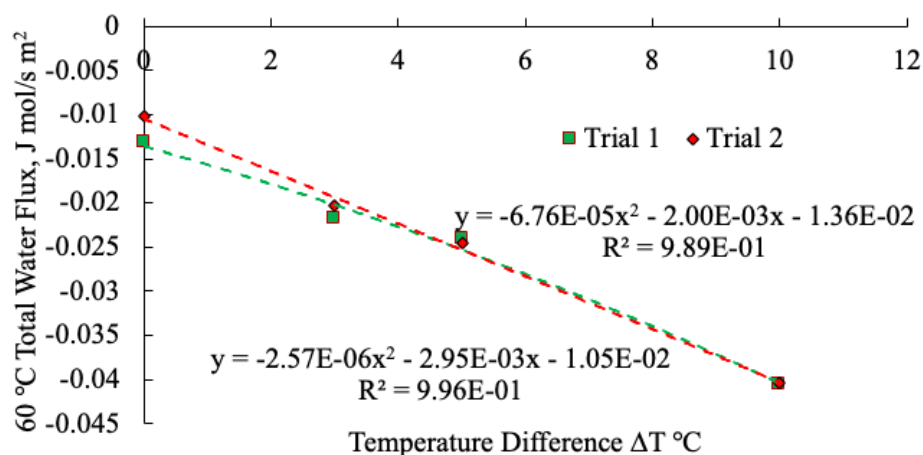


Figure 3.6.10 Total Water Flow Data used to get Thermal Osmosis [80]

The total water flow data was refitting to a trendline that does not go through the origin. The data is fit to a polynomial instead of the linear trendline. The direction of the flow was in the direction of cathode to anode which is also the hot to cold direction, and this is the total water flow.

When there is no thermal gradient, there still is water flow across the membrane, confirming that other fluid drivers are present, this could be from electro-osmotic drag or back diffusion. The total water flow is increasing with temperature difference. The thermal osmosis portion of the total water flow needs to be determined along with the thermal osmosis transport coefficient. There is inconsistency with the electroosmotic drag coefficients and back diffusion coefficients, and this makes it difficult to extract electro-osmotic drag and back diffusion. Liquid water will introduce two-phase flow into the system. The thermal osmosis portion of the total water flow needs to be determined along with the thermal osmosis transport coefficient.

Thomas et al [81] conducted thermal osmosis experiments with fixed temperature difference between the anode and cathode and ran the experiments with a variable current density, the total water flow vs current density is shown in Figure 3.6.11:

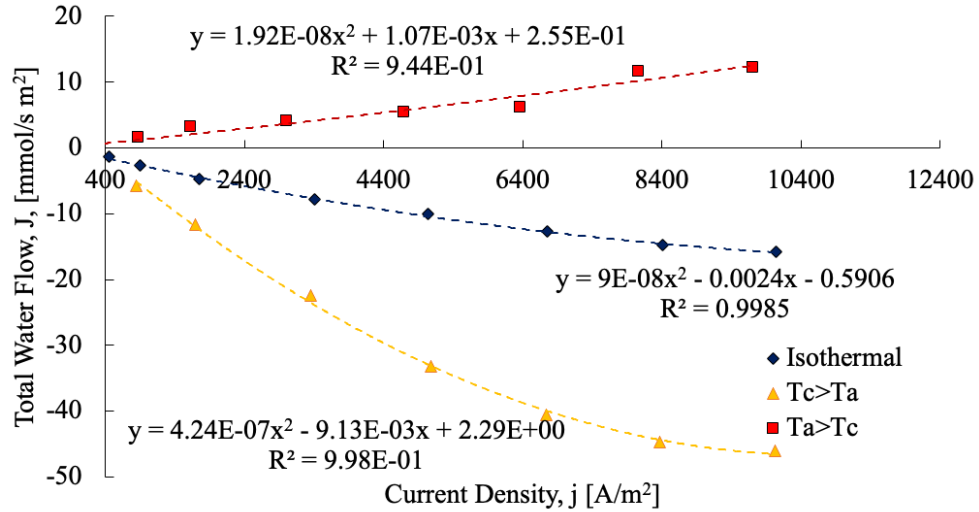


Figure 3.6.11 Total Water Flow Data used to get Thermal Osmosis [81]

In all three cases, the total water flow trendlines do not go through the origin, indicating that other fluid drivers besides electro-osmotic drag are present. All three cases were fit to polynomials, a linear case was not used, the total water flow was in the direction of hot to cold in all cases even when the anode was warmer than the cathode. There is a possibility of liquid water being present because the anode and cathode was fully humidified so subtracting the isothermal case from the other two cases for determining thermal osmosis is not viable because there could be changes in the electro-osmotic drag and back diffusion coefficient. There was water flow across the membrane when there was no temperature across the membrane which is a result of electro-osmotic drag and back diffusion. The total water flow needs to be broken down into its electro-osmotic drag, back diffusion and thermal osmosis components without assuming any fluid transport coefficient.

This evidence also indicates that the water flowing in the hot to cold direction also. The data in its present form can be used to compute the electro-osmotic drag coefficients, but it is also desirable to get the impact of thermal osmosis also. The data can be reformatted to obtain inside on thermal osmosis; this is done by replotting the data against the temperature difference and the current is fixed. The total water flow must be decomposed to confirm the direction of thermal osmosis along with the magnitude.

In all cases, the total water flow is not completely linear, there are regions on linearity. The only case that has all the water flow in the direction anode to cathode is when the anode is warmer than the cathode, this indicates that the temperature driven water flow is in the direction of hot to cold. In the isothermal and the case where the cathode is warmer than the anode has the water flow in the direction of cathode to anode. The replotted data is shown in Figure 3.6.12:

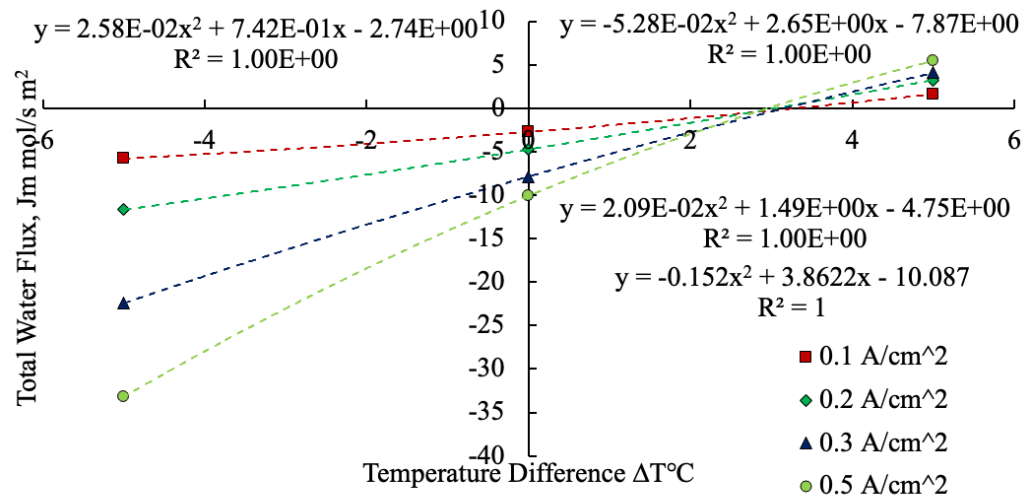


Figure 3.6.12 Total Water Flow Data used to get Thermal Osmosis [81]

The total water flow data is fit to a polynomial and not a linear trendline, as the current density increases, the trendline is shifted further away from the origin. There is total water flow across the membrane when there is no thermal gradient. The total water flow is in the direction of hot to cold, the data in the present form does allow for the thermal osmosis portion of the total flows as well as the thermal osmosis transport coefficient to be computed. The thermal osmosis portion needs to be extracted to better understand it.

In the cases the current density was fixed that the data was replotted against the thermal gradient, in the case where the anode is cooler than the cathode this is reflected by -5°C temperature difference, in the case where the cathode is warmer than the anode this is denoted by the 5°C temperature difference, and for the isothermal cases the temperature difference is 0°C . The data shows that when the anode is warmer than the cathode the total water flow is in the direction of anode to cathode and when the cathode is warmer than the anode, the total water flow is in the direction of cathode to anode.

The temperature driven component of water flow seems to be going in the hot to cold direction. Also, when there is no temperature difference the water flow across the membrane, will contain electro-osmotic drag and back diffusion. With the inconsistencies in the electro-osmotic drag and back diffusion coefficients it makes it difficult to extract these fluid drivers. The thermal osmosis coefficient was also not known.

Kjelstrup [82] replicated Kim and Mench [75],[76] thermal osmosis work to explain thermal osmosis through Non-Equilibrium Thermodynamics (NET), originally the trendline data was forced through the origin, it was believed that other fluid drivers are present, as a result the initial data is replotted to where the trendline is not forced through the origin as shown in Figure 3.6.13:

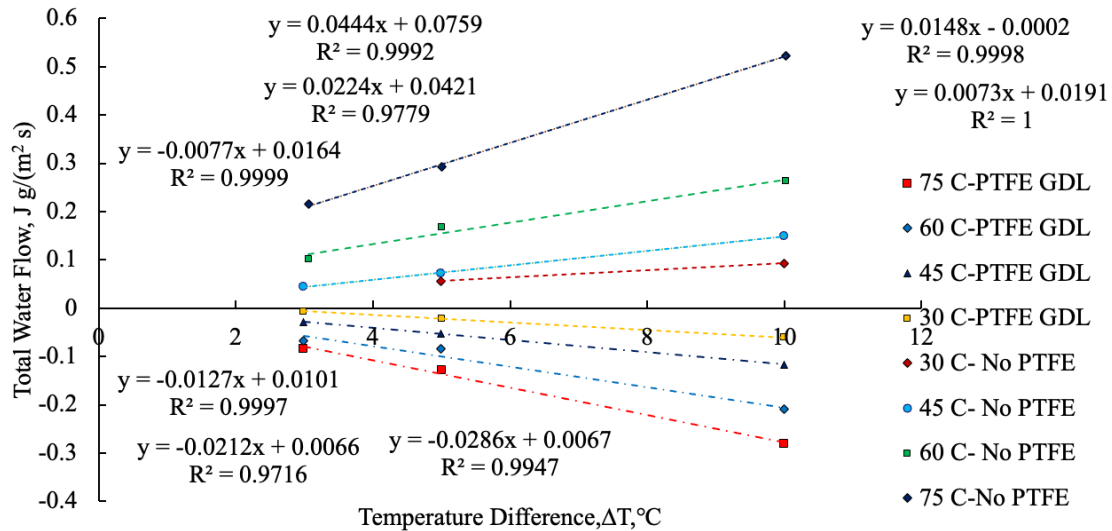


Figure 3.6.13 Total Water Flow Data used to get Thermal Osmosis [82]

The total water flow data is fit to a linear trendline and not a polynomial, and the trendline is not forced through the origin. The new trendlines does show there are other fluid driver present in the experiment. It is not known how much the thermal osmosis and the other fluid drivers contribute to the total water flow. In this case with the hydrophobic gas diffusion layer (GDL) the total water flow was in the direction of hot to cold, when the hydrophobic PTFE was removed the direction of the water flow was in the direction of cold to hot. As in Kim and Mench's [75],[76] thermal osmosis data, the experiments

were conducted with liquid water, and the direction of thermal osmosis did match Kim and Mench's results [75],[76].

It is noted that when the trendline was not forced through the origin, a constant did appear in the trendline. In some of the cases the constant was the same sign as the slope of trendline but in other cases the constant was the opposite sign of the trendline which suggested the other fluid driver is working against thermal osmosis. The consensus obtained was that for hydrophobic cases the water flow was in the direction of hot to cold and for the hydrophilic cases the water flow was cold to hot. Since a lot of the experiments forced the trendline through the origin, the direction of the water flow will be correct but magnitude would be incorrect a deeper dive in the data is required. The thermal osmosis portion of the total water flow needs to be extracted from the data as well as the thermal osmosis transport coefficient.

Bozkurt et al [83] performed thermal osmosis experiments with liquid water and hydrophobic and hydrophilic material, their initial trendline was forced through the origin, it is believed that other fluid drivers are present and these fluid drivers must be isolated from the thermal osmosis data. The hydrophobic data is replotted and the trendline is not forced through the origin as shown in Figure 3.6.14:

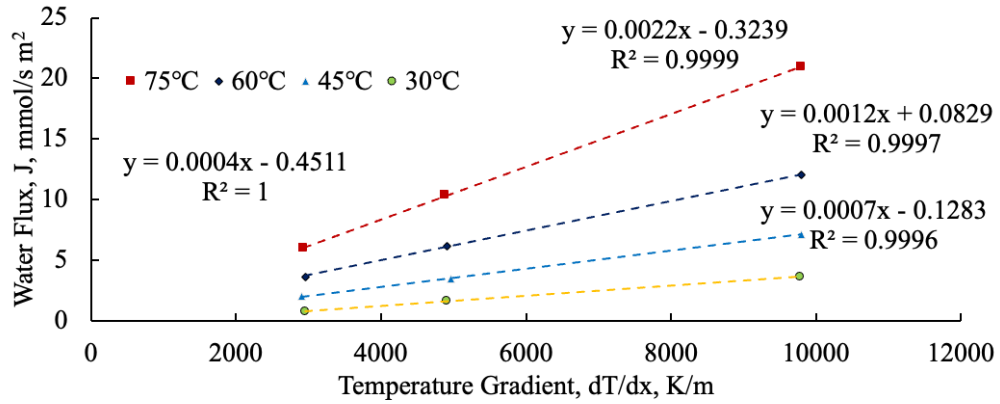


Figure 3.6.14 Total Water Flow Data used to get Thermal Osmosis [83]

The experimental data can be fit to a linear trendline, the slope of the line is positive indicating the temperature driven component is in the direction of hot to cold. Also, from the linear trendline, a constant is generated in some of the cases the constant is positive indicating that the other fluid driver is moving in the same direction of thermal osmosis. When the constant is of the opposite sign of the slope of the trendline, the other fluid driver is opposing thermal osmosis. The thermal osmosis portion of the total water flow needs to be computed. Thermal osmosis is unknown portion of the total water flow.

Bozkurt et al [83] also evaluated hydrophilic material with liquid water as before the total water flow trendline was forced through the origin neglecting the impact of other fluid driver present in the experiment. The first step involves refitting Bozkurt et al [83] thermal osmosis data where the trendline does not go through the origin as shown in Figure 3.6.15:

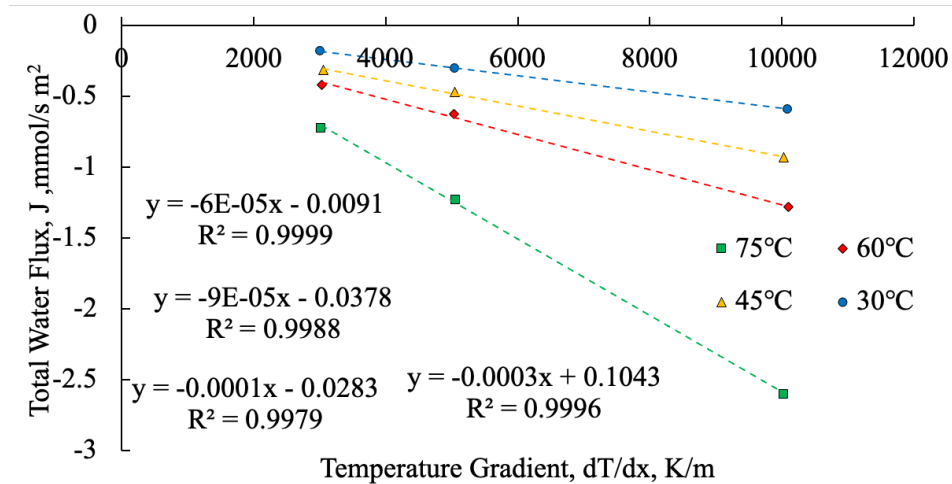


Figure 3.6.15 Total Water Flow Data used to get Thermal Osmosis [83]

The total water flow data was fit to a linear trendline, a polynomial was not needed.

The slope of the trendline is negative indicating that the temperature driven water flow was in the direction of cold to hot. There is also a constant from the linear trendline indicating that there is another fluid driver present.

There is a constant from trendline and in some instances it is the same sign as the slope of the trendline if so, the other fluid driver will move in the same direction of thermal osmosis and in cases where the constant is the opposite sign of the slope the other fluid driver will work against thermal osmosis.

In cases where thermal osmosis is in the same direction of the other fluid driver, thermal osmosis will be overstated, and when thermal osmosis is in the opposite direction of the fluid driver thermal osmosis will be understated. The fluid flow is so small, and high accuracy is required, and thermal osmosis cannot be over or understated. The thermal

osmosis portion of the total water flow along with the thermal osmosis transport coefficient need to be computed.

Tasaka et al [84] conducted thermal osmosis experiments with liquids and different membrane. Tasaka et al [84] had shown two trendlines, the first one is where the water flow was forced through the origin, and the second one is where the water flow was not forced through the origin. Tasaka et al [84] thermal osmosis was not observed for Nafion 417 even at a temperature difference of 12 K, this implies that thermal osmosis is not continuous or significant. The plot of the thermal osmosis data not forced through the origin is shown in Figure 3.6.16:

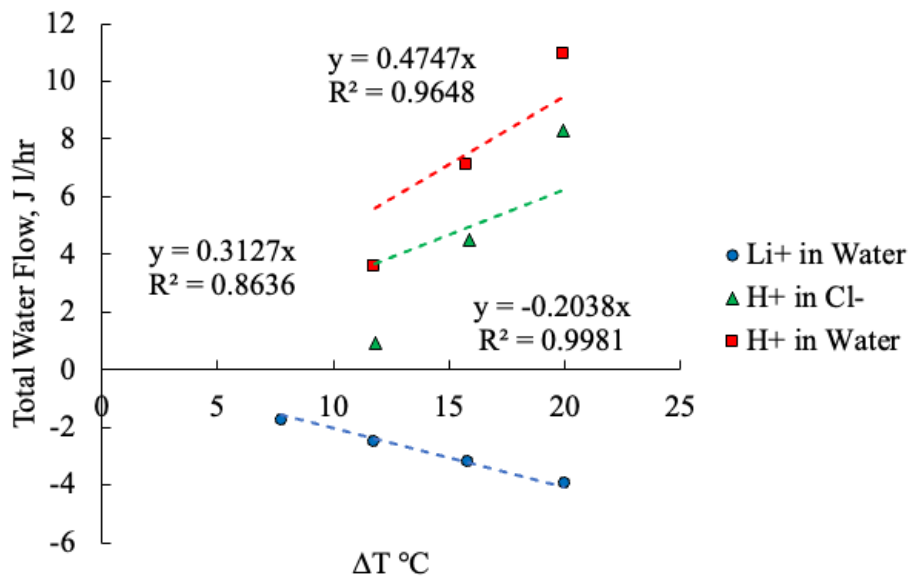


Figure 3.6.16 Total Water Flow Data not forced through origin [84]

The total water flow data was fitted to a linear trendline that does go through the origin, by doing this it assumes that all the water flow is from thermal osmosis, and it assumes

that thermal osmosis is continuous. The data needs to be examined where the trendline is not forced through the origin.

Tasaka et al [84] assumed the cold to hot direction is positive. The data trendline does not go through all the data points for the hydrogen ion cases. The slope for the lines is positive for the hydrogen ions (H^+), and for the lithium ion (Li^+) is negative, indicating the water flow that the thermal osmosis flow for hydrogen ions is cold to hot and in the cases for the lithium ions the water flow was in the direction of hot to cold. The correlation for the lithium ions was the best, but the hydrogen ions cases were not the best trendline fit, the lowest $R^2=.8636$, according to the graph the data is skewed, this also does not explain why thermal osmosis flow is only seen at temperature differences above 12 K. Also, there is big difference between the slope of the hydrogen ion lines, the first one is .4747 l/ (hr. °C) and .3127 (l/hr. °C) This process assumed that no other fluid drivers are present and does not explain the non-continuous behavior of thermal osmosis. The second attempt to refit the data with the data fit to a linear trendline where the data is not forced through the origin as shown in Figure 3.6.17:

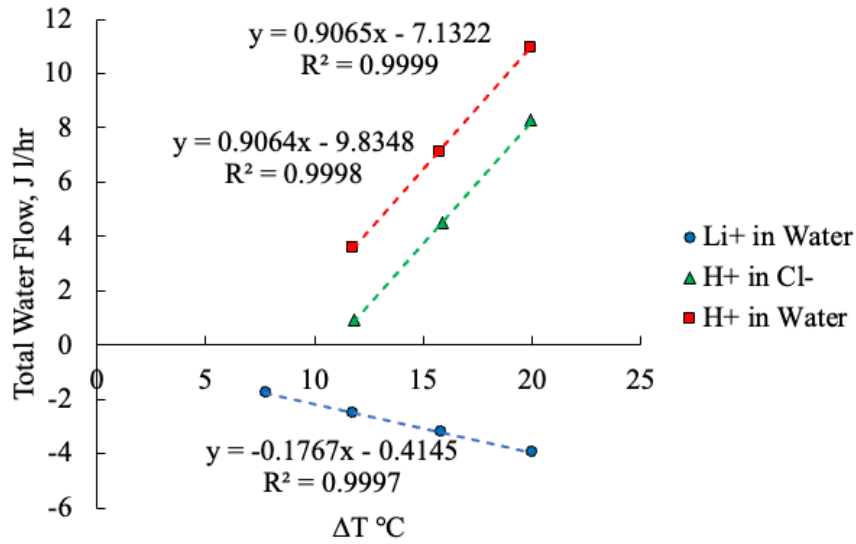


Figure 3.6.17 Total Water Flow Data forced through origin [84]

The total water flow data was refitted to a linear trendline that does not go through the origin, as a result there is a constant from the linear trendline. The constant from the trendline indicates that other fluid drivers are present. The new trendline show that there is a constant in all three cases, In the case of hydrogen ions the constant is the opposite sign indicating that the other fluid driver is opposing thermal osmosis. The slopes of the two hydrogen ions are almost identical the slopes .9065 and .9064 l/ (hr. $^\circ\text{C}$). The opposing fluid driver should create a point where no water flow will occur and once the temperature difference is above this point then thermal osmosis will be seen.

The direction of water flow is cold to hot, no change in the direction but the magnitude will be different. The results here will properly report thermal osmosis water flow. The thermal osmosis portion of the total water flow needs to be extracted along with the thermal osmosis transport coefficient. The lithium-ion thermal osmosis does not change

in direction compared to the new trendline fit, the constant produced from the linear fit is negative indicating it is moving in the same direction of thermal osmosis. The correlation is good for thermal osmosis correlation.

Tasaka et al [85] performed thermal osmosis with CM-3, CM-4 and CM-5 membranes as before their data shows two trendlines, the first one where the trendline is forced through the origin and the second one is where the data is not forced through the origin, the data is going to replotted both way to obtain insight on thermal osmosis fluid flow. The replot of the data where the flow is forced through the origin is shown in 3.6.18:

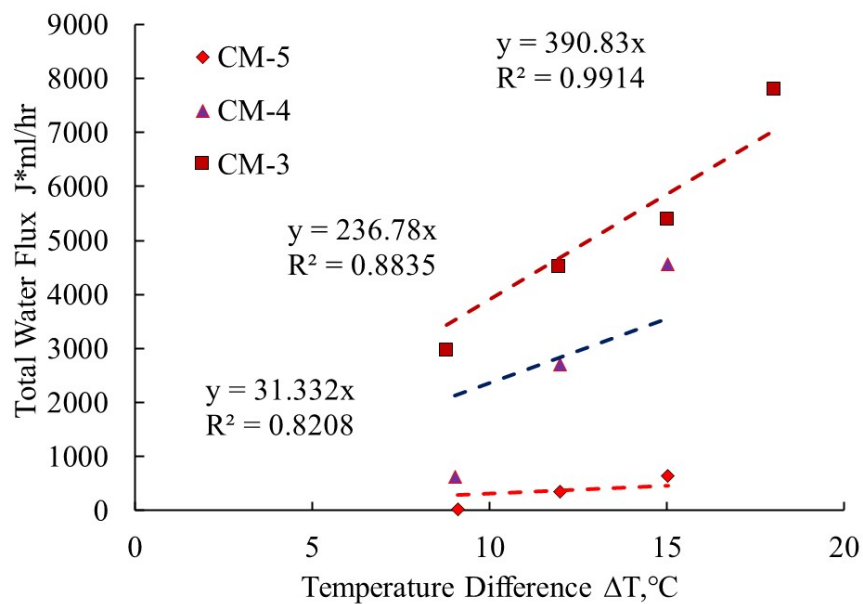


Figure 3.6.18 Total Water Flow Data not forced through origin [85]

The first scenario involved forcing the linear trendline through the origin, but doing this it assumes that the total water flow is equal to thermal osmosis. The slope of the lines are positive indicating that the temperature driven flow is in the direction of cold to hot.

There is good correlation for one of the trendlines specifically the CM-3 the $R^2 = .9914$, the other correlations ranged from 0.82 to 0.88, ideally a R^2 between 0.9-1 and would be ideal. The trendlines seemed to be skewed for the CM4 and CM5 membranes. The next step involves refitting the data to where the trendline is not going through the origin as shown in Figure 3.6.19:

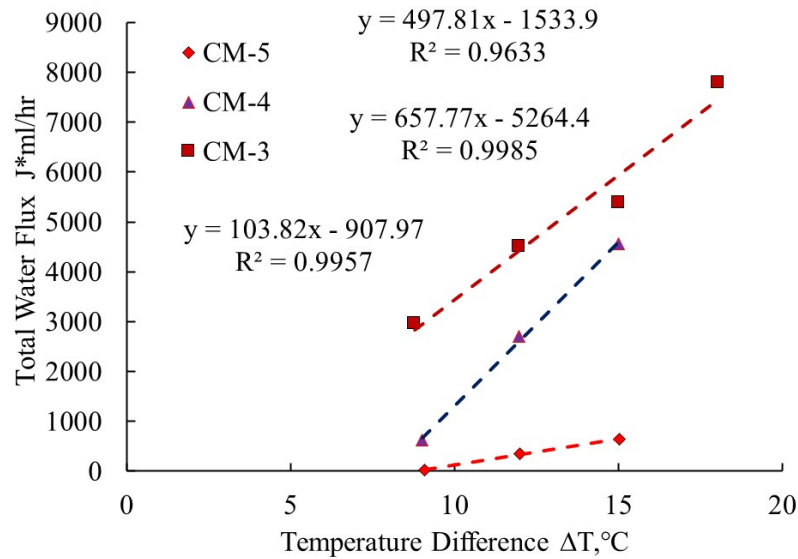


Figure 3.6.19 Total Water Flow Data not forced through origin [85]

The total water flow data was fitted to a linear trendline that is not forced through the origin. By fitting the data to the linear trendline it assumes that not of the total water flow is from thermal osmosis. The new trendline does not change the direction of the water flow it only changes the slope. In all the cases the slope is positive indicating that thermal osmosis fluid flow is moved in the cold to hot direction. The constant from trendline is of the opposite sign of the slope indicating that the other fluid driver is opposing thermal osmosis. With the slope of the trendline and the constant opposite signs there is a region which will appears where thermal osmosis water flow will not occur. There appears to be

other fluid drivers appear to be present and these fluid drivers must be considered when determining thermal osmosis. With the proposed approach the thermal osmosis portion of the total water flow needs to be extracted along thermal osmosis transfer coefficient.

D'Ilario et al [86] also performed thermal osmosis experiments with and without pressure components, their original data involved forcing the water flow through the origin as shown in Figure 3.6.20. The total water flow data is fitted to a linear trendline that is forced through the origin, as a result it assumes that all the total water flow is from thermal osmosis. The slopes of the trendlines are positive and the direction which coincides the cold to hot direction. The correlation of the data to the trendline does show a good fit to the data for both cases, the no pressure case does provide the best correlation with an R^2 of 0.99, when the pressure component is added, the correlation does decrease to an R^2 of 0.9845.

The slope of the trendlines does also increase when the pressure component is added the slope changes from 1.3214 mg/ (hr. cm^2 °C) to 1.772 mg/(hr. cm^2 °C). It is possible that pressure components are added to the thermal osmosis. The next step is to replot the original data where the data is not forced through the origin as shown in Figure 3.70:

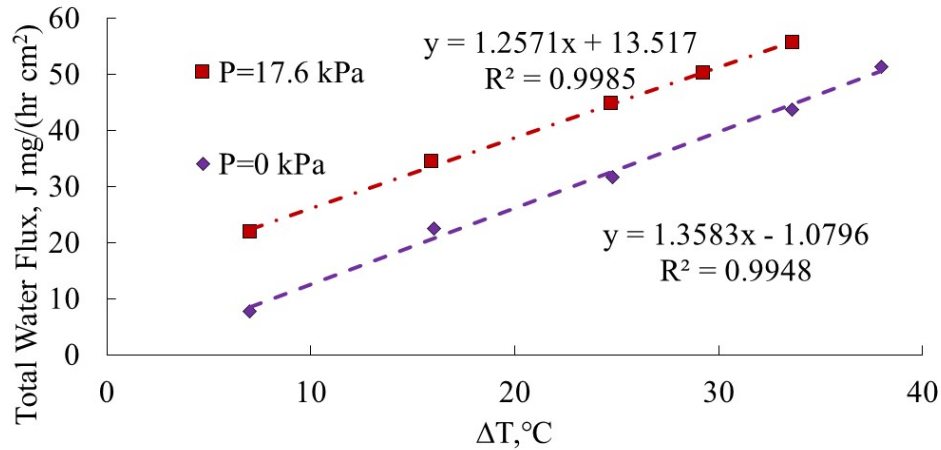


Figure 3.6.20 Total Water Flow Data not forced through origin [86]

The total water flow data is fitted to a linear trendline. The constant from the trendline indicates that another fluid driver is present and thermal osmosis is a portion of the total water flow. In both new trendlines, the slopes are positive and there is no change in the direction of thermal osmosis, and the correlations are better for both R^2 correlation are 0.99. In the case where there is no pressure component the constant from the trendline fit is negative indicating that it is working against thermal osmosis, and for the pressurized case the constant from the trendline fit is positive. The slopes of the line are much closer compared to the cases forced through the origin, the slopes from the second are 1.2571 mg/ (hr. cm²) to 1.3583 mg/ (hr. cm²).

The thermal osmosis portion of the total water flow must be extracted from the total water flow along with the thermal osmosis transport coefficient. Thermal osmosis cannot be measured by itself, it is measured along with other fluid drivers, and the thermal osmosis portion of the total water flow needs to be extracted to determine its contribution

to the total water flow. If the thermal osmosis is not extracted properly it will lead to either over or under reporting the true results.

3.7 Forcing the Total Water Flow through the Origin

The mass flowrate across the membrane is not measured directly it is measured indirectly and as a result the total mass flux is measured, and it is the summation of all the fluid effects present. When forcing the data trendline through the origin it assumes that all the fluid flow is from the one measured driver, as a result the other drivers will be lumped into the data which could overstate or understate the results.

In the instance of experiments where the electro-osmotic drag is being measured Bieshevel and Dykstra [62] had noted that electro-osmotic drag is measured into experiments with and without current and the difference is the electro-osmotic drag. The proposed approach could extract electro-osmotic drag with only one experiment.

According to the Nernst-Planck equation as shown in equation 16 and equation 17 there are two components electro-osmotic drag and back diffusion. The thermal effects are neglected. In an experiment where the current is varied, and the concentration gradient is held constant, then the back diffusion will be constant and if the trendline is forced origin then equation 17 will be simplified to 92.

$$J_{Total} = n_d(\lambda) \frac{j}{F} - D(\lambda) \frac{\partial c}{\partial x} \quad (92)$$

The forcing of the total water flow for electro-osmotic drag experiment will results in neglecting the back diffusion. In cases to where the water flow in the direction of cathode to anode, this will under report the electro-osmotic drag coefficient and when the direction of back diffusion is anode to cathode the electro-osmotic drag coefficient will be over reported. With the heat and water management important in the fuel cell overstating electro-osmotic drag will overstate how much water will be on the cathode like what Nguyen and White [32] saw in their fuel cell modeling.

In cases where the current density is fixed and concentration gradient is varied like in Ge et al [48] forcing through the origin will neglect the electro-osmotic drag will be neglected, this can be demonstrated by taking equation 16 and forcing it through the origin as shown in equation 93.

$$J_{Total} = n_a(\lambda) \frac{j}{F} - D(\lambda) \frac{\partial c}{\partial x} \quad (93)$$

In the case of thermal osmosis there are two driving mechanism the pressure and thermal gradient as shown in equation 34. In the case where the thermal gradient is varied and pressure is help constant then the pressure-based term will be neglected as shown in equation 121.

$$-J_v = D^*[\Delta s \Delta T - v_s \Delta \pi] \quad (94)$$

In cases where the temperature is fixed and the pressure difference is varied and the trendline is forced through the origin then the temperature driven component will be neglected as shown in equation 95.

$$-J_v = D^*[\Delta s \Delta T - v_o \Delta \pi] \quad (95)$$

Siemer et al [16] had used Non-Equilibrium Thermodynamics (NET) as a result there three fluid drivers, the chemical potential gradient, thermal gradient and voltage gradient as shown in equation 96.

$$J_{water} = -\frac{D_T}{T} \frac{dT}{dx} - l_{ww} \frac{d\mu}{dx} + \frac{n_d}{F} j \quad (96)$$

The same logic of forcing trendlines through the origin can be applied to NET. The NET approach does respect thermal osmosis. In addition to the pressure component Honda et al [102] had noted the Soret effect which is a mass transfer from the combination of thermal gradient. Along with the Soret effect there is the Dufour effect, which is the energy transported from the concentration gradient. The Dufour effect depends the substance, on the phase of the material, and the Lewis (Le) number. The Lewis number is the mass diffusion coefficient (D) divided by thermal diffusivity (α) as shown in equation 97.[114]

$$Le = \frac{D}{\alpha} \quad (97)$$

The Soret and Dufour effects are secondary effects from the concentration gradient and thermal gradient. Soret and Dufour effect are different for liquids compared to gases. Liquids and gases have difference diffusion coefficient, density and behave differently.

3.8 Water Vapor

In the PEM fuel cell, the goal is to keep water in vapor form, on the cathode of the PEM fuel cell, water is generated if the liquid water is not removed flooding will occur which is why the water balance across the membrane is one of the most important items with the PEM fuel cells. According to Ge et al [48] the electro-osmotic drag coefficient is not a function of temperature when the water is in its vapor form. Equation 116 is used for the hydration state of the membrane when the membrane is exposed to water vapor. The electro-osmotic drag coefficient is much higher for liquid water compared to water vapor. The back diffusion coefficient is also increasing with the hydration state of the membrane.

Phase Change Induced (PCI) cannot occur when only water vapor is present, water only exists as a vapor but when liquid is present PCI can occur. Thermal Osmosis research has been done with liquids only Fu et al [78], Thomas et al [81] and Zaffou et al [80], note that Thomas et al [81] and Zaffou et al [80] experiments were performed with 100% RH,

which introduces the risk that liquid water will be present. Fu et al [78] performed experiments with the cold side fully humidified and varied the hot side relative humidity up to 85% which also introduces the risk of liquid water being present. Other thermal osmosis experiments were performed with liquid water so it is not known if these experiments will correlate to water vapor. Thermal osmosis in gases will need to be explored more. In cases where liquid is separated by porous media, the Lewis number is on the order of 10^{-2} . When porous media separates gases, Lewis number 10^2 therefore the Dufour effect in gases cannot be neglected but can be in liquids. Experimentation performed on liquids would not have the Soret and Dufour effect whereas experiments done with gases will account for the Soret and Dufour Effect. Other sources have contradicted Newman [117] and R Byron Bird et al [118]. For instance, W. Hort et al [119] and Al-Farhany [120] have noted that the Dufour effect is significant in gases but not in liquids.

Hort [119] says that the Dufour effect depends on the Lewis Number. The Lewis number is a ratio of the thermal diffusion to mass diffusion; the Lewis number can also be expressed as the thermal boundary layer to concentration boundary layer just like how the Prandtl number is a ratio to thermal boundary layer to viscous boundary layer. Table 3.8-1 shows the Lewis Numbers for water, hydrogen, nitrogen and oxygen in a methane/hydrogen environment.

Table 3.8-1 Lewis Number for Fuel Cell Gases [119]

Gas	Lewis Number
Hydrogen(H ₂)	0.29
Nitrogen (N ₂)	1.04
Oxygen(O ₂)	1.10
Water (H ₂ O)	0.89

Since the Lewis number is close to unity for fuel cell reactants, it can be assumed the thermal diffusion boundary layer and concentration boundary layer are the same.

Therefore, the Dufour effect and Soret effect cannot be neglected. In addition, the porous media does couple heat and mass transfer together. The Lewis number is also linked to the Dufour effect, and the Lewis number is significant in reacting systems. In the PEM fuel cells chemical reactions will be taking place, therefore neglecting the Dufour effect is not valid in a fuel cell.

The effects of thermal osmosis should be added to the existing PEM fuel cell model, and the results should be compared to existing models. To fully understand thermal osmosis, the mechanism behind it must be understood. An additional note due to the Schroeder Paradox, membrane move for water through it when exposed to liquid compared to vapor, typically vapor should move freely compared to liquid. The membrane properties do change with hydration state of the membrane.

3.9 Liquid Water

For successful operation of the fuel cell, the goal is to keep the liquid water out of the cathode catalysts layer to prevent flooding which will reduce fuel cell efficiency.

The hydration state of the membrane is computed differently with liquid water, as shown in equation 98.

$$\lambda(a_w) = 1 < a_w < 3 = 14 + 1.4a_w \quad (98)$$

Based on empirical coefficient models, electro-osmotic drag coefficients are much higher for liquid water compared to water vapor. Springer et al [33] had a piecewise function for electro-osmotic drag for liquid and vapor. Also, there is a difference in empirical back diffusion coefficients, for water vapor and liquid water, Springer et al [33] empirical model does have the higher back diffusion for liquid water.

Other empirical models show back diffusion for liquid water is greater than the back diffusion coefficient for water vapor. In the cases of electro-osmotic drag for liquid water is a function of temperature as Ge et al [40] noted. Kusoglu and Weber [5] also noted that the electro-osmotic drag coefficient does increase with temperature for liquid water and other researchers have confirmed this as shown in Figure 2.3.9. It is possible that these higher transport coefficients are impacted by the Schroeder Paradox. The Paradox needs to be examined further. The phenomenon is known but not addressed in electro-osmotic drag.

3.10 Phase of Water Present in Experiment

In the fuel cell/porous media there are four possibilities, there is vapor on both sides of the membrane, liquid on one side and vapor on the other, there is vapor on the side and liquid on the other and lastly there is liquid on both sides. For a vapor/vapor scenario there would only be three modes of water transport available, they are electro-osmotic drag, back diffusion and single-phase thermal osmosis. Note in cases where the relative humidity on one side of the membrane gets to high liquid water can form and transition into two-phase region where liquid water form. This is essential to be able to predict when this transition is because it will impact the phase of water and what equations to use for total water flow.

These experiments consist of Yan et al [25], Fu et al [27], Cai et al [31], Nguyen and White [32], Barragan et al [34], Colinart et al [36], Adachi [37], Ye et al [38], Ito et al [39], Ge et al [40], Bezamalinovic et al [41], Reid [42], Aotani et al [43], Weber and Newman [69], Gandomi et al [70], Atiyeh et al [71], Yau et al [72], Chadha et al [73], Zaffou et al [80], Thomas et al [81] and some instances in the experiments involved some two phase work but there water not a distinction where this transition was. Both experiments were conducted with fully humidified reactants.

The second type of experiment with liquid on one side and vapor on the other would be a methanol-based fuel cell like Ren et al [61],[63] where the anode which cooler in the fuel cell. In this scenario the liquid is on the cooler side of the membrane. In this scenario, two

phase water will exist and the modes of water transport that are available are electro-osmotic drag, back diffusion, single phase thermal osmosis and membrane distillation.

The third type of experiment with vapor on one side and liquid on the other consisted of experiments where the liquid was on the warmer side of the membrane like in instances where the liquid is on the cathode and the vapor is on the cooler side of the membrane. In this scenario, two phase water will exist and the modes of water transport that are available are electro-osmotic drag, back diffusion, single phase thermal osmosis and membrane distillation. The liquid/vapor and vapor/liquid experiments are as follows:

Yan et al [25], Fu et al [27], Adachi [37], Ye et al [38], Ge et al [48], Ren et al [61], Ren et al [63], Yau et al [72]. There could also be cases where the experiment was done isothermal is Makoto. In the last scenario is with liquid on both sides of the membrane. In this case there could be electro-osmotic drag, back diffusion and osmotic distillation.

The total water flow experiments that fall into this domain are as follows: Barragan et al [34], Kim and Mench [75] [76] , Villaluenga [77], Kjelstrup [82], Bozkurt et al [83], Tasaka et al [84][85][87][88][92][93][95][98], D’Llario and Canella [86], Mengual and Gaarchia-Lopez [89], Paglicua et al [90], Rastogi et al [96], Kiyono et al[94], Bellucci et al [97], Gaeta et al [100], Voellmy et al [101], Honda et al [102]. In the cases where liquid is present, osmotic distillation, membrane distillation can be present, in cases where vapor is present osmotic distillation and membrane distillation will not be present.

3.10.1 Three variable equations of state

Typical equation of state for thermodynamics system consist of two variables and relationships obtained between the two variables is done through Maxwell's mixed partial derivative. If the Nernst-Planck equation is assumed to be an equation of state, then then a relationship between electro-osmotic drag and back diffusion can be obtained. If the thermal osmosis term is introduced to the Nernst Planck equation, then the same logic cannot be used as a result a three variable method was introduced to get relationships of three-variable systems. [135]

4 Results

The total water transfer coefficient can be used to obtain the total water flow across the membrane, and an empirical function can be obtained for either the total water flow as a function of current density or concentration difference or a thermal gradient. The empirical data fit can be used along with the theoretical equation to solve for the transport coefficients and obtain that portion of the total water flow. The first group examined is the total water flow experiments.

4.1 Total Water Flow

Yan et al [25] initially reported the total water transfer coefficient and the total water flow was obtained; the theory is applied to exact the electro-osmotic drag from the total water flow and solve for the back diffusion without assuming an empirical model. The computed electro-osmotic drag coefficient is shown in Figure 4.1.1:

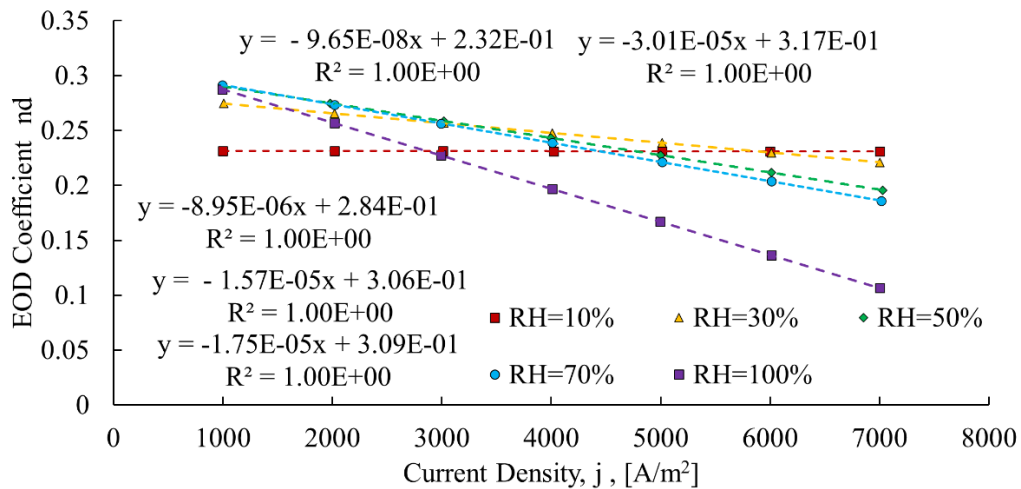


Figure 4.1.1 Computed Electro-Osmotic Drag Coefficient [25]

All the cases the electro-osmotic drag coefficient is changing with current density. The electro-osmotic drag coefficient is decreasing with current density, the decrease in electro-osmotic drag for the 100% RH case was the most severe. The EOD coefficient was least impacted when the cathode inlet relative humidity was case 10% RH. The water formation in the cathode is a function of current density; this case will introduce two-phase flow which would introduce liquid water. When liquid water is introduced other modes of water transports such as membrane distillation will occur. The cathode side of the membrane is at a higher temperature than the anode which will create a vapor pressure difference.

With the electro-osmotic drag coefficient obtained the electro-osmotic drag portion of the total water flow and the back diffusion portion can be obtained. The extracted electro-osmotic drag coefficient was gained by breaking down the total water flow. The composition of the total water flow is shown in Figure 4.1.2:

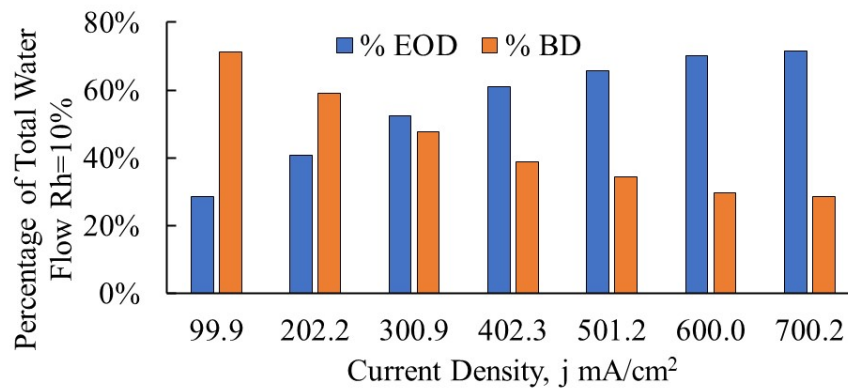


Figure 4.1.2 Computed Portion of Total Water Flow [25]

The anode relative humidity was fixed to 100% while the cathode RH was varied. When the cathode RH was low electro-osmotic drag can move for water flow across the membrane compared to back diffusion. In the 100% RH cathode at higher current density specifically 700 mA/cm² has back diffusion exceeding electro- osmotic drag. The back diffusion is being assisted by the membrane distillation. The total water flow was never broken down until today. The composition of the total water flow is new information by data mining the existing total water flow data.

Yan et al [25] also conducted an experiment with a fixed current density and variable relative humidity, based on the total water flow the electro-osmotic drag and back diffusion were computed. The computed back diffusion is shown in Figure 4.1.3:

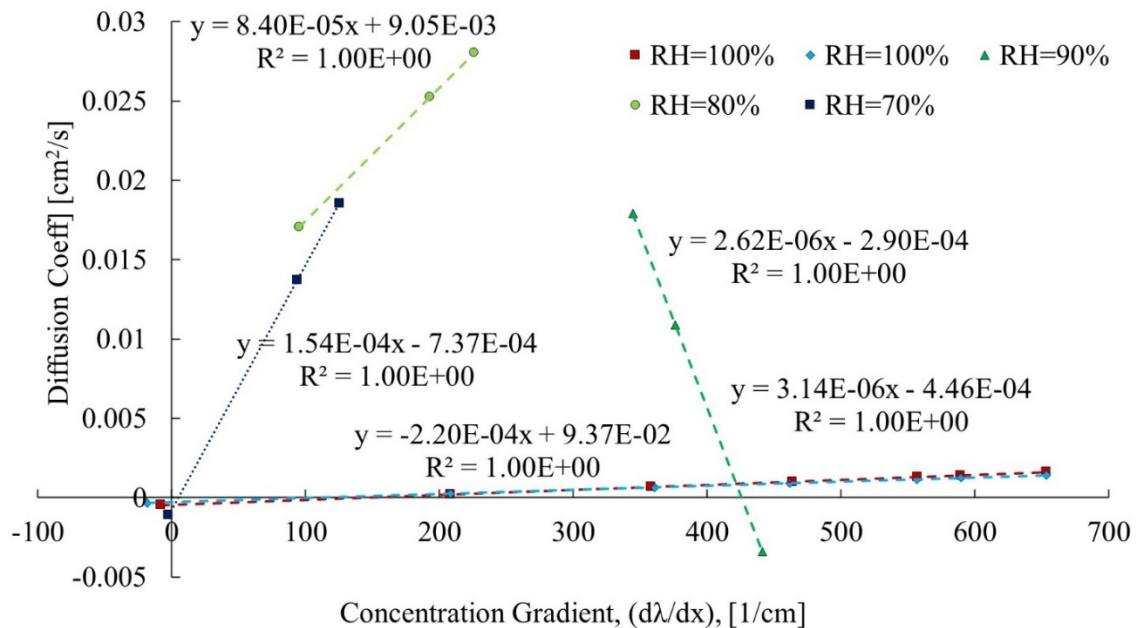


Figure 4.1.3 Computed Back Diffusion Coefficient [25]

The back diffusion coefficient is a function of the concentration gradient. In the 70% RH, and 80% RH it is increasing with the concentration gradient, this could be due changing membrane properties but at the 90% RH case the back diffusion coefficient was decreasing with the concentration gradient. This would occur with liquid water is present in the fuel cell, membrane/osmotic distillation will take place and move water in the direction of liquid to vapor due to the vapor pressure difference. The 100% RH cases show a small increase in the back diffusion coefficient; this occurs because the membrane is saturated and it no longer absorbing water. In general, the back diffusion coefficient is changing with the concentration gradient, and it is dependent on the hydration state of the membrane. With the current density fixed and the back diffusion portion known, the electro-osmotic drag portion and the electro-osmotic drag coefficient can be obtained. The electro-osmotic drag coefficient is shown in Figure 4.1.4:

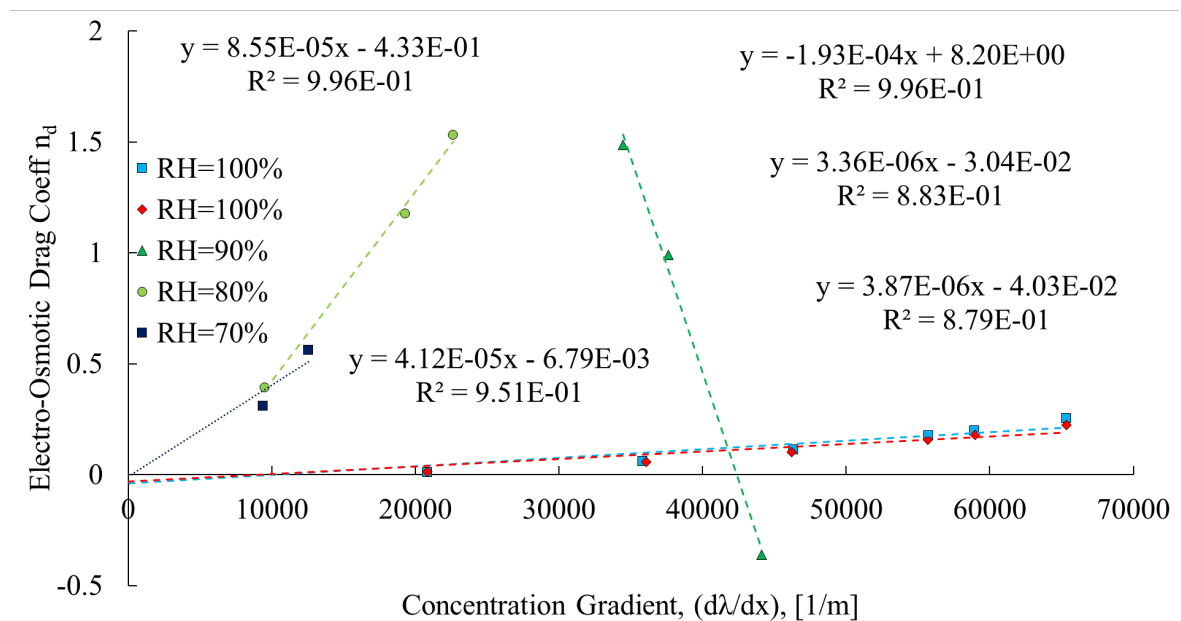


Figure 4.1.4 Computed Electro-osmotic Drag Coefficient [25]

The electro-osmotic drag coefficient is changing with the relative humidity and the concentration gradient. In this case the electro-osmotic drag is also dependent on the concentration gradient. In the case of the 70 % RH and 80% RH the electro-osmotic drag coefficient is increasing with concentration gradient. In the case of the 90% RH the electro-osmotic drag coefficient is decreasing with the concentration gradient, this is due to the liquid water formation and inducing membrane distillation/osmotic distillation in the direction of liquid to vapor. The 100% RH cases show the smallest changes in electro-osmotic drag this is due to the membrane being saturated.

Yan et al [25] did not breakdown the total water flow into its electro-osmotic drag and back diffusion component, nor did they provide a breakdown of the total water flow. In the Yan et al [25] experiments the total water flow through the membrane was non-linear which does not coincide with the Nernst Planck equations, there are regions of the of the trendline fit that are linear and the total function not linear.

In the case where the relative humidity is 100% there is high probability that liquid water is present, in lower relative humidity, there is lower probability of water, note that water is generated in the fuel cell. The total water flow in three of the cases is examined further to demonstrate that there is two -phase water flow as shown in Figure 4.1.5:

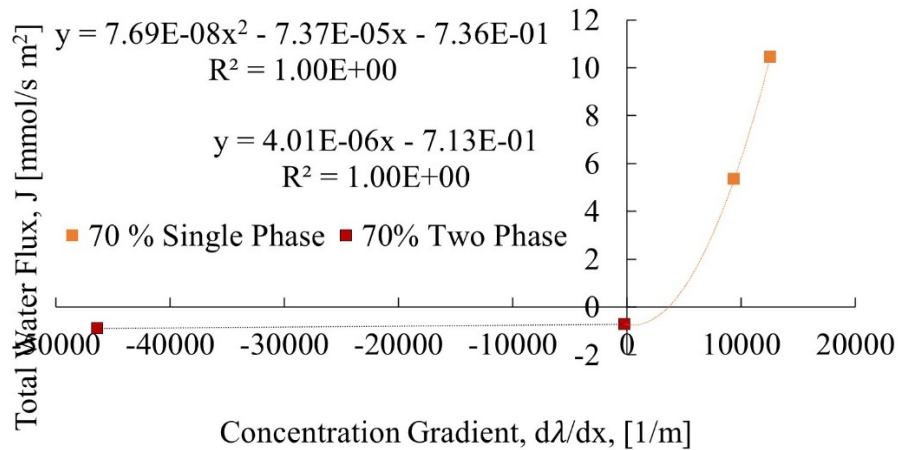


Figure 4.1.5 Total Water Flow Further Examined [25]

The total water flow was broken down into two regions, the single-phase region and the two-phase region, each region had a different trendline fit. The total water flow across the membrane cannot be defined with a continuous function, it can be defined with a piecewise function analogue between laminar, transition and turbulent flow. The total water flow was broken down into its electro-osmotic drag, and back diffusion portion of total water flow as shown in Figure 4.1.6:

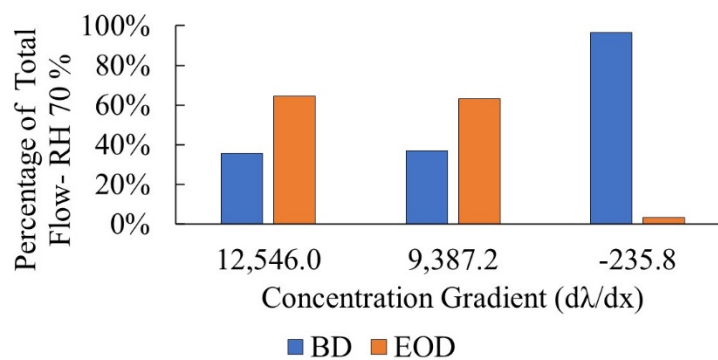


Figure 4.1.6 Composition of total Water flow [25]

In the two-phase region, the back diffusion portion of the total water flow exceeds the back diffusion. In the cases where the anode is at 100% the electro-osmotic drag exceeds back diffusion. The electro-osmotic drag and back diffusion can now be compared to back diffusion. Higher anode relative humidity supports electro-osmotic drag. This break down was not performed by Yan et al [25]. In the two-phase region the back diffusion is dominant over the electro-osmotic drag, this could be a result of osmotic distillation/ membrane distillation driving water in the direction of liquid to vapor. Yan et al [25] did not break down the total water flow into its electro-osmotic drag and back diffusion components nor did they provide the transport coefficients. Yan et al [25] has also examined the impact of hydrogen flow on the total water flow has, and the electro-osmotic drag portion of the total water flow was computed as shown in Figure 4.1.7:

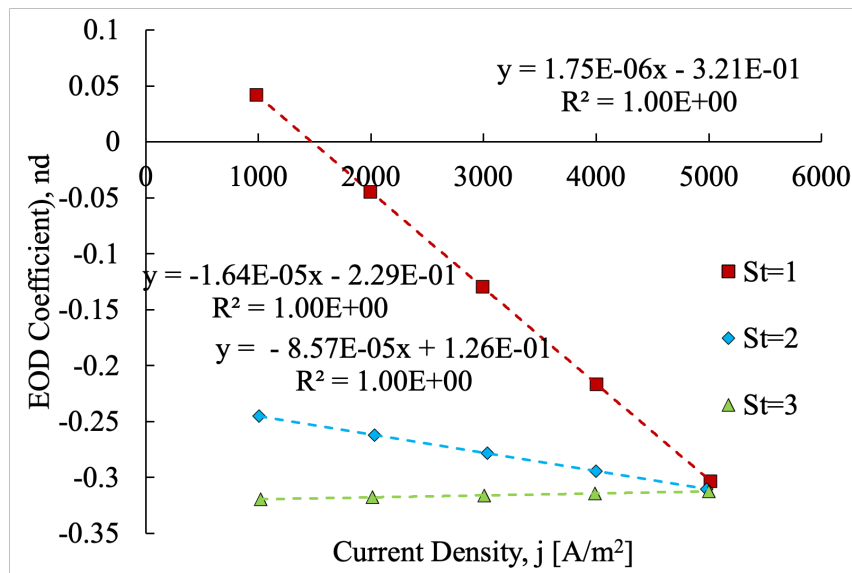


Figure 4.1.7 Computed Electro-Osmotic Drag Coefficient [25]

In this experiment the cathode was fully humidified, and the anode was only humidified to 20%, and this is the reason why the direction of flow is cathode to anode. In all the cases the electro-osmotic drag coefficient was changing with current density implying that current density does impact electro-osmotic drag. It also shows the hydrogen flowrate does impact electro-osmotic drag also. In all three cases the electro-osmotic drag coefficient is decreasing with current density but when the Stoichiometry is 1 shows the greatest decreases. The data mining shows that the electro-osmotic drag coefficient is also a function of current density. The total water flow is also broken down in its electro-osmotic drag and back diffusion components as shown in Figure 4.1.8:

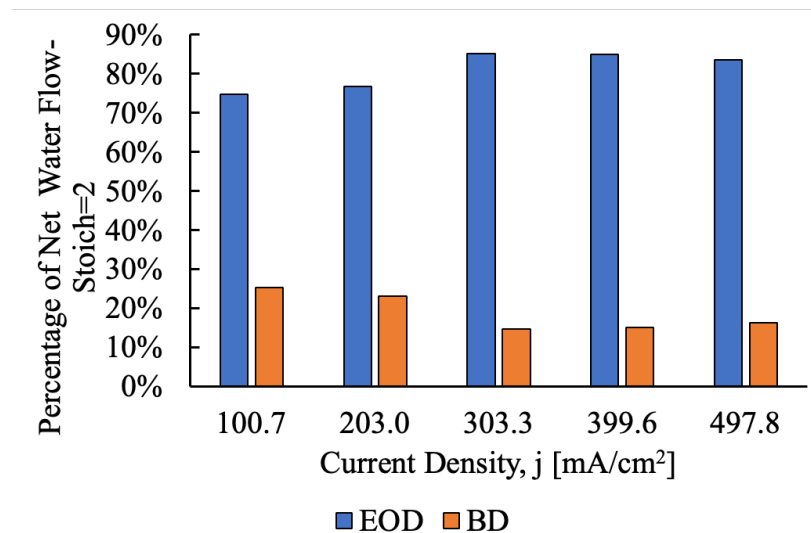


Figure 4.1.8 Computed Total Water Flow [25]

The computed transport coefficients and breakdown of the water flow were not provided by Yan et al [25]. In Yan et al [25] other experiment the current density was varied to extract back diffusion. In all the cases the electro-osmotic drag exceeded back diffusion. The results were analyzed with the proposed method and the back diffusion. The electro-

osmotic drag coefficient was extracted out of the data the coefficient did come up out of range of reported values. The calculated EOD coefficient is shown in Figure 4.9.

There seems to be error in the electroosmotic drag coefficient which would be impacting results this is one case that could be error in the measurements. The case examined was with constant current density and variable current density, the calculated electro-osmotic drag coefficient is shown in Figure 4.1.9:

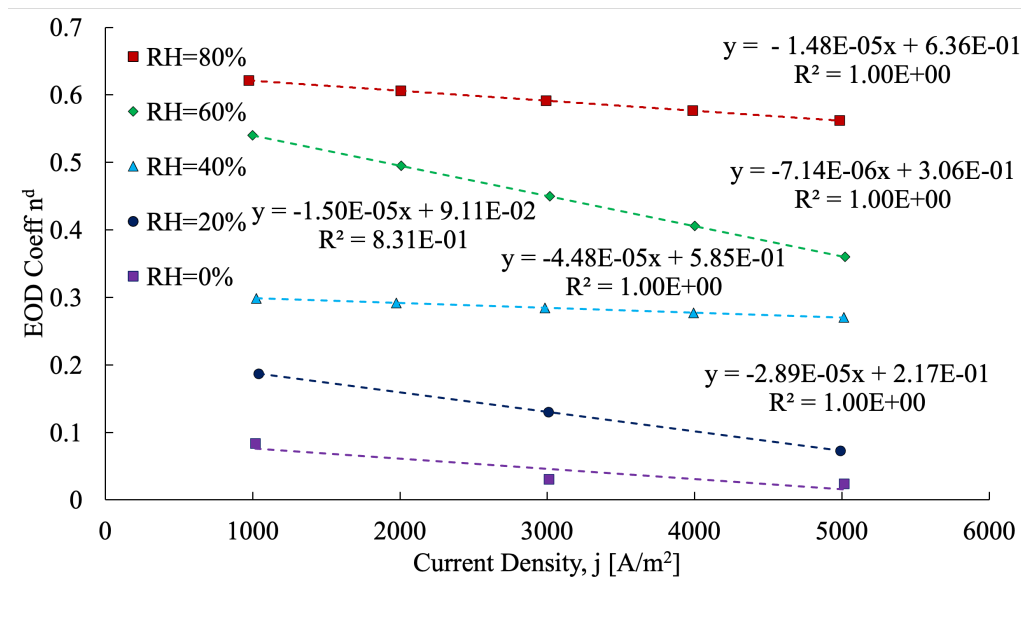


Figure 4.1.9 Computed Electro-osmotic drag coefficient [25]

The electro-osmotic drag is changing with current density, and the electro-osmotic drag is function of current density. The higher the relative humidity, the higher starting electro-osmotic drag coefficient. There are two factors influencing the total water flow, the first one being the voltage gradient is decreasing with current density. The other factor could be the liquid water on the cathode, at a higher relative humidity, there is a higher

probability of liquid water on the cathode, and this would induce water flow in the direction of liquid to vapor. The determination of electro-osmotic drag was done by data mining the existing data. The total water flow is broken down into its fundamental components as shown in Figure 4.1.10:

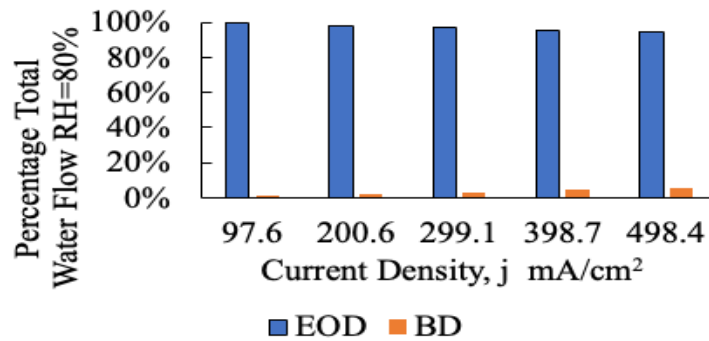


Figure 4.1.10 Total Water Flow Composition [25]

Yan et al [25] did not provided a breakdown of the total water flow into electro-osmotic drag and back diffusion. In the 80% case the electro-osmotic drag exceed back diffusion mainly due to the anode hydration. The breakdown of the total water flow is new insight gained from the total water transfer coefficient. Yan et al [25] objective to determine how relative humidity impacts total water flow across the membrane. The total water flow not broken down into electro-osmotic drag and back diffusion component and no understanding of electro-osmotic drag and back diffusion is obtained. The proposed approach allowed for the experimental data to be used to compute the electro-osmotic drag and back diffusion component of the total water flow without assuming an empirical model for the electro-osmotic drag and back diffusion coefficient. The Cai et al [31] total water flow was examined, and the electro-osmotic drag coefficient was extracted from the total water flow as shown in Figure 4.1.11:

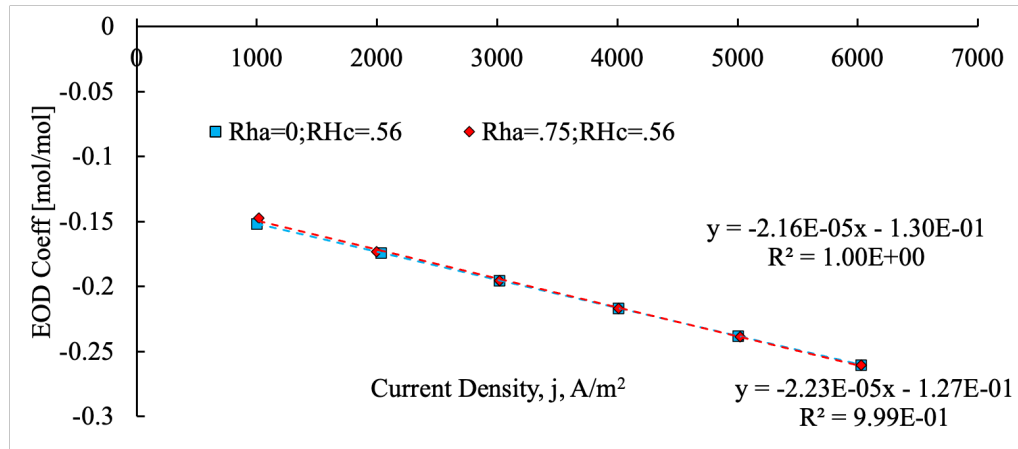


Figure 4.1.11 Electro-osmotic drag coefficient determination [31]

The electro-osmotic drag coefficient was calculated based on the total water flow. The electro-osmotic drag is decreasing with current density. The electro-osmotic drag is a function of current density. The approach does not rely on any of the electro-osmotic drag and back diffusion coefficient models. When the anode is humidified, the electro-osmotic drag does increase, the negative flow is a result of the non-humidified anode. The water generation on the cathode will impact the back diffusion. With the computed electro-osmotic drag coefficient, the electro-osmotic drag component is obtained, and it is subtracted from the total water flow to obtain the back diffusion. The breakdown of the total water transfer coefficient does show that electro-osmotic drag is a function of current density, this was not provided by the total water transfer coefficient. The total water flow is broken down and is shown in Figure 4.1.12.

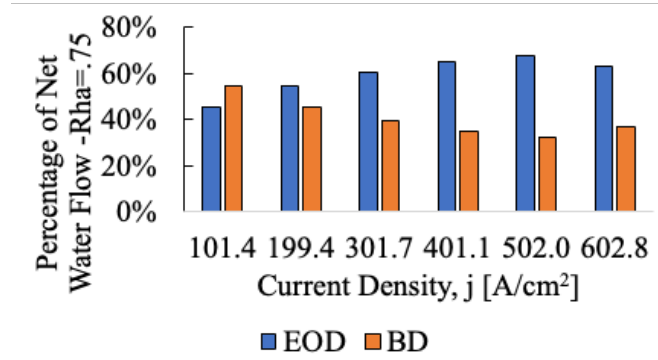


Figure 4.1.12 Total Water Flow Composition [31]

Cai et al [31] kept results in terms of the total water transport coefficient and did not break down the total flows into its electro-osmotic drag and back diffusion components. At higher current densities the electro-osmotic drag dominates over back diffusion.

Barragan et al [34] initially reported the volumetric flux and not the mass flux, the electro-osmotic drag coefficient will be a volume flow calculation. The computed electro-osmotic drag is shown in Figure 4.1.13:

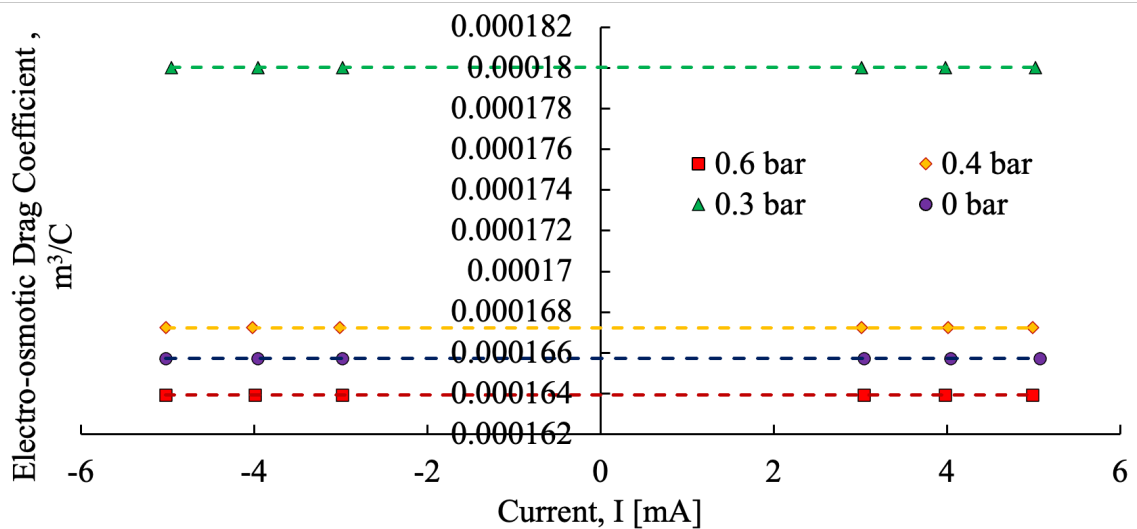


Figure 4.1.13 Computed Transport Coefficient [34]

Barragan et al [34] experimental data does provide insight on how other fluid drivers will impact the make-up of the total water flow. Based on the linear fit the electro-osmotic drag coefficient is independent of current density, the electro-osmotic drag coefficient is constant, this could be a result of the experiment conducted in a liquid environment.

With the electro-osmotic drag portion of the total flow determined from the EOD coefficient, the other fluid driver can be found, and the composition of total water flow is shown in Figure 4.1.14:

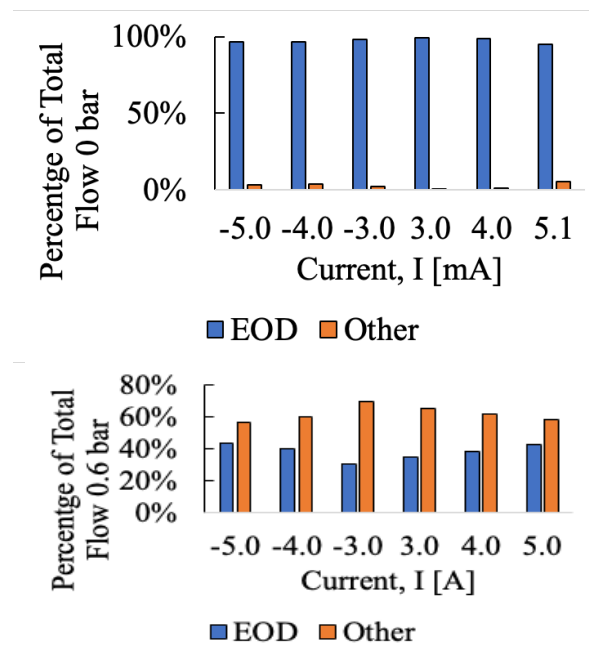


Figure 4.1.14 Total Fluid Flow Decomposition [34]

The total water flow experiment was performed in liquid water, and all the trendline fits were linear. The slope of the linear trendline is a constant and the electro-osmotic drag coefficient is constant. The direction of sign of the current does influence the direction of total water flow. In the case of no pressure, the electro-osmotic drag portion of the total water flow was greater than 90%, as the pressure component is increased the electro-

osmotic drag portion of the total water flow ranges from 30-68%. As the pressure component increases, the pressure component of the total water flow increases. The pressure component does influence the total water flow.

The experiments were also performed liquid, and it was possible to fit the data to a linear trendline. Other total water flow cases where water vapor was present, a polynomial fit was required. The linear fit for the total water flow does fit coincide with the limitations of the Nernst Planck equation. The proposed method took existing data and broke it down and extracted the electro-osmotic drag and pressure-based component without assuming on the electro-osmotic drag coefficient.

Choi et al [35] total water flow was further examined to determine the electro-osmotic drag coefficient as shown in Figure 4.1.15. The electro-osmotic drag coefficient does change with current density.

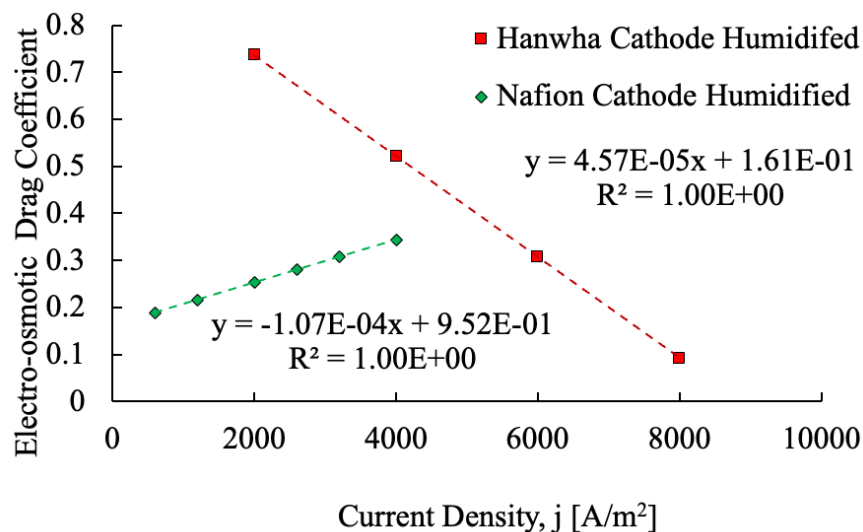


Figure 4.1.15 Computed Electro-Osmotic Drag Coefficient [35]

In the Nafion membrane the electro-osmotic drag is increasing with current density and in the Hanwha membrane the electro-osmotic drag coefficient is decreasing with current density, the data shows that the electro-osmotic drag is a function of current density. By analyzing the total water flow. The total water flow composition was also determined, the composition of the total water flow is shown in Figure 4.1.16:

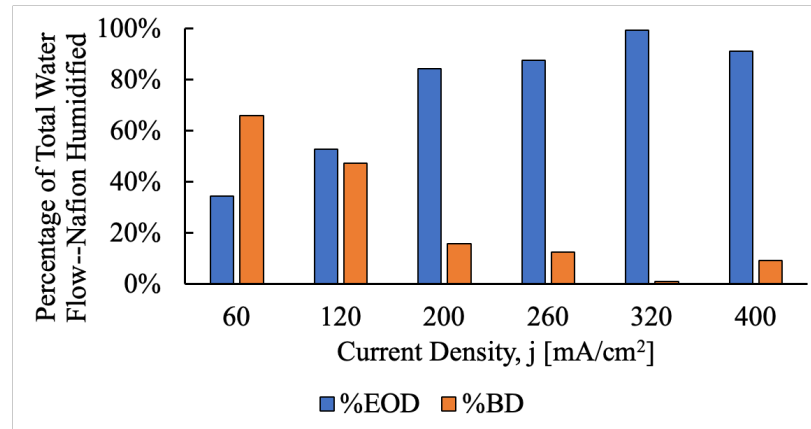


Figure 4.1.16 Composition of Total Water Flow [35]

In the case of Nafion, the back diffusion portion of the total water flow at low current densities, but as the current density increased, the electro-osmotic drag portion of the total water flow increased. The composition of the total water flow was not provided by Choi et al [35]. The composition of the total water flow is new insight gained with the research.

Colinart et al [36] data is used to compute the electro-osmotic drag coefficient and the composition of the total water flow. The electro-osmotic drag coefficient is shown in Figure 4.1.17:

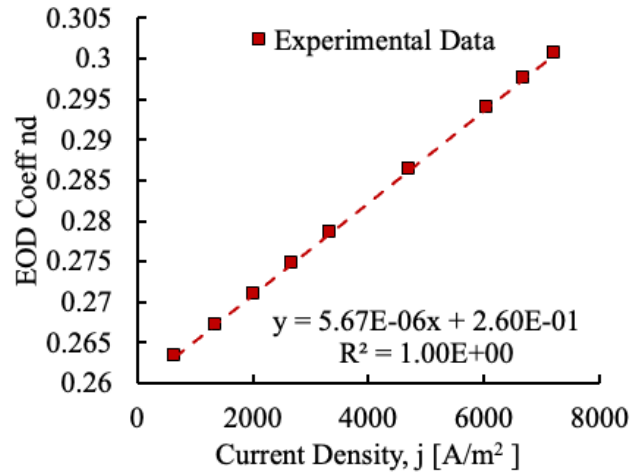


Figure 4.1.17 Computation of Electro-osmotic drag coefficient [36]

The total water flow is used to compute the electro-osmotic drag coefficient and the electro-osmotic portion of the total water flow. The electro-osmotic drag coefficient is positive indicating that the water flow is in the direction of anode to cathode and the coefficient is increasing with current density. The electro-osmotic drag is increasing with current density, and it is a function of the current density. The dependency of electro-osmotic drag coefficient on current could relate to the voltage gradient. The other factors that could influence the electro-osmotic drag is the thermal gradient and/or the presence of liquid water. The liquid water will drive flow in the direction of liquid to vapor. The composition of the water flow is shown in Figure 4.1.18:

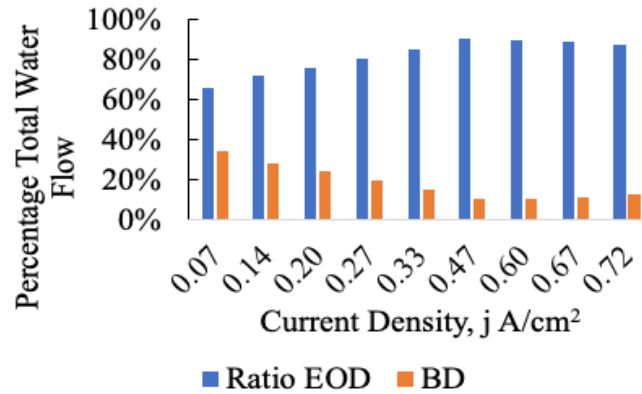


Figure 4.1.18 Computation of Electro-osmotic drag coefficient [36]

The composition of the water flow shows that electro-osmotic drag does exceed back diffusion for all cases. Colinart et al [36] did not provide a breakdown of the total water this allows us to compare the fluid drives to one another. Colinart et al [36] did not break down the total water flow into its electro-osmotic drag and back diffusion component. The total water flow was decomposed into electro-osmotic drag and back diffusion components without using an empirical model for electro-osmotic drag. The data mining has shown that electro-osmotic drag is a function of current density, there needs to be a better understanding why the electro-osmotic drag changes with current density.

Adachi [37] total water flow cases are individually examined, and the fluid transport properties are further examined, and the total portion of the water flow is computed. In Adachi [37] total water flow with variable current density is analyzed and the computed electro-osmotic drag is shown in Figure 4.1.19:

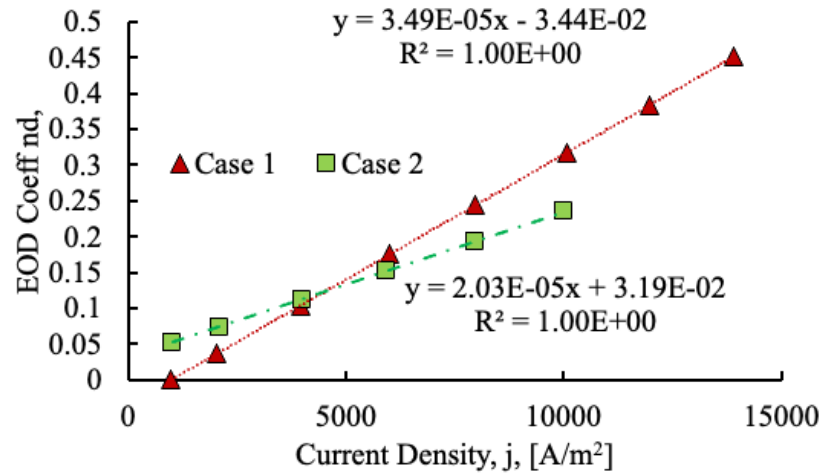


Figure 4.1.19 Computation of Electro-osmotic drag coefficient [37]

In both cases the electro-osmotic drag is increasing with current density and the values computed fall within the range of electro-osmotic drag empirical models. The peak electro-osmotic drag coefficient was 0.5, Adachi assumed and EOD coefficient and in one case the computed value was 0.5, his assumption is only valid at one data point. All the other electro-osmotic drag coefficients are less than 0.5. The data also shows that the electro-osmotic drag is a function of current density. The electro-osmotic drag coefficient is continuously changing and the assumed constant value of 0.5 is not valid. The composition of the total water flow is shown in Figure 4.1.20:

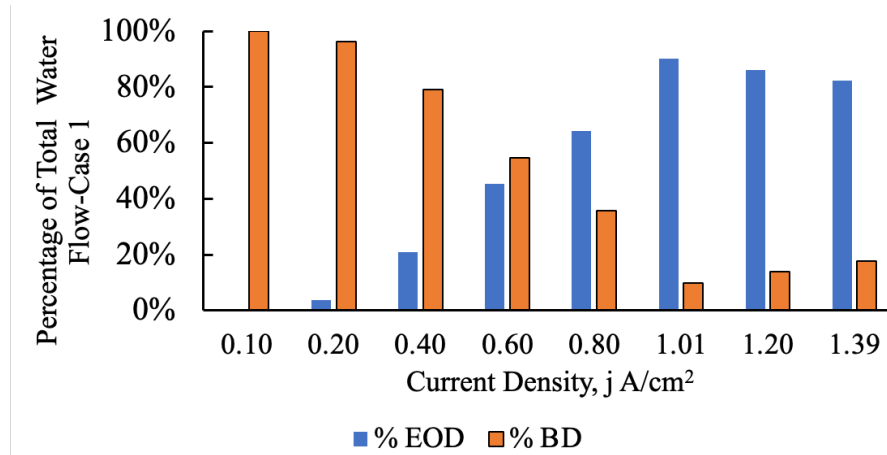


Figure 4.1.20 Computation of Total Water Flow Composition [37]

The analysis of the data shows that the electro-osmotic drag coefficient ranges from 0.1 to 0.5 which does not match the assumption made on the electro-osmotic coefficient.

The total water flow was broken down into its components without assuming an electro-osmotic drag coefficient, it was determined with the experimental data. In case 1 the back diffusion exceeded electro-osmotic drag at low current densities but at higher current densities electro-osmotic drag exceed back diffusion.

The breakdown of the total water flow and the computation of the electro-osmotic drag were not done by Adachi [37], instead the electro-osmotic drag coefficient was assumed. Adachi [37] had also examined membrane thickness and its impact on electro-osmotic drag; the data was used to compute the electro-osmotic drag is shown in Figure 4.1.21:

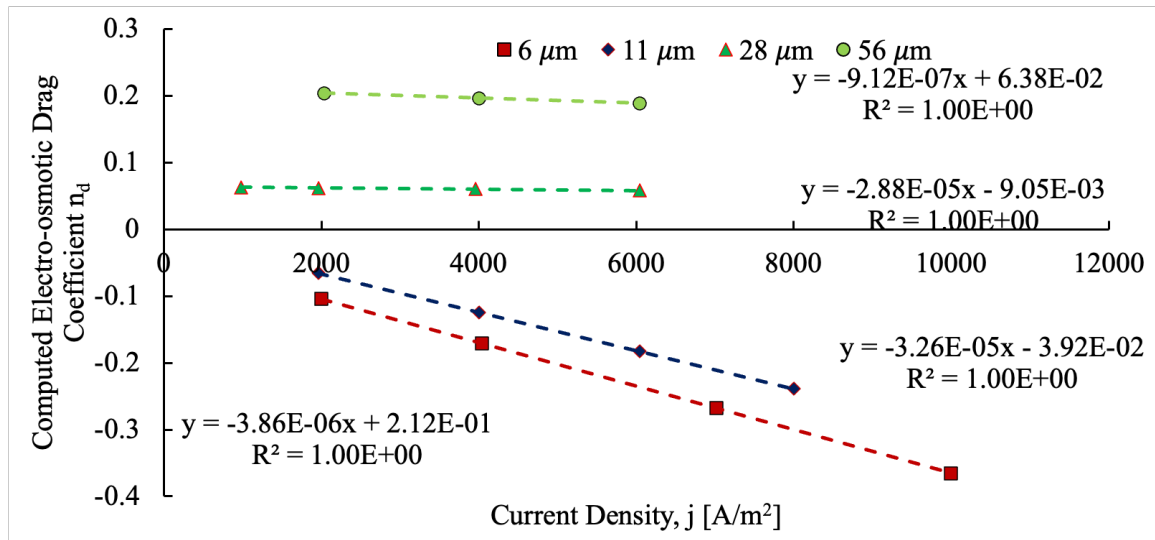


Figure 4.1.21 Computation of Electro-osmotic drag coefficient [37]

The thicker membranes promote more electro-osmotic drag and suppress back diffusion because the concentration gradient get smaller. The thinner membranes promote back diffusion, this is the main reason why the electro-osmotic drag coefficient is negative. The thicker membrane will reduce the back diffusion. The total water flow is in the direction of anode to cathode because of the reduced back diffusion.

All cases of electro-osmotic drag coefficient are a function of the current density. The electro-osmotic drag does decrease with current density. In the case of thicker membranes, the electro-osmotic drag coefficient is positive and for thinner membrane the electro-osmotic drag coefficient is negative indicating it is going in the opposite direction, the thinner membrane promotes a larger concentration gradient and increasing back diffusion. The composition of the total water flow is shown in Figure 4.1.22. The thickness of the membrane impacts the concentration gradient across the membrane.

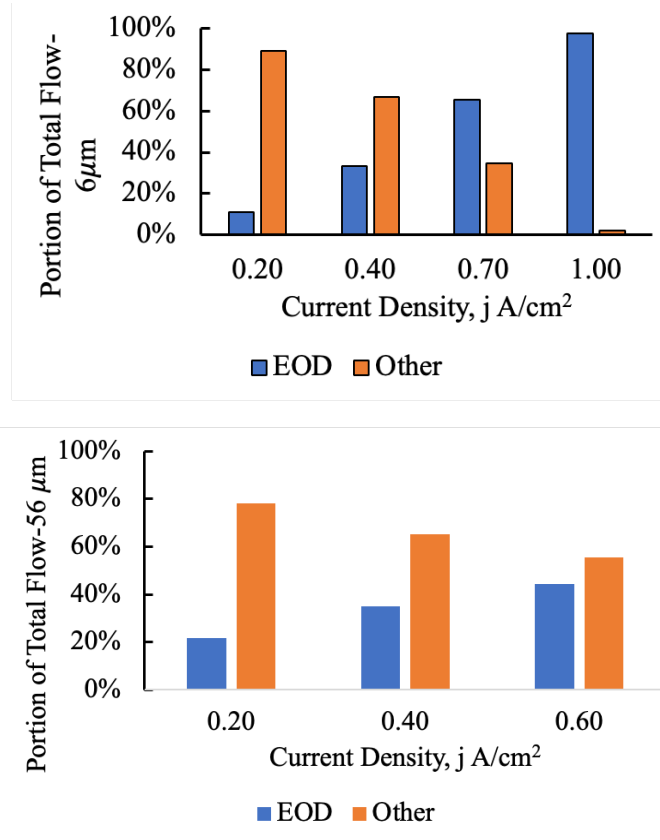


Figure 4.1.22 Composition of Total Flux [37]

The thinner membranes like the 6 and 11 μm promote back diffusion; the back diffusion portion of the total water flow exceeds electro-osmotic drag. In the case of the 140 μm the back diffusion exceeds electro-osmotic drag at lower current densities but as current density increases so does the electro-osmotic drag portion of the total water flow. The total water flow across the membrane was not broken down into its electro-osmotic drag and back diffusion components. The experimental data was processed to determine the electro-osmotic drag and back diffusion without assuming an electro-osmotic drag and back diffusion coefficient. The results were kept in terms of the total water flow; no

attempts were made to break down the total water flow. The cathode is humidified, and the anode is not humidified this breakdown of the total water flow, and the computation of electro-osmotic drag were not performed by Adachi [37]. Adachi [37] liquid and vapor experiments and vapor and vapor experiments are examined in detail. The back diffusion coefficient is computed for the liquid and vapor scenario, and the vapor and vapor scenario were computed as shown in Figure 4.1.23:

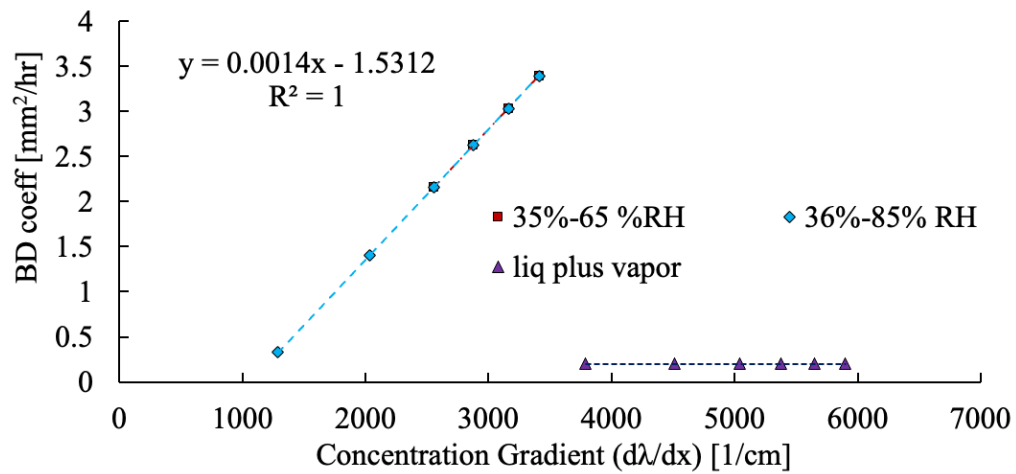


Figure 4.1.23 Computation of Back Diffusion coefficient [37]

The back diffusion coefficient does change with the concentration gradient, for the vapor/vapor scenario. In the case of the liquid/vapor scenario the back diffusion coefficient does not change with the concentration gradient. When the membrane is the vapor/vapor scenario, the membrane is not fully saturated, and the diffusion coefficient is changing with the concentration gradient because the membrane is not saturated.

When the membrane is in contact with liquid, the membrane can be saturated, and the membrane hydration state would not be changing. In the liquid and vapor scenario the

water in the direction was in the direction of liquid to vapor. Since this experiment was done isothermally the reason the water flow was in the direction of liquid to vapor was membrane or in this case osmotic distillation. The back diffusion coefficient is constant for the liquid water and vapor scenario. Adachi [37] had noted a lower water temperature compared to the vapor. The data also confirms the membrane properties are dependent on the hydration state. The properties of the membrane are impacted by the phase of water present. The total water flow was not broken down by Adachi [37]. The back diffusion for the vapor-vapor scenario was had the diffusion coefficient change with the concentration gradient.

Adachi [37] examined pressure driven flow across the membrane also. With the linear trendline fit the slope of the line is the pressure driven component. The trendline was not forced through the origin. The computed pressure coefficient is shown in Figure 4.1.24:

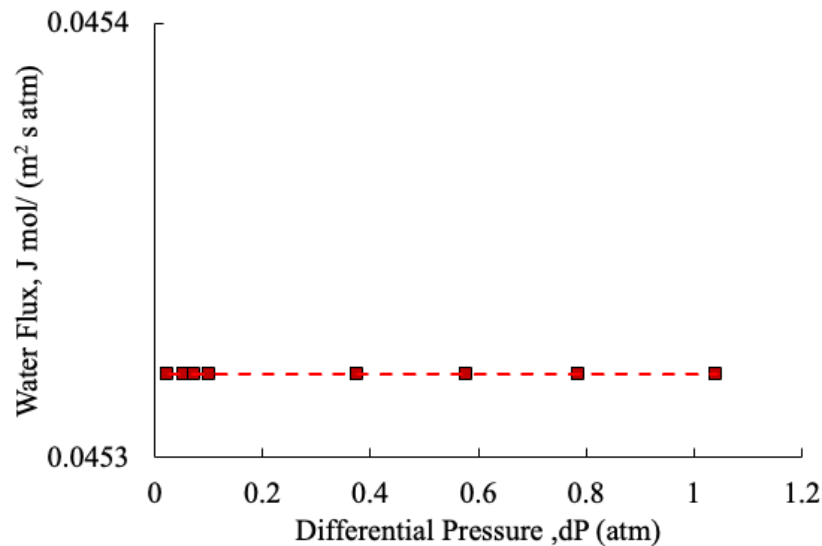


Figure 4.1.24 Pressure Coefficient for Transport [37]

The pressure transport coefficient is constant based on the derivative of the linear trendline. The pressure transport coefficient is independent of pressure gradient. With the pressure transport coefficient being determined, the pressure-based component of the total water flow can now be determined, and it is subtracted from the total water flow. The composition of the total water flow is shown in Figure 4.1.25:

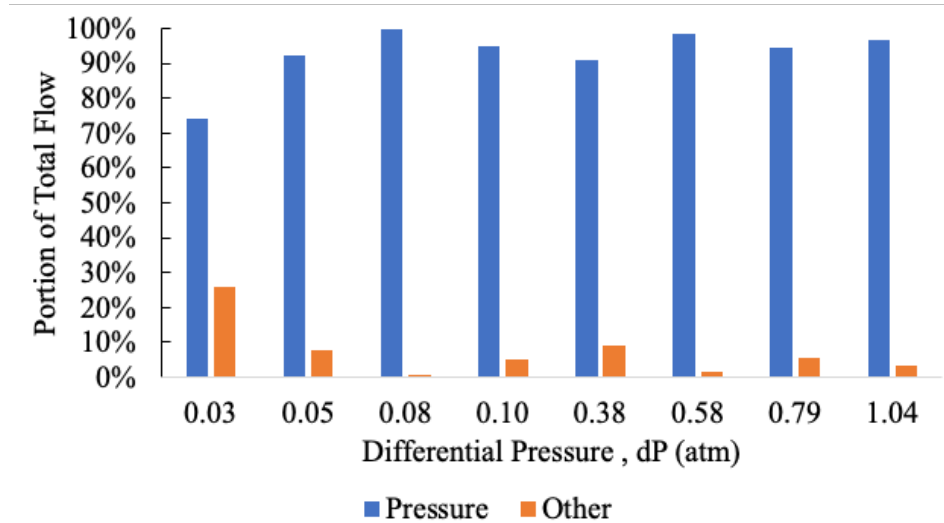


Figure 4.1.25 Composition of Total Water Flow [37]

The composition of the total flow ranges from 73%-96% and this shows that other fluid drivers are present, this driver is in the same direction of the pressure component.

The other component could be neglectable when the pressure component is 96% but accuracy is required, this requires that the pressure-based flow be broken down to obtain accuracy and precision. This shows that not all the fluid flow is from the pressure gradient. The separation of the total water flow was not performed on the data; the separation of the total water flow comes from data mining the data.

The next experiment that was examined is the results with anode and cathode humidified with a variable current. With the total water flow the electro-osmotic drag coefficient is computed as shown in Figure 4.1.26:

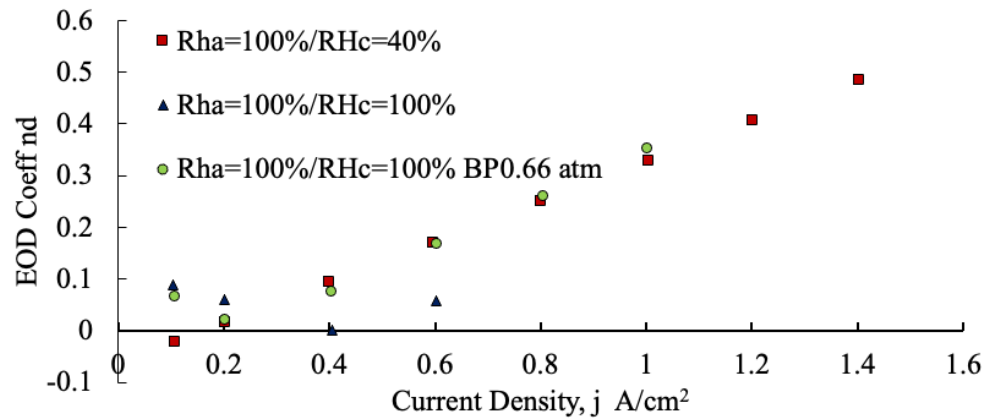


Figure 4.1.26 Electro-Osmotic Drag Coefficient computed [37]

In two of the three cases the electro-osmotic drag is increasing with current density, and when the anode and cathode were fully humidified the electro-osmotic drag coefficient decreases and at 0.4 A /cm² it starts increasing. The electro-osmotic drag portion of the total water flow is extracted, and it is changing with current density. In the case shown the electro-osmotic drag does increase with current density and is positive in current densities greater 0.2 A/cm². The total water flow composition is shown in Figure 4.1.27:

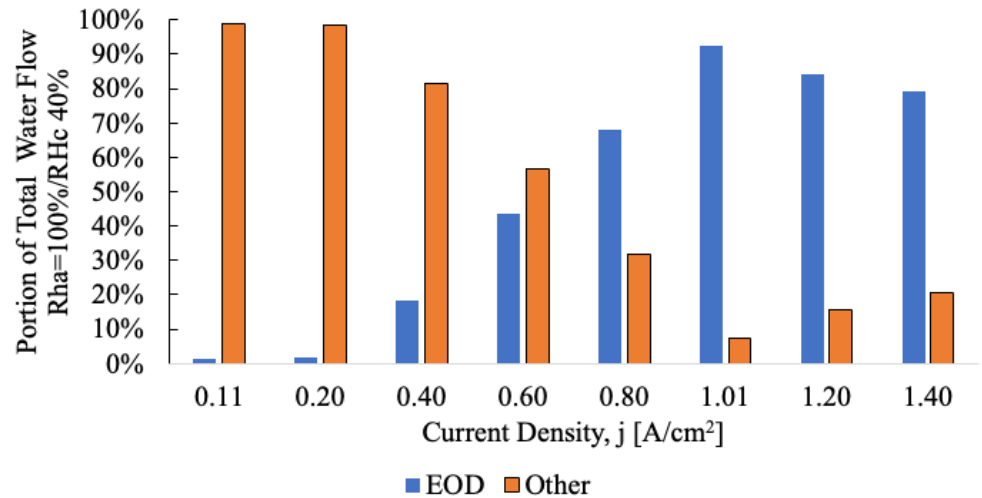


Figure 4.1.27 Electro-Osmotic Drag Coefficient computed [37]

The total water flow was broken down into its fundamental components. At lower current densities the back diffusion portion of the total water flow exceeds electro-osmotic drag. At higher current densities the electro-osmotic drag portion of the total water flow exceeds back diffusion. This breakdown was not done by Adachi [37]. The breakdown of the total water flow does provide understanding of electro-osmotic drag and back diffusion. In the last case where liquid water is flowing with a differential pressure, the slope of the trendline was used to determine pressure transport coefficient. The trendline was not forced through the origin. The pressure coefficient is shown in Figure 4.1.28:

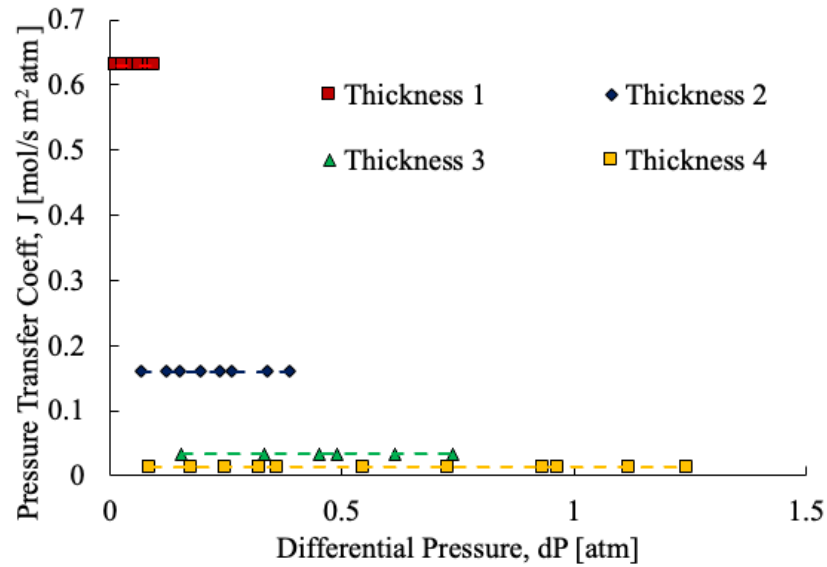


Figure 4.1.28 Pressure Transfer Coefficient [37]

The pressure-based coefficient is constant based on the slope of total water flow trendline. The pressure transfer coefficient is not a function of differential pressure. The pressure transport coefficient can now be used to compute the pressure component of the total water flow. The composition of the total water flow is shown in Figure 4.1.29:

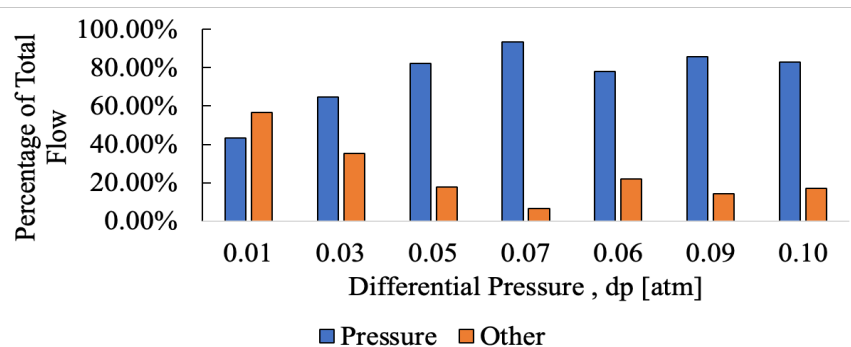


Figure 4.1.29 Total Water Flow Composition [37]

Based on the total water flow breakdown, the pressure-based component of the total flow ranges from 43-96%. Other fluid drivers are present and, in any experiment, where the water flow is indirectly measured, the total water flow must be broken down. The other fluid driver is not neglectable it can be a major driver at lower pressure differences but at higher pressure difference the other component it is a small component of the total pressure flow. To maintain accuracy and precision, the proposed process should be used to only extract the desired driver from total water flow, total water flow needs to be broken down for all cases to ensure the desired fluid driver is isolated.

Ito et al [39] ran water flow experiments and their data was used to compute the electro-osmotic drag coefficient, and the total water flow composition break down. The total water flow is used to compute the electro-osmotic drag coefficient as Figure 4.1.30:

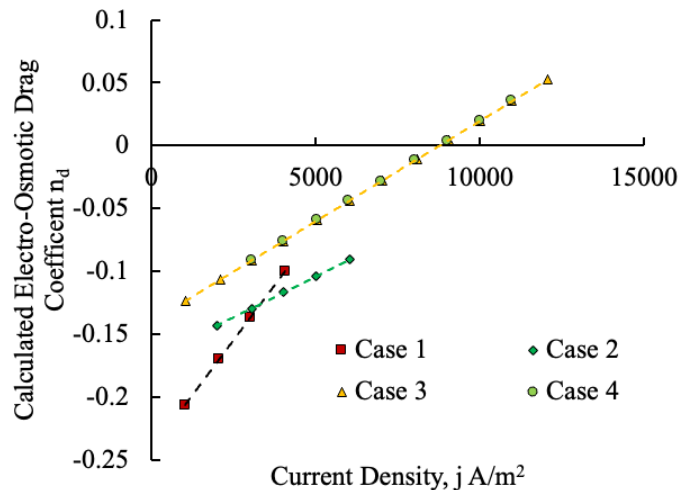


Figure 4.1.30 Computed Electro-osmotic Drag Coefficient [39]

The electro-osmotic drag coefficient is a function of current density in each case. In two of the three cases the electro-osmotic drag is negative, in one case the electro-osmotic

drag is positive at higher current density. In case number 4 the electro-osmotic drag does become positive while in the other cases it is negative. The negative electro-osmotic drag coefficient indicates that the electro-osmotic drag is going in the direction of cathode to anode, the fuel cells tested did have a Microporous Layer (MPL) and when liquid water is present is till induce membrane distillation in the direction of liquid to vapor. The water generated on the cathode side is dependent on the current density, if over saturation of air occurs then liquid water will be generated. Now that the total water flow is broken down the composition of the total water flow can be evaluated. The total water flow is broken down into its components as shown in Figure 4.1.31:

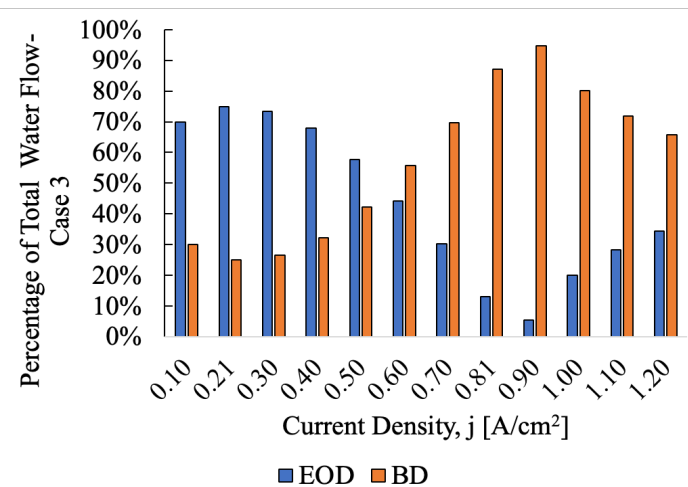


Figure 4.1.31 Total Water Flow Composition [39]

At lower current densities, the electro-osmotic drag does exceed back diffusion but when the current density is greater than 0.6 A/cm², the back diffusion does exceed electro-osmotic drag, this could be due to the thermal gradient across the fuel cell as well as the liquid water on the cathode inducing membrane distillation. The thermal gradient was not reported so it was possible to break down the total water flow further. The electro-

osmotic drag coefficient and the breakdown of the total water flow was not provided by Ito et al [39]. There is not any consistency is electro-osmotic drag and back diffusion some of the cases electro-osmotic drag is greater than back diffusion and some cases back diffusion exceeds electro-osmotic drag.

In the experiments there are two fluid drivers assumed electro-osmotic drag and back diffusion. The total water composition has electro-osmotic drag dominant in some cases and back diffusion in other cases. At higher current densities the back diffusion is dominant. The total water transfer coefficient can be used for a cell-to-cell comparison but does not provide an insight on electro-osmotic drag or back diffusion. More can be obtained when analyzing the total water flow across the membrane.

Ge et al [40] total water flow was examined that compute the electro-osmotic drag coefficient and the composition of the total water flow. The calculated electro-osmotic drag is shown in Figure 4.1.32:

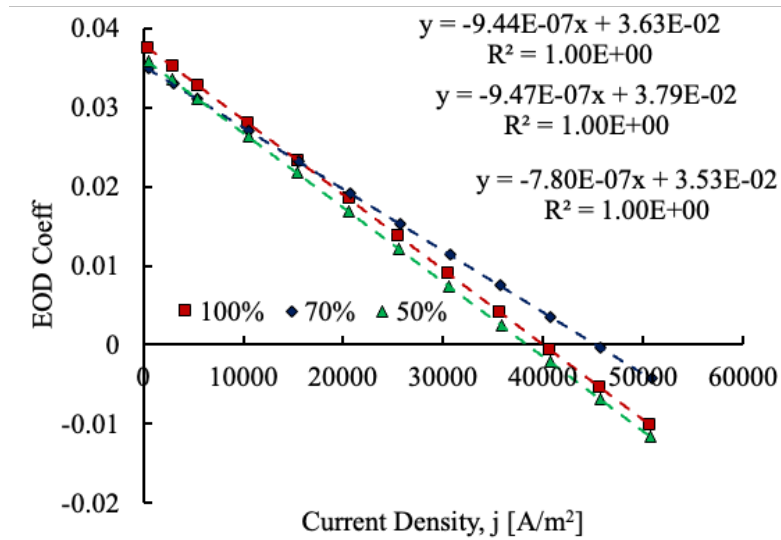


Figure 4.1.32 Calculated Electro-osmotic Drag Coefficient [40]

The electro-osmotic drag coefficient is decreasing with current density; this confirms that electro-osmotic drag is a function of the current density. The electro-osmotic drag coefficient starts off positive and does turn negative at higher current densities, this could be due to the thermal gradient as well as the liquid water formation on the cathode. The fuel cell voltage does decrease with current density and when the fuel cell voltage decreases the thermal gradient increases. The other reason is that the membrane hydration state is changing based on the total water flow across the membrane.

The total water flow reported was in the in the direction of cathode to anode, and typically electro-osmotic drag goes from anode to the cathode. The electro-osmotic drag is coming up negative due to it flowing anode to cathode. The electro-osmotic drag coefficient is changing with current density. The electro-osmotic drag was calculated

with the experimental data, and it was not obtained from an empirical model. The composition of the total water flow is shown in Figure 4.1.33:

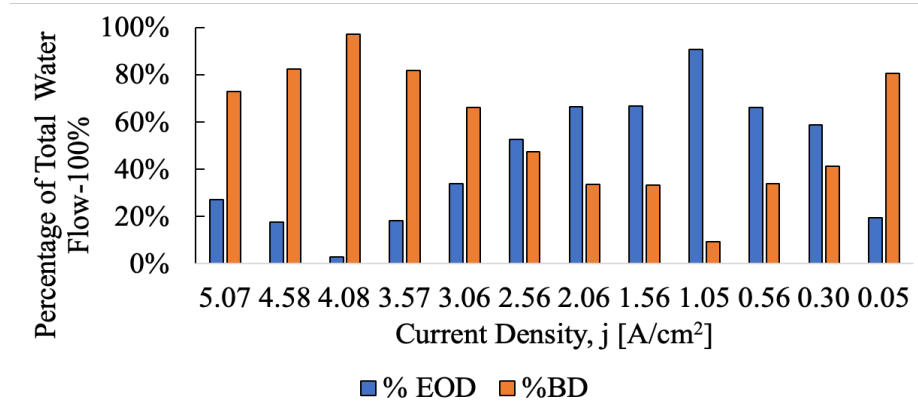


Figure 4.1.33 Composition of Total Water Flow [40]

At high current density, the back diffusion exceeds electro-osmotic drag and at mid current densities the electro-osmotic drag exceeds back diffusion and at low current density the back diffusion exceeds electro-osmotic drag. Electro-osmotic drag and back diffusion portion of the total water flow change with current density. The dominant mode of water transport does vary with the inlet conditions as well as the current density, some cases electro-osmotic drag dominates and other cases back diffusion dominates. The determination of electro-osmotic drag coefficient and the total water flow break down was not provided by Ge et al [40].

Bezamalainovic [41] reported the total water flow across the membrane but did not provide a breakdown of the total water flow and did not compute the electro-osmotic drag coefficient. The calculated electro-osmotic drag coefficient is shown in Figure 4.1.34:

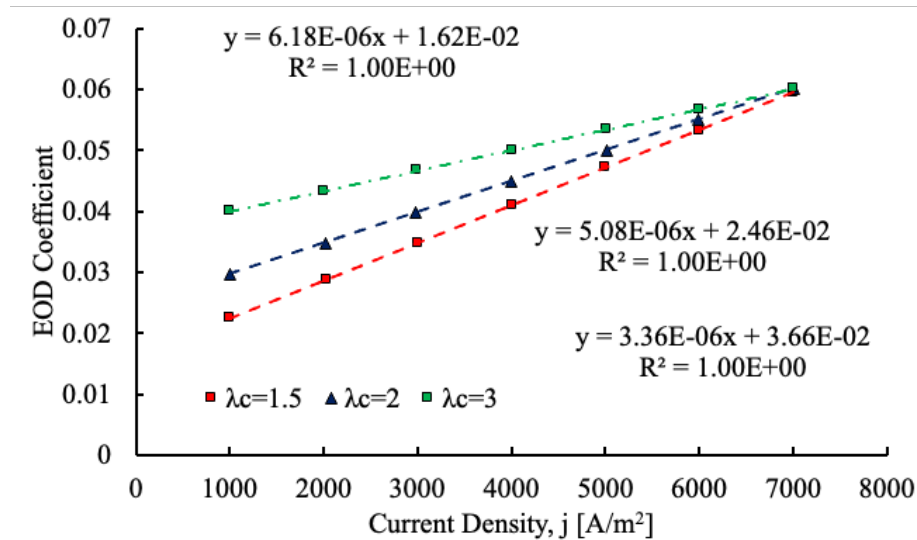


Figure 4.1.34 Calculated Electro-Osmotic Drag Coefficient [40]

The electro-osmotic drag coefficient does increase with current density, but the change is rather small from .02 to .06, this is very small change. This is a high temperature fuel cell, and the goal is to keep water in the vapor form. The electro-osmotic drag coefficient did stay positive because membrane distillation will not occur is water is in vapor form. The electro-osmotic drag coefficient is function of current density this is due to the change in the hydration state of the membrane as well as the change in the voltage gradient across the membrane. The electro-osmotic drag was not computed by Bezamalinovic [41]. The total water flow for each case was broken down into its drivers the composition of the drivers is shown in 4.1.35:

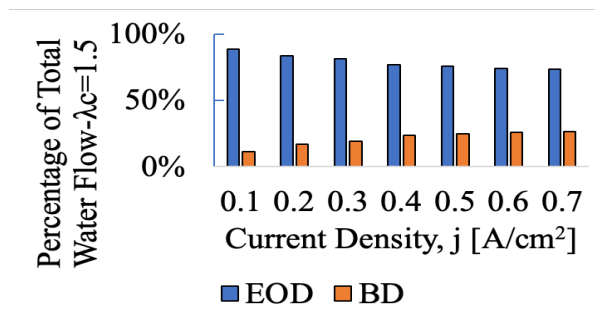


Figure 4.1.35 Composition of Total Fluid flow [40]

In the high temperature fuel cell, the electro-osmotic drag does exceed back diffusion in all cases, the high temperature fuel cell does not have liquid water which can introduce membrane distillation. The mass flow of air does impact the total water flow across the membrane. The insight gained is that the electro-osmotic drag does change with current density and this change is small compared to the lower temperature fuel cells. The composition of total fluid flow is shown in Figure 4.1.35.

Park and Caton [133] performed experiments with the objective to determine the electro-osmotic drag coefficient under variable current density, and they found that the electro-osmotic drag coefficient decreases with increasing current density. Park and Caton proposed two theories: the first is that water formation on the cathode increases back diffusion. The second is that with increased current density, more protons are transported to the cathode, but with increased back diffusion the net number of water molecules decreases.

Reid [42] performed fuel cell testing and the electro-osmotic drag and back diffusion portion of the total water flow were not calculated. The total water flow data was used to calculate the electro-osmotic drag coefficient as well as the composition of the total water flow. The calculated electro-osmotic drag coefficient is shown in Figure 4.1.36:

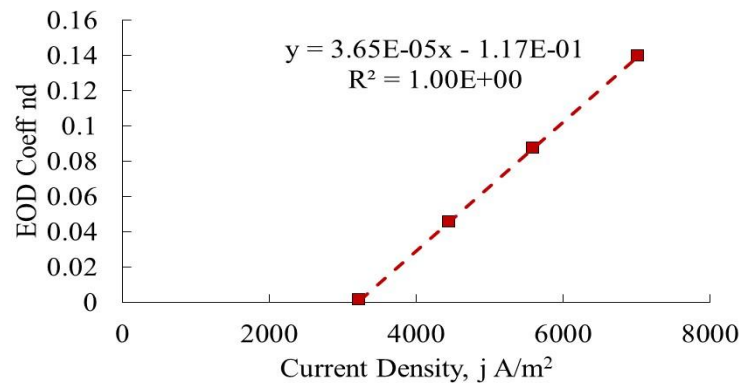


Figure 4.1.36 Calculated Electro-Osmotic Drag Coefficient [42]

The electro-osmotic drag coefficient is increasing with current density; this also confirms that electro-osmotic drag coefficient is a function of current density. The linear relationship of the electro-osmotic drag comes from the polynomial fit of the total water flow plotted against current density. The membrane properties are changing with the hydration state of the membrane. The other reason for the change in electro-osmotic drag could be a result of the changing of the discharge voltage with current density. The breakdown of the total water flow is shown in Figure 4.1.37:

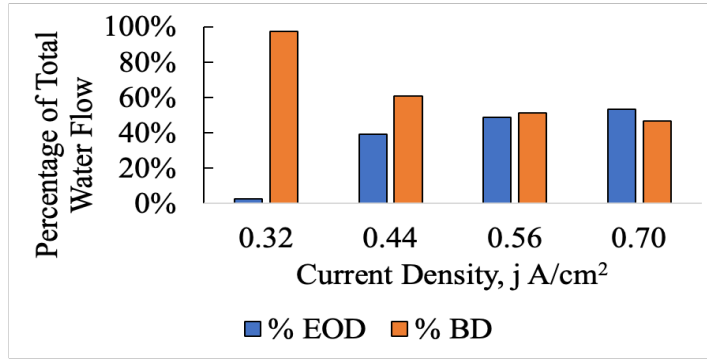


Figure 4.1.37 Composition of Total Water Flow [42]

At low current density, back diffusion exceeds electro-osmotic drag at all cases except for 0.7 A/cm². At lower current densities it is expected that electro-osmotic drag to contribute very little because of the low current Reid [42] did not break down the total water flow to gain insight into electro-osmotic drag and back diffusion.

Anotani et al [43] performed experiments on the fuel cells and with their calculated total water flow data, the electro-osmotic drag coefficient and composition of total water flow.

The computed electro-osmotic drag coefficient is shown in Figure 4.1.38:

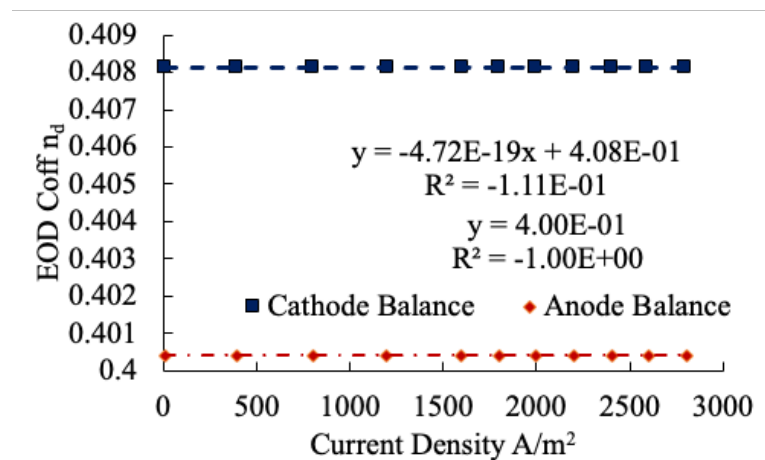


Figure 4.1.38 Calculated Electro-Osmotic Drag Coefficient [43]

This is one case where the electro-osmotic drag coefficient was constant during operation, this is a result of the linear fit of the total water flow data. The two electro-osmotic drag coefficients come from the anode and cathode balance, the cathode water balance. The calculated value for electro-osmotic ranges from 0.4 to .408. The computed electro-osmotic drag coefficient can be used to compute the electro-osmotic drag, and the back diffusion portion of the total water flow can be obtained. The composition of the total water flow is shown in Figure 4.1.39:

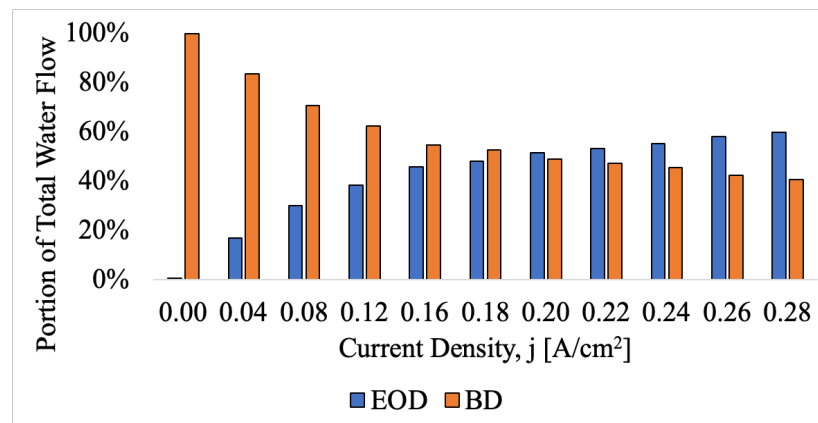


Figure 4.1.39 Composition of Total Water Flow [43]

At lower current densities, the back diffusion portion of the total water flow exceeds electro-osmotic drag and as the current density increases the electro-osmotic drag portion of the total water flow increases. Anotani et al [43] did not fully analyze the total water flow across the membrane. The proposed approach allows for the calculation of the electro-osmotic drag and back diffusion portion of the total water flow based on the experimental data.

4.2 Electro-Osmotic Drag Analysis and Back Diffusion Analysis

When total water flow is indirectly measured, the total water flow is the summation of all fluid drivers are present. In electro-osmotic drag experiments the total water flow was forced through the origin, which will assume that all the water flow is from electro-osmotic drag and no other fluid drivers are present.

Ren et al [61] conducted experiments with a methanol fuel cell. In the methanol fuel cell liquid is on one side of the membrane and water vapor. The computed electro-osmotic drag coefficient is shown in Figure 4.2.1:

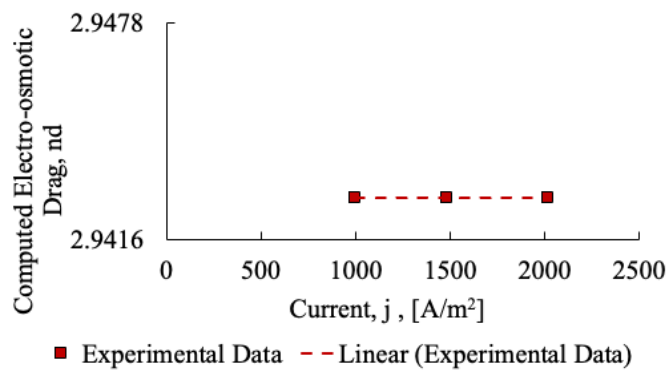


Figure 4.2.1 Calculated Electro-Osmotic Drag [61]

The electro-osmotic drag coefficient is not changing with current density; this is a result of the linear fit of the total water flow data. The linear fit could be result of the liquid on the anode side of the membrane. The cathode side is humidified air. The constant value of the electro-osmotic drag coefficient is a result of the membrane properties not changing because the membrane is saturated. In this case with liquid on the anode, the membrane properties are not changing because the membrane is fully hydrated. Also,

with the liquid on the anode and water vapor on the cathode like Adachi [37] experiment membrane distillation/osmotic distillation will be present. The direction of the membrane distillation would be anode to cathode just like in electro-osmotic drag. Membrane distillation would be augmenting electro-osmotic drag. Since there is liquid water present on the anode, the Nernst-Planck equation is applicable. The composition of the total water flow is shown in Figure 4.2.2:

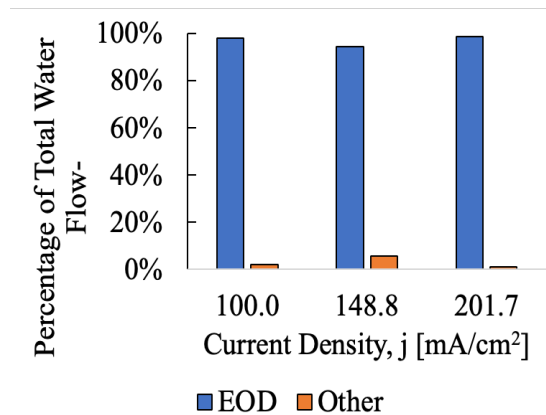


Figure 4.2.2 Total Water Flow Composition [61]

The electro-osmotic drag portion of the water flow is between 94-98%, electro-osmotic drag is not the only fluid driver present in the total water flow and forcing the trendline through the origin does lump in the other fluid driver. The other fluid drivers are present, and not all the total water flow is electro-osmotic drag. The other fluid driver ranges from 2-6%. By forcing through the origin, it will be accounted for the other fluid driver; to maintain accuracy and precision the total water flow needs to be broken down into its primary fluid drivers. In this case the back diffusion is 2-6% of the total water flow. The heat and water management of the fuel cell require accuracy and precision.

Ren et al [61] also examined the methanol fuel cell at different conditions and like their other case the total water flow was forced through the origin, and this neglects the other fluid drivers. A linear trendline was used to fit the data because liquid is on the anode side and humidified air is on the cathode side. The computed electro-osmotic drag is shown in Figure 4.2.3:

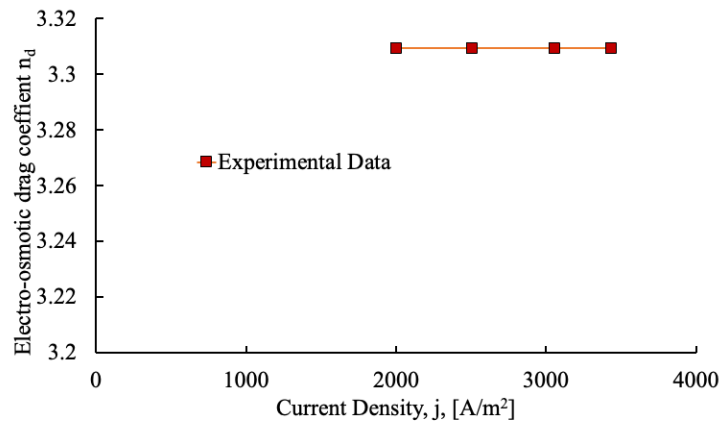


Figure 4.2.3 Computed Electro-Osmotic Drag Coefficient [61]

As in the other methanol fuel cell case, the electro-osmotic drag coefficient is not changing with current density which indicates that in this environment the electro-osmotic drag is independent of current density. The constant electro-osmotic drag coefficient is a result of the linear fit of the total water flow, and it is a result of the membrane being saturated. The computed electro-osmotic drag coefficient is constant because of the liquid on the anode side of the membrane and falls into the domain of the Nernst-Planck equation, note cases with water vapor do not follow a linear fit. The

computed electro-osmotic drag is higher than the value Ren et al [61] reported because when the other fluid. The total water flow composition is shown in Figure 4.2.4:

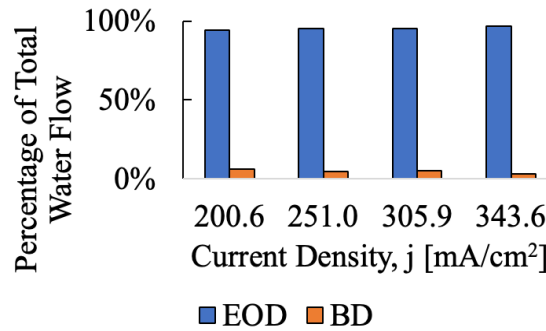


Figure 4.2.4 Composition of Total Water Flow [61]

As before the 95% of the total water flow is electro-osmotic drag and about 5% of total flow is back diffusion, this will skew the true electro-osmotic drag coefficient. The new method does calculate a different electro-osmotic drag coefficient free of the back diffusion. The fuel cell is sensitive to heat and water management, accuracy is required. A more accurate the coefficient models the better the water management which can mitigate fuel cell flooding. With the liquid water present on one side of the membrane distillation/osmotic distillation will occur which will augment electro-osmotic drag. The total water flow must be broken down into its primary fluid drivers and analyzed, and the total water flow trendline should not be forced through the origin.

Ren et al [63] also ran experiments at different temperatures, the total water flow data is used to compute the electro-osmotic drag coefficient as well the composition of total water flow. Ren et al [63] also forced the data trendline through the origin. The

experiment was conducted with liquid on the anode and humidified air on cathode. The computed electro-osmotic drag coefficient is shown in Figure 4.2.5:

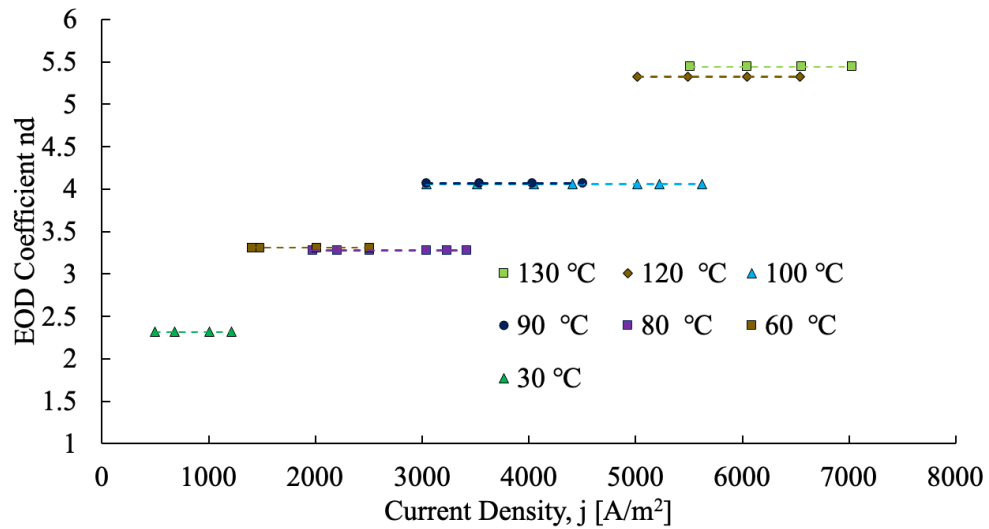


Figure 4.2.5 Computed Electro-Osmotic Drag Coefficient [61]

The electro-osmotic drag coefficients are constant over the current density, indicating that the electro-osmotic drag is independent on the current density. This is a result of the membrane being saturated with liquid water on the anode. The membrane properties are not changing in a liquid environment. The electro-osmotic drag coefficient increased with temperature; this is a result of membrane/osmotic distillation because saturation pressure will increase with temperature, the vapor pressure of water is increasing with temperature. The membrane distillation will occur on the direction of liquid to vapor; the higher temperature will increase membrane distillation because of the increase in vapor pressure. The composition of the total water flow is shown in Figure 4.2.6:

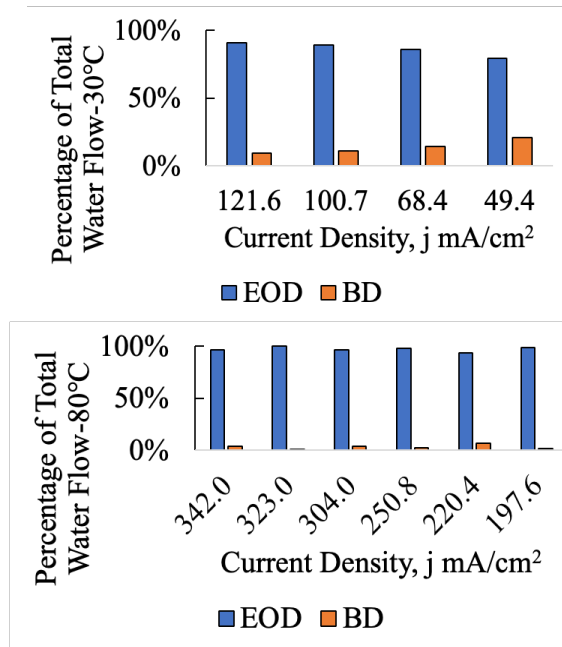


Figure 4.2.6 Composition of Total Water Flow [61]

The electro-osmotic drag portion of the total water flow is 98-99%. The higher percentage of electro-osmotic drag occurred at 100°C. The electro-osmotic drag is also augmented by membrane distillation because of the liquid at the anode and the water vapor on the cathode. As the temperature increases the electro-osmotic drag portion of the total water flow is increasing. At 30°C the electro-osmotic drag portion of the total water flow ranged 79-91%, at lower temperatures the vapor pressure is much lower, and this will produce less membrane distillation. The direction of membrane distillation will be in the direction of anode to cathode due to the liquid water at the anode. Both membrane distillation and electro-osmotic drag are in the same direction, so it looks like a larger electro-osmotic drag, but it is being added by membrane distillation.

The total water flow across membrane cannot be forced through the origin, due to the presence of other fluid drivers. The total water flow must be broken down into its fundamental fluid drivers. The other fluid driver ranges from 1-20%. In the instance where the other fluid driver is 1%, it could be considered neglectable but when the other fluid driver is 20% it is not neglectable. The total water flow must be analyzed for each case to obtain an accurate electro-osmotic drag and back diffusion transport properties.

Lee et al [64] total water data was examined to determine the electro-osmotic drag coefficient as well as the composition of the total water flow, the initial data was not forced through the origin, but all the data was lumped together. The calculated electro-osmotic drag is shown in Figure 4.2.7:

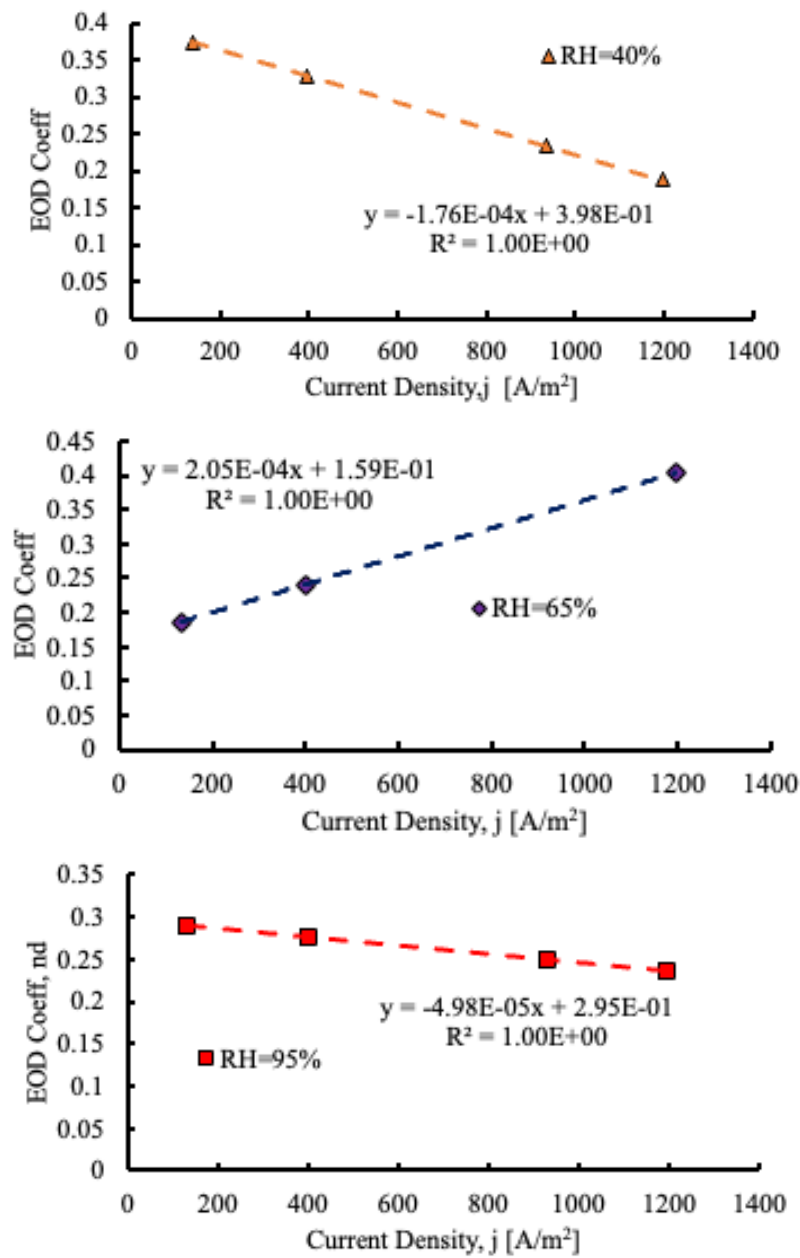


Figure 4.2.7 Computed Electro-osmotic drag coefficient [64]

The calculated electro-osmotic drag coefficient is a function of current density. In the 40% RH and 95% RH cases the electro-osmotic drag coefficient is decreasing with

current density, but the 65% RH case shows the electro-osmotic drag coefficient is increasing with current density. The initial plot of assumed that electro-osmotic drag is independent of current density. All the cases that the electro-osmotic drag coefficient is a function of current density. The membrane properties are changing along with the voltage gradient across the membrane. The composition of the total water flow is shown in Figure 4.2.8:

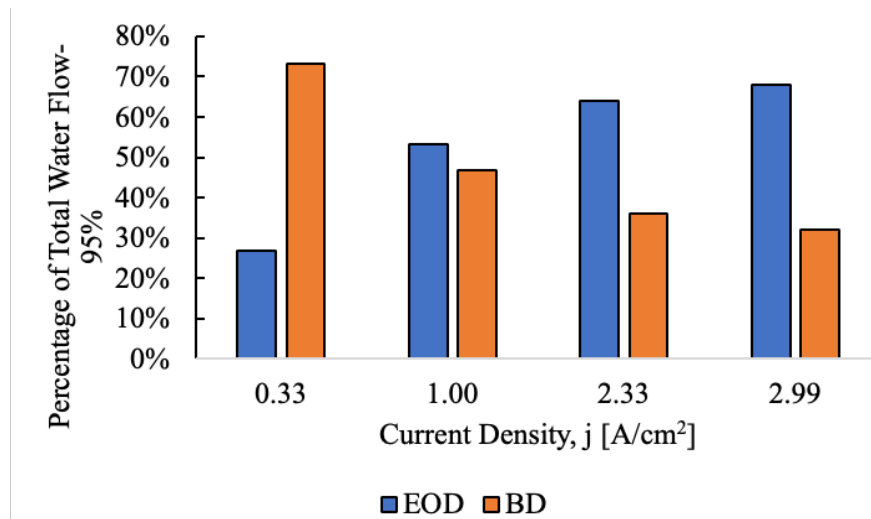


Figure 4.2.8 Composition of Total Water Flow [64]

The total water flow is composed of electro-osmotic drag and back diffusion and Lee et al [64] was correct not to force the total water flow through the origin but the electro-osmotic drag coefficient depends on relative humidity and current density this is reason why the total water flow must be separated based on relative humidity. At lower current densities the back diffusion exceeds electro-osmotic drag but as current density increases electro-osmotic drag exceeds back diffusion.

Husar et al [65] examined water flow in different scenarios the first scenario was hydraulic permeation, the original data was forced through the origin, and this assumes that other fluids drivers are neglected. The data was used, and the pressure transfer coefficient was obtained, and the composition of the total water flow is obtained. The pressure transfer coefficient is shown in Figure 4.2.9:

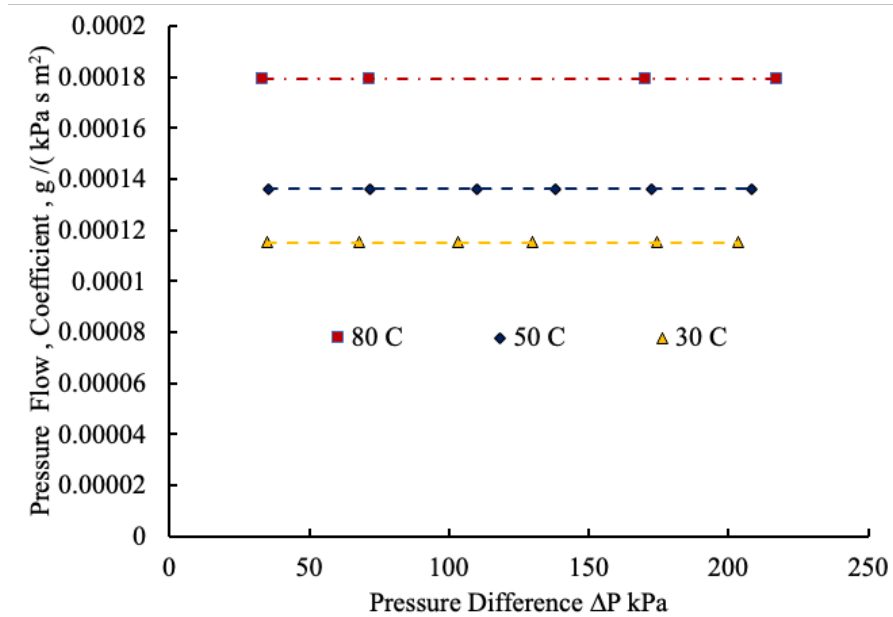


Figure 4.2.9 Pressure Transfer Coefficient [65]

The pressure transport coefficient is constant for each based on the linear trendline. The constant pressure transport coefficient indicates that it is independent of the pressure gradient. With the data trendline, the pressure-based component needs to be isolated from the total water flow. The pressure component of the total water flow is shown in Figure 4.2.10:

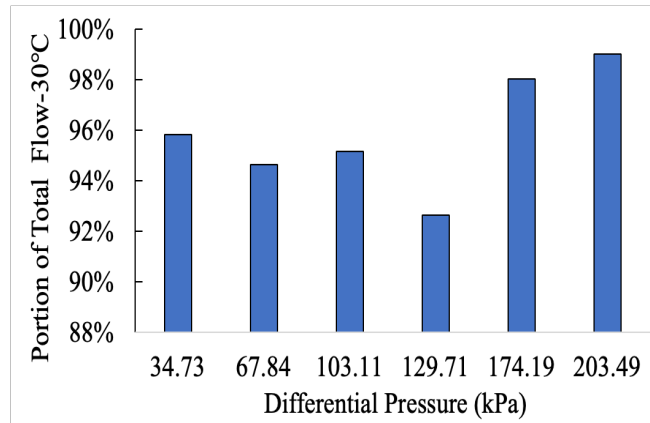


Figure 4.2.10 Pressure Component of the Total Water Flow [65]

Not all the total flow is pressure-based flow, the pressure component ranges from 92-99%. The proposed method has been used to break down the total water flow into its components and to determine transport coefficient without assuming a transport coefficient. Not all the total water flow is pressure driven there is a component that comes from other fluid drivers. The total water flow must be broken down in all cases. The electro-osmotic drag experiment was also examined, and the electro-osmotic drag was calculated based on the total water flow data and the calculated electro-osmotic drag is compared to the reported result shown in Figure 4.2.11.

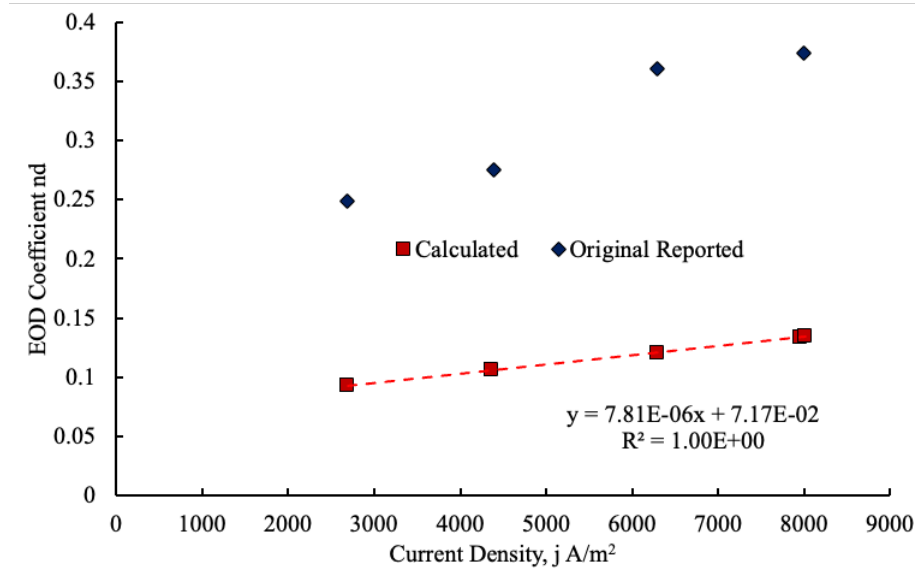


Figure 4.2.11 Comparison of Electro-osmotic drag coefficient [65]

The calculated electro-osmotic drag is lower than the reported results. The electro-osmotic drag coefficient is also changing with current density. The calculated electro-osmotic drag is lower than the reported results. The difference in electro-osmotic drag coefficient will lead to less water on the cathode. One common agreement is the electro-osmotic drag coefficient is a function of current density. Only the total water flow data was used to obtain the electro-osmotic drag coefficient. The composition of the total water flow is shown in Figure 4.2.12:

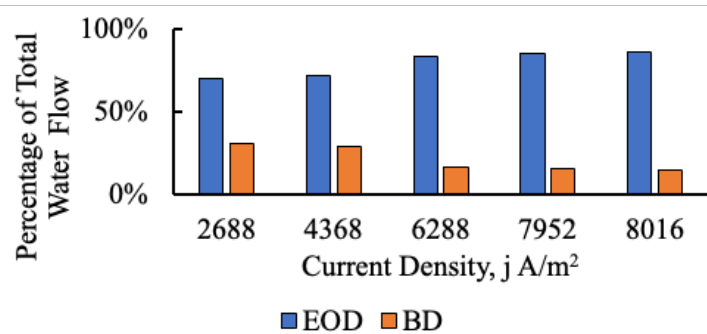


Figure 4.2.12 Composition of the Total Water Flow [65]

The total water flow is composed of electro-osmotic drag and back diffusion; in all cases the electro-osmotic drag exceeds back diffusion. Husar et al [65] did not break down the total water flow into its primary fluid driver components, the total water flow can be broken down without assumption any transport coefficient.

Ye et al [46] performed electro-osmotic drag experiments with hydrogen pump, the total water flow data was examined and the electro-osmotic as well as the composition of the total water flow. Ye et al [46] had also forced the trendline through the origin. The electro-osmotic drag coefficient is shown in Figure 4.2.13:

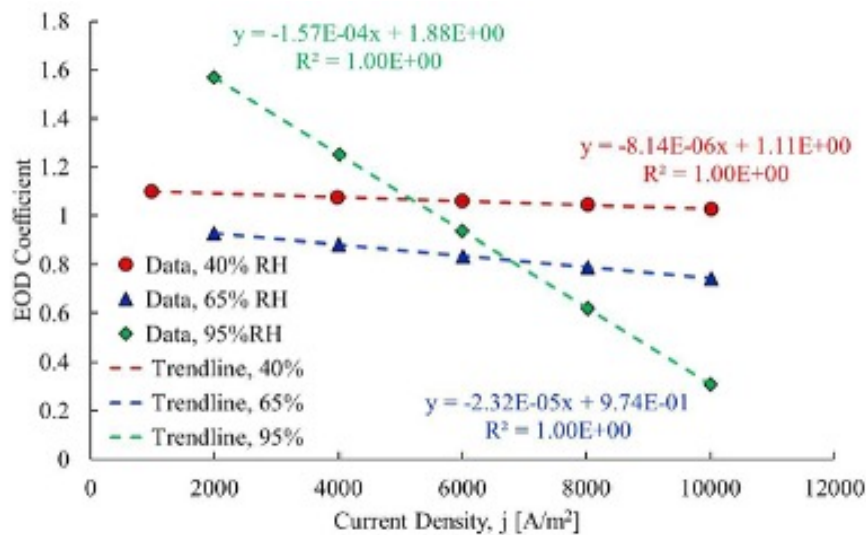


Figure 4.2.13 Calculated Electro-Osmotic Drag Coefficient [46]

The calculated electro-osmotic drag is changing with the relative humidity along with the current density, the most severe decrease is for the 95% RH case. Ye et al [46] had stated that the electro-osmotic drag does not change with current density. The major decrease for in current density could be a result of the membrane distillation/osmotic distillation

moving water from the cathode to the anode. At high relative humidity there is high probability of liquid water which will introduce membrane distillation. The composition of the total water flow is shown in Figure 4.2.14:

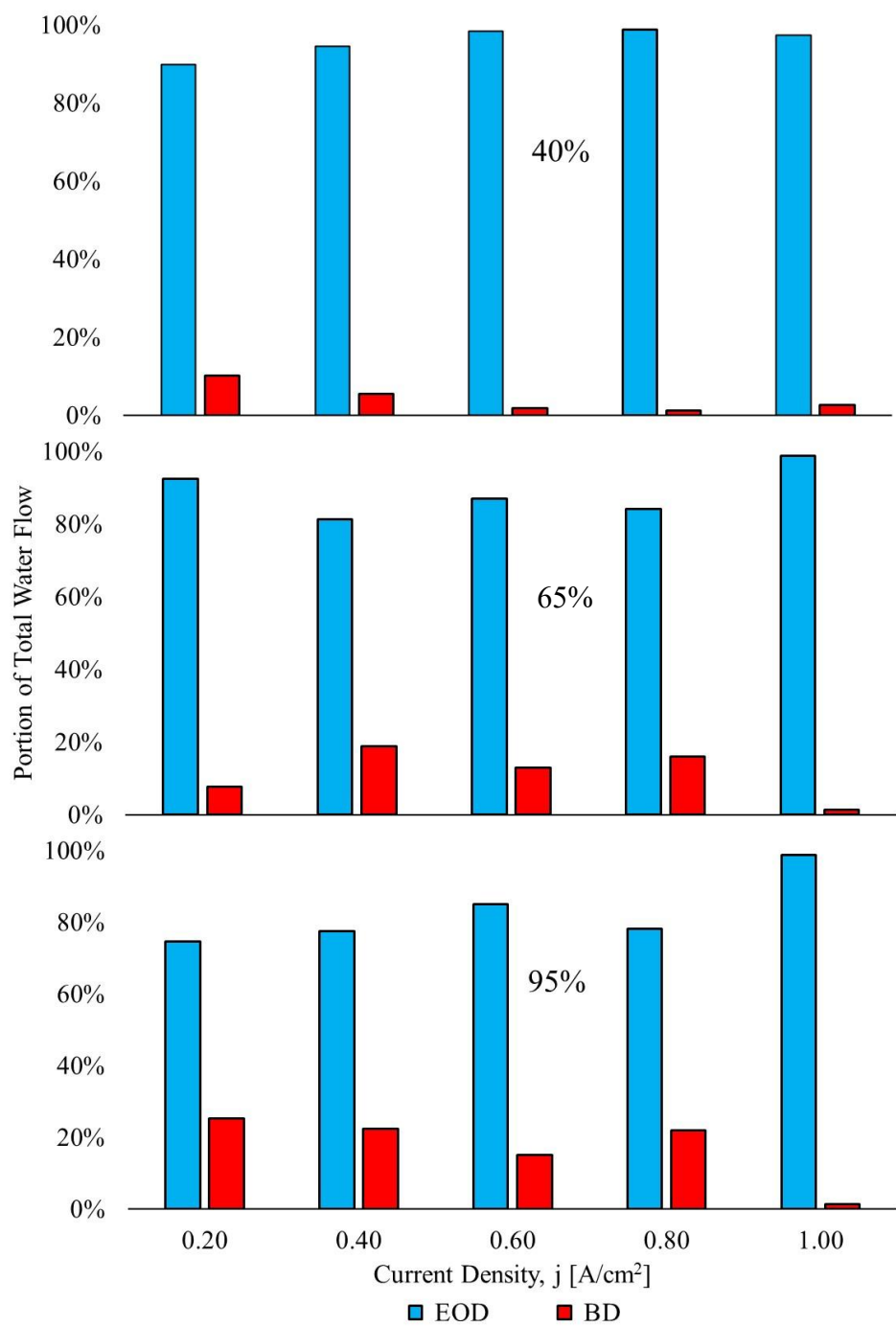


Figure 4.2.14 Composition of Total Water Flow [46]

Ye et al [46] had assumed that back diffusion was neglectable, but the back diffusion component of the total water flow is not neglectable. The back diffusion portion of the total water flow is up to 20% of the total water flow. The data analysis does show that the electro-osmotic drag coefficient is a function of current density especially at the 95% RH case where it has the greatest decrease. This decrease is a result of liquid water on the cathode inducing membrane distillation and pushing water back toward the anode. The other factor influencing the change in the electro-osmotic drag coefficient is the changing properties of the membrane.

In Ye et al [46] electro-osmotic drag the total water flow was forced through the origin neglecting other fluid driver. The refitted was used to compute the electro-osmotic drag coefficient. The back diffusion is portion of the total water flow is not neglectable and forcing through the origin is not good assumption. The total water flow needs to be broken down without making any assumptions and it can be done with the proposed approach.

Ge et al [48] data was processed using the total water flow to compute the electro-osmotic drag and back diffusion portions of the total water flow. The computed coefficients for the electro-osmotic drag and back diffusion for the 303 K are shown in Figure 4.2.15. Ge et al [48] calculated electro-osmotic drag is shown for comparison.

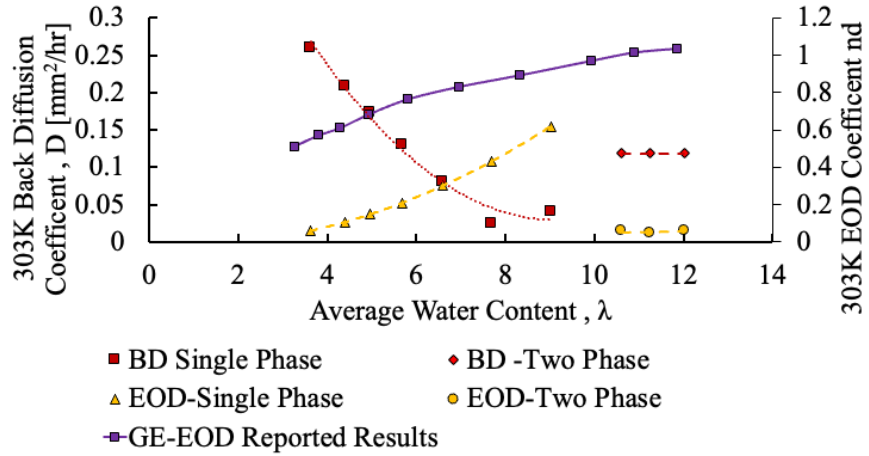


Figure 4.2.15 Calculated Coefficients for 303K [48]

The results show that calculated electro-osmotic drag coefficient is lower than Ge et al [48] and in increasing with water content. The back diffusion is decreasing with membrane water content. The differences are a result of the back diffusion model chosen by Ge et al [48] compared to the calculations done without assuming a back diffusion coefficient. In the two-phase region of the test the electro-osmotic drag constant value. The composition of the total water flow is shown in Figure 4.2.16:

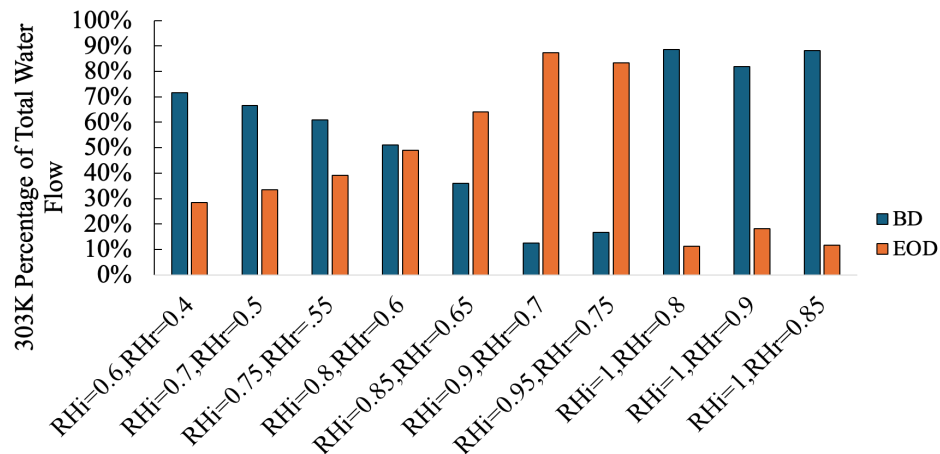


Figure 4.2.16 Composition of Total Water Flow [48]

In the cases where the relative humidity is 100% the back diffusion exceeds electro-osmotic drag. Both electro-osmotic drag and back diffusion play a role on the water transport and in some of the cases electro-osmotic drag dominates and in other conditions the back diffusion dominates. It is noted that in the single-phase region the transport properties change but when two phase is achieved the transport coefficients are constant.

As in the 303K case, the case the two-phase region has a constant back diffusion and constant electro-osmotic drag coefficient. In the single-phase region the back diffusion and electro-osmotic drag coefficient are changing with the membrane water content. In these cases, the current density is fixed, and it is not known how to how electro-osmotic drag changes with current density. The electro-osmotic drag and back diffusion coefficient are different in the single and two-phase regions. The electro-osmotic drag coefficient and back diffusion coefficient are constant in the two-phase region and changing in the single-phase region. The calculated electro-osmotic drag is much lower than the reported electro-osmotic drag although the increase in the Ge et al model [48]. The back diffusion coefficient is decreasing with water content.

The back diffusion portion of the water flow is dominate over the electro-osmotic drag except for one case. The total water flow can be broken own without assuming a back diffusion or electro-osmotic drag coefficient and the results will be independent on one another. In the electro-osmotic drag cases only one case was not forced through the

origin. Lee et al [64] did account for the other drivers but did not decompose the total water flow into its components.

Ren et al [61],[63] and Ye et al [46] had forced the data trendline through the origin and neglected other fluid drivers, their electro-osmotic drag coefficient will have the other drivers lumped in and it will not be the true coefficient, nor did they provide the breakdown the total water flow. By forcing the trendline through the origin their assumption of total water flow equal to electro-osmotic drag means that 100% of the fluid flow is from the one driver and the other drivers will be lumped in.

In summary, when the total water flow is indirectly measured, the total water flow will be summation of all the fluid drivers present. There is not a need to assume an electro-osmotic drag or back diffusion coefficient to determine one of the fluid drivers.

The theoretical model along with the experimental data can be coupled together to determine one of the transport coefficients, and then that fluid driver then the other driver can be obtained by subtracted from the total.

The second point is that when the data trendline is forced through the origin, it assumes that off the total water flow is from the measured fluid driver, when data is examined further, there are other fluid drivers that need to be extracted, and this can be done with the proposed method. Chadha et al [73] performed back diffusion experiments with Nafion, and their data had single-phase and two-phase data, but it was not clear if they

forced their data through the origin, the data plotted against the concentration of difference and the results were reexamined. The calculated back diffusion coefficient is shown in Figure 4.2.17:

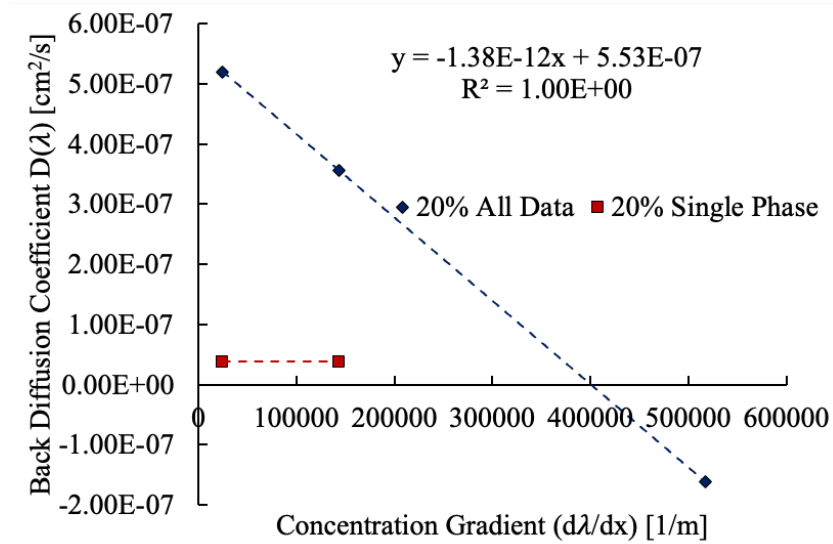


Figure 4.2.17 Calculated Back Diffusion Coefficient [73]

The back diffusion coefficient is decreasing with the concentration gradient which confirms that the back diffusion coefficient is a function of the concentration gradient. The back diffusion coefficient is a function of the hydration state of the membrane and with the membrane hydration state changing so is the back diffusion coefficient. When the single-phase data is extrapolated it diverges from the two-phase results indicating that another fluid driver is present, the two-phase data difference is theorized that membrane distillation/osmotic distillation is present. The constant from the trendline indicates that another fluid driver is present in the experiment. Chadha et al [73] assumed all water flow across the membrane is from back diffusion, with further analysis and not all the water

flow is from back diffusion. The composition of the total water flow is shown in Figure 4.2.18:

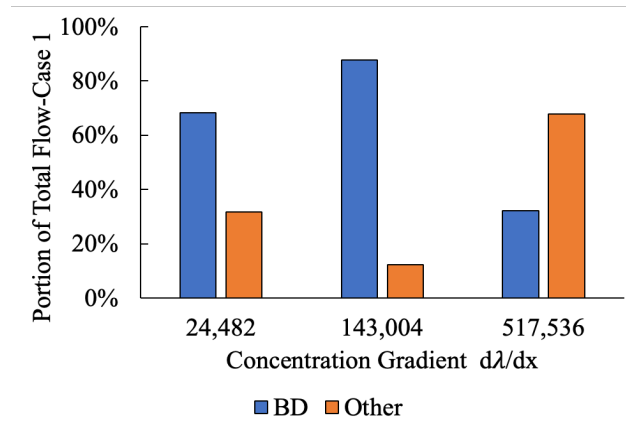


Figure 4.2.18 Back Diffusion portion of total water flow [73]

The total water flow is made up of back diffusion and other fluid drivers, so it is not safe to assume that all the total water flow is from back diffusion. The highest percentage of back diffusion is 94% and the lowest is 34%. The total water flow must be examined fully even in back diffusion experiments.

4.3 Thermal Osmosis

There are two forms of thermal osmosis, single-phase, and two-phase (Membrane distillation), the general agreed theory for thermal osmosis is that for liquids in contact with a hydrophilic membrane fluid will move from cold to hot, and for hydrophobic membrane the direction of flow is from hot to cold. Not all membranes are purely hydrophobic or hydrophilic such as Nafion. It is not known if the same logic for liquids will transfer over gases. When thermal osmosis experiments are conducted the total water

flow is indirectly measured and the total water flow will contain other fluid drivers. When some researchers looked at thermal osmosis data, they had forced the trendline through the origin like in the electro-osmotic drag coefficient experiment. As in the other osmotic pressure case, the empirical model could be coupled with a theoretical model to determine the coefficient transport for osmotic pressure but based in other cases the proposed method shows that the total fluid flow is not the same as the osmotic pressure fluid flow. The reprocessed data shows that other fluid drivers are present besides osmotic flow.

Kim and Mench [75] first thermal osmosis experiment involved measuring the total water flow on a Nafion membrane at different temperatures. The total water flow data was refitting to a linear trendline that is not forced through the origin as shown in Figure 4.3.1:

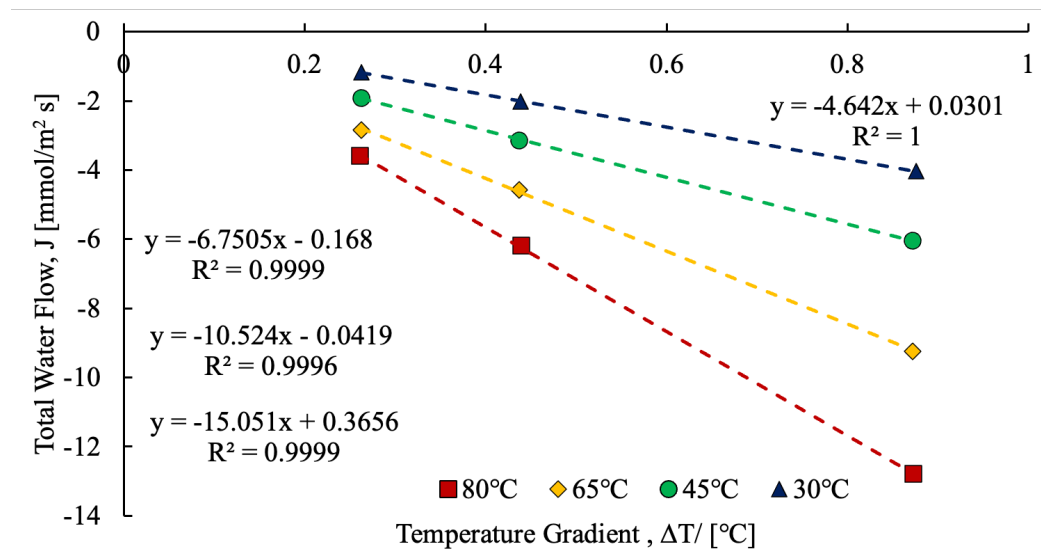


Figure 4.3.1 Thermal Osmosis Total Water Flow Not Forced Through the Origin [75]

The total water flow data is successfully fit to a linear trendline that is not forced through the origin. All the cases do show a constant from the new trendline, in two of the cases it is positive and the other two cases it is negative. The two positive constant cases have the other fluid drive working against thermal osmosis and in the other case when the constants are negative the other fluid driver is working with thermal osmosis.

In the cases with liquid water the thermal osmosis coefficient is a constant which indicates it is not a function of the thermal gradient, this could be due to the membrane being saturated. The thermal osmosis portion of the total water flow is going against the thermal gradient, indicated by the negative slope of the trendline. The slope of the linear trendline is used to compute the thermal osmosis coefficient, and with the thermal osmosis coefficient known the thermal osmosis portion of the total water flow can be computed as shown in Figure 4.3.2:

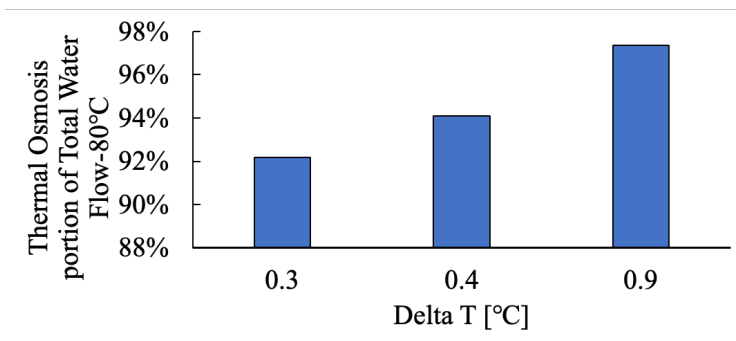


Figure 4.3.2 Thermal Osmosis Portion of Total Water Flow [75]

Not all the total water flow is from thermal osmosis, a portion of it is from another fluid driver. The thermal osmosis portion of the total water flow ranges from 92-98%. The

composition of the total water flow shows thermal osmosis is not the only fluid driver present. In any thermal osmosis experiment, the total water flow needs to be broken down into its components. Like in the total water flow, electro-osmotic drag, and back diffusion experiments the total water flow needs to be broken down into its fundamental fluid drivers.

Tasaka et al [95] examined thermal osmosis in liquids, the experiments measured shows two different curve fits, one case where the trendline was forced through the origin and the second where the trendline is not forced through the origin. By forcing through the origin, it assumes that no other fluid drivers are present so at no temperature difference there should be fluid flow but with other drive present this is not true. The correlation to the data is not the best fit of the for two out of the three cases. The current data trendline does not address seeing thermal osmosis below a discrete temperature difference. The data is reexamined to where the trendline is not forced through the origin as shown in Figure 4.3.3:

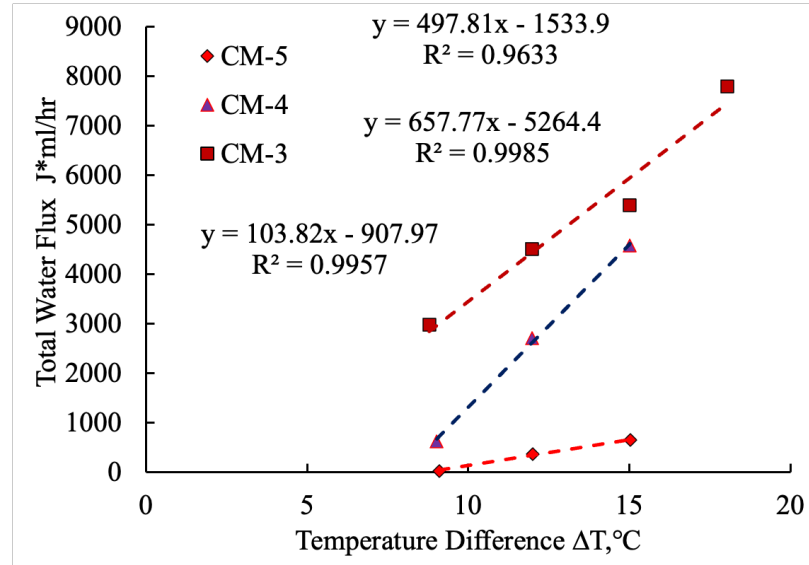


Figure 4.3.3 Current Total Water Flow Data with the trendline not forced the origin [95]

The linear fit does produce a constant in all the cases the constant fluid driver is opposing thermal osmosis, it is masking it. The slopes of the trendline indicate that the assumed direction of the thermal osmosis is correct and the constant from the data fit indicated that there is another fluid driver opposing thermal osmosis. There is a point where no flow will occur. The zero-flow point is solved for by setting the mass flux to zero and determining at which temperature thermal osmosis will appear. The calculated temperatures differences are in Table 4.3-1:

Table 4.3-1 Determination When Thermal Osmosis will be seen

Material	a₁	a₀	Zero Flow Temperature Difference
	ml/(hr °C)	ml/hr	°C
CM-3	497.81	-1533.9	3.08
CM-4	657.77	-5264.4	8.00
CM-5	103.82	-907.97	8.75

In the case of the CM-3 membrane thermal osmosis is seen above a temperature difference of 3K, and for the CM-4 membrane thermal osmosis seems above a temperature difference of 8K and in the CM-5 membrane thermal osmosis is seen above 8.75 K. The reason why thermal osmosis is seen above a certain temperature difference is because other fluid drivers are present, this is why forcing the trendline through the origin is not correct, the trendline that is not forced through the origin is the correct one to use. The thermal osmosis coefficient is not changing with the thermal gradient which indicates that it is not a function of the thermal gradient, this could be a result of the thermal osmosis experiment being conducted in liquid water. The slope of the trendlines is used to compute the thermal osmosis transport coefficient. The known thermal osmosis transport coefficient along with the temperature difference are used to calculate the thermal osmosis portion of the total water flow as shown in Figure 4.3.4:

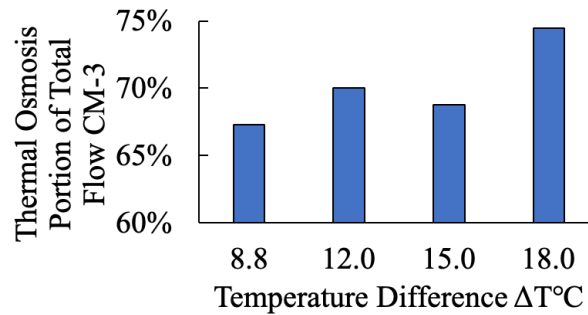


Figure 4.3.4 Current Total Water Flow Data with the trendline not forced the origin [95]

The thermal osmosis portion of the total water flow ranges from 67-75%, this confirms that other fluid drivers are present and that thermal osmosis cannot be measured by itself. The total water flow even in a thermal osmosis experiments must be broken down into its fundamental fluid drivers.

Bozkurt et al [83] also examined thermal osmosis for hydrophobic and hydrophilic material in a liquid water environment, as in other cases the thermal osmosis. The total water flow is replotted for the hydrophobic and hydrophilic material to where the trendline is not forced through the origin. By not forcing through the origin, it is assumed that not the measured fluid flow is from thermal osmosis. The linear trendline indicates that the transport properties are not changing with respect to the thermal gradient. The constant from the trendline fit confirms that other fluid drivers are present. The slope of the trendline is positive indicating that the temperature driven water flow moving with the thermal gradient. The constant from the trendline is sometimes positive and sometimes negative, in the cases the constant is positive the other fluid driver is working

with thermal osmosis and when the sign of the constant is negative the fluid driver is working against thermal osmosis.

The experimental data is fit to a linear trendline, the slope of the trendline is negative indicating that thermal osmosis is moving against the thermal gradient. In some cases, the constant from the trendline fit is the same sign of thermal osmosis indicates that the other fluid driver is moving in the same direction of thermal osmosis, if the constant is of the opposite sign of the slope, the fluid driver is opposing thermal osmosis. The slopes of the trendlines are used to compute the thermal osmosis transport coefficient. The calculated thermal osmosis transport coefficient for the hydrophobic case is shown in Figure 4.3.5:

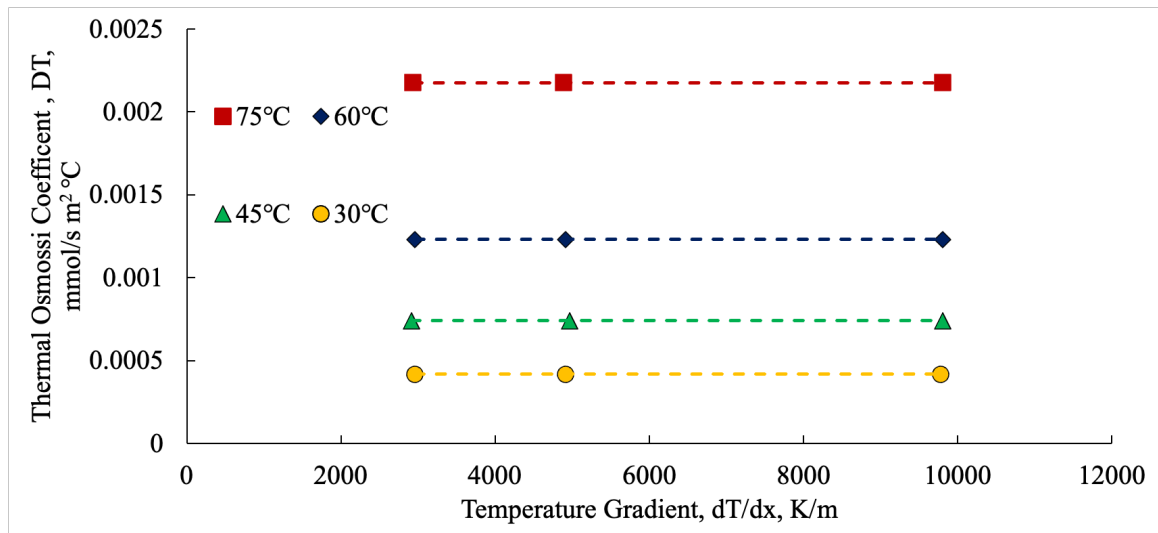


Figure 4.3.5 Hydrophobic Thermal Osmosis Transport Coefficient [83]

The thermal osmosis coefficient does not change with temperature difference. The same process is following for the hydrophilic case as shown in Figure 4.3.6 The thermal osmosis transfer coefficient is constant throughout the test conditions.

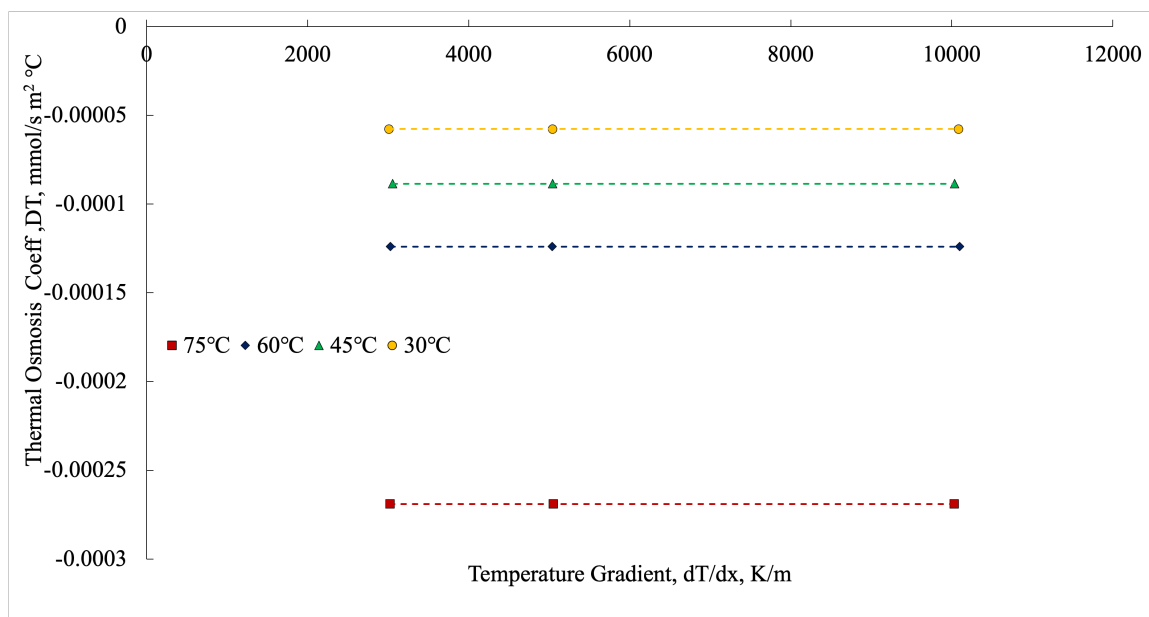


Figure 4.3.6 Hydrophilic Thermal Osmosis Transport Coefficient [83]

With the thermal osmosis coefficients known, the thermal osmosis portion of the water flow can be computed, and it can be extracted for the total water flow. The thermal osmosis portion of the total water flow for the hydrophobic case is shown in Figure 4.3.7:

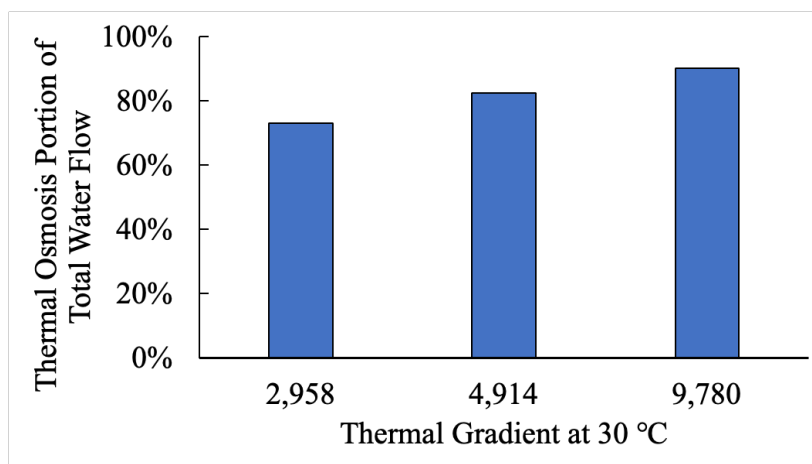


Figure 4.3.7 Hydrophobic Thermal Osmosis Portion of Total Water Flow [83]

The thermal osmosis portion of the total water flow ranges from 73% to 99%, and the other fluid driver contributes 1 to 27%. The other fluid driver contribution of the total water flow does continuously change. The same process is done on the hydrophilic thermal osmosis experiment, and the thermal osmosis portion of the water flow is shown in Figure 4.3.8:

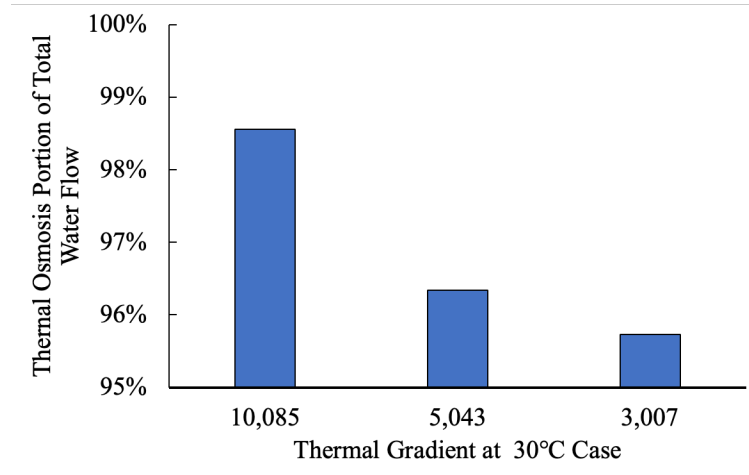


Figure 4.3.8 Hydrophilic Thermal Osmosis Portion of Total Water Flow

The impact of temperature on the thermal osmosis transport coefficient for the hydrophobic and hydrophilic cases was examined. The absolute value of the thermal osmosis coefficient was originally taken by Bozkurt et al [83] and both the hydrophobic and hydrophilic cases were treated the same. The thermal osmosis transport coefficient for the hydrophobic case is plotted against temperature as shown in Figure 4.157:

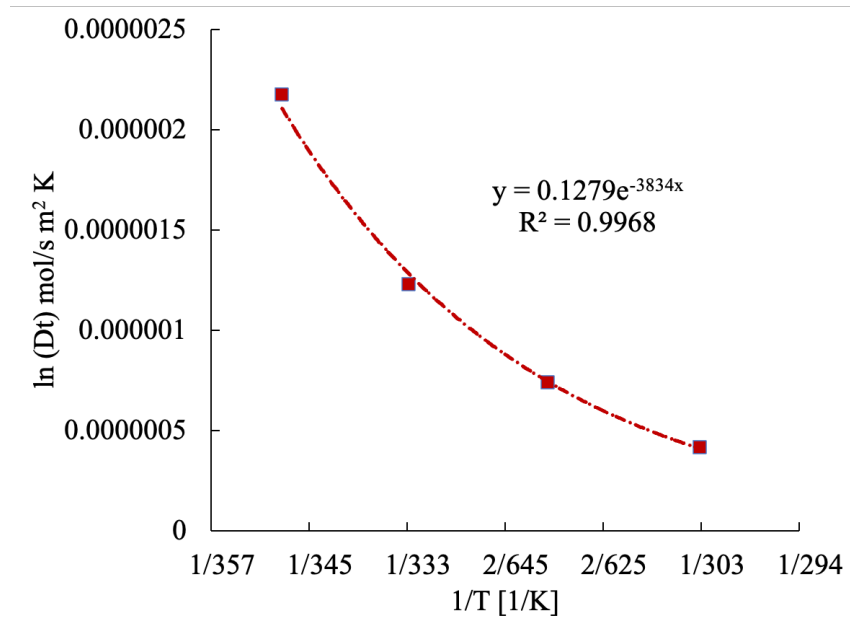


Figure 4.3.9 Thermal Osmosis Transport Coefficient variation with Temperature for Hydrophobic Scenario [83]

The experimental data fit to an exponential trendline which has occurred in all hydrophobic material. For the hydrophobic material energy is required for liquid water to move across the membrane, and this energy is the heat of vaporization. Liquid water can only pass through a hydrophobic membrane via membrane distillation. The same process is repeated for the hydrophilic case as shown in Figure 4.158:

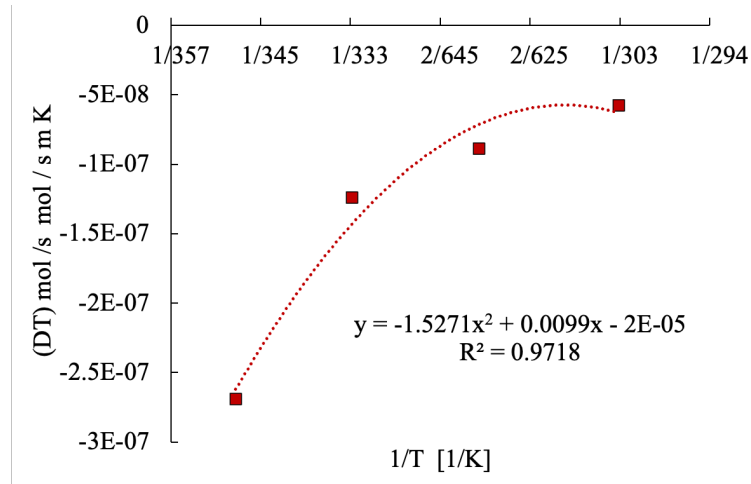


Figure 4.3.10 Thermal Osmosis Transport Coefficient variation with Temperature for Hydrophobic Scenario [83]

In the hydrophilic scenario, the exponential data fit was not obtainable due to the negative value, but the exponential fit was not obtainable with the negative value. Bozkurt et al [83] did also take the absolute value for the hydrophilic case but both the hydrophobic and hydrophilic cases are being treated the same way but have a different transport mechanism. For the hydrophobic case the thermal osmosis would be two-phase thermal osmosis where there is a phase change involved and then when the water vapor passes through the membrane it then condenses just like in membrane distillation. In the hydrophilic case, there is no phase change involved, and this thermal osmosis would be single phase. The transport mechanisms completely different which is why the thermal osmosis transport coefficients trends are different. Bozkurt et al [83] assumed that the total water flow was all thermal osmosis, instead of assuming other fluid drivers were present. The data was processed, and the thermal osmosis portion of the total water flow

was obtained along with the thermal osmosis transport coefficient. It is confirmed that other fluid drivers are present and the total water flow data did other fluid drivers present.

Tasaka et al [84] examined thermal osmosis with Nafion and different ions originally the data was shown with two data trendline, the first one with the trendline forced through the origin and the second one where the trendline was not forced through the origin. One note Tasaka et al [84] noted was thermal osmosis was not observed at a temperature difference even at 12K. The two data trendlines are examined individually. The case where the trendline is forced through the origin is examined first as shown in Figure 4.3.11:

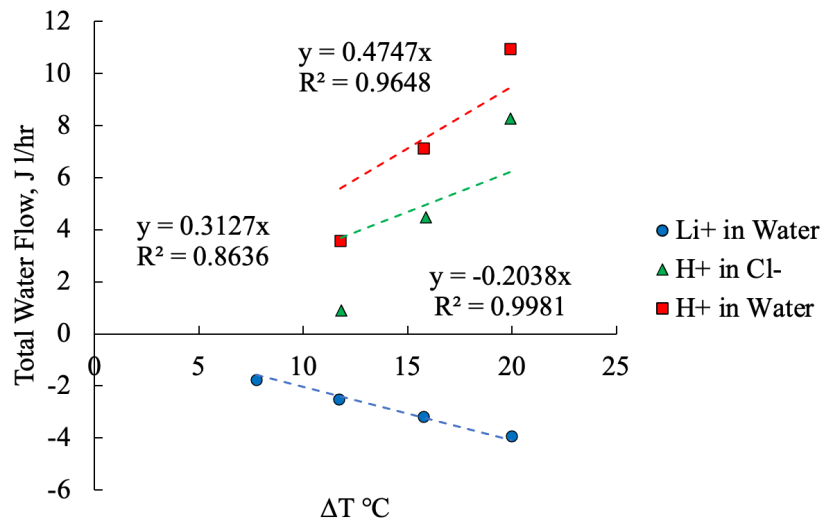


Figure 4.3.11 Thermal osmosis in Nafion with the trendline forced through the origin. [84]

The two hydrogen ion cases do not provide a good fit, but the lithium ion does provide a good fit, the thermal osmosis for the hydrogen ion scenario is going from cold to hot and the lithium ions is going from hot to cold. The current set up assumes that no other fluid

drivers are present and it does not resolve the statement no thermal osmosis has been below a 12K temperature difference. The second trendline is plotted where the trendline is not forced through the origin as shown in Figure 4.3.12:

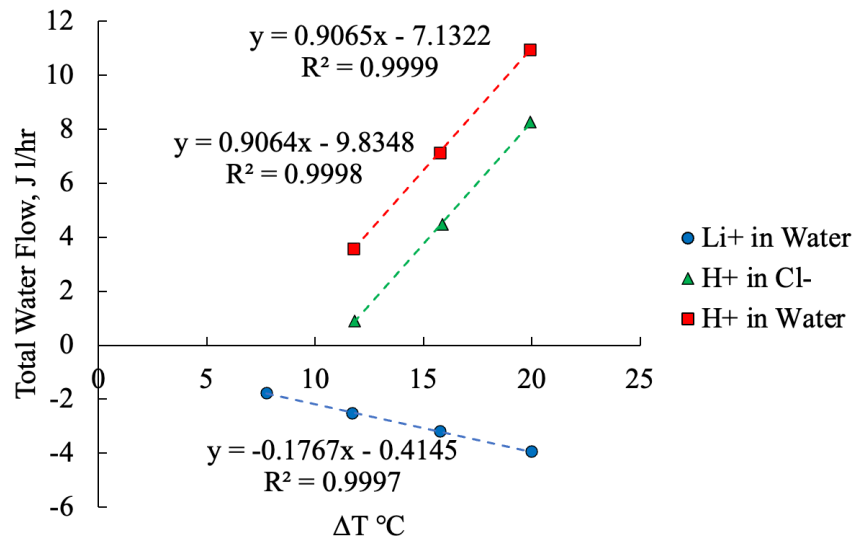


Figure 4.3.12 Thermal osmosis in Nafion with the trendline not forced through the origin. [84]

The same approach was taken with all three trendlines and it was found all results improved. The trendline fit is better fit compared to the first scenario. There is no change in the direction in thermal osmosis. In the hydrogen ion cases, the constant from the trendline is of the opposite sign of the slope, this indicates that there a point where the no flow is seen, the mass flux across the membrane is set to zero and the temperature difference where no flow will occur. The results are shown in Table 4.3-2:

Table 4.3-2 Determination of the No-Flow Point

	a_1	a_0	Zero Flow Portion Temperature Difference
Case	l/(hr. °C)	l/hr.	°C
Li ⁺	-0.4145	-0.1767	-2.3
H ⁺ /HCl	0.9064	-9.8348	10.9
H ⁺ /Water	0.9065	-7.1322	7.9

The no-flow point will occur at approximately 10.9 K, which is close to 12K. This confirms that thermal osmosis is continuous, there is just another fluid driver present, and it is working against thermal osmosis. This confirms that the total water flow cannot be forced through the origin. The total water flow is composed of thermal osmosis and another fluid driver. The slope of the trendline is taken to compute the thermal osmosis transport coefficient and with the transport coefficient known and the thermal gradient known the thermal osmosis portion is known. The thermal osmosis portion of the water flow is shown in Figure 4.3.13:

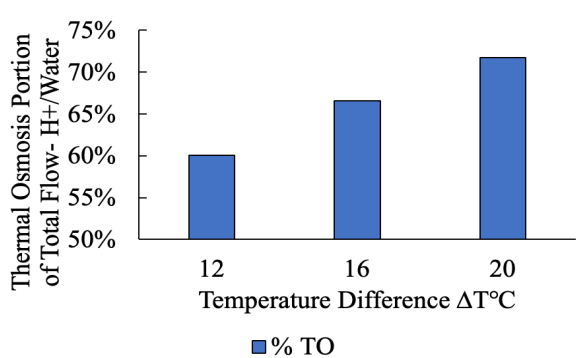


Figure 4.3.13 Thermal osmosis portion of total water flow. [84]

The thermal osmosis portion of the total water flow ranges from 52%-89%. The other fluid driver ranges from 11% to 48%. This shows that thermal osmosis is a portion of the total water flow. Like with total water flow, electro-osmotic drag, back diffusion and thermal osmosis experiments, a single fluid driver cannot be measured by itself. One of the critical errors made was forcing a linear trendline through the origin, this assumes that no-other fluid drivers are present and all the fluid flow comes from thermal osmosis. When the data was fitting to a new trendline that is not forced through the origin it assumed that other fluid drivers were present and it required the extraction of the thermal osmosis portion of the total water flow.

When the theoretical model and experimental data were used to determine the thermal osmosis coefficient at each data point. With the thermal osmosis coefficient determined free of other fluid drivers the contribution of thermal osmosis to the total water flow can be determine along with its direction. The type of trendline fit will determine how the thermal osmosis coefficient changes with the thermal gradient, in cases where there is a polynomial fit, the thermal osmosis coefficient will vary linearly with the thermal gradient. When a linear fit is used, the thermal osmosis coefficient will be constant and independent of the thermal gradient. In the thermal osmosis experiments with liquid, the thermal osmosis coefficient is constant because the membrane is considered saturated, when water vapor is present, the membrane properties will be changing, and its transport coefficient will depend on the hydration state of the membrane. In the cases of the hydrophobic membrane, liquid water will be transported in the direction based on the

vapor pressure difference, since the vapor pressure is a function of temperature the direction will be hot to cold when liquids are on both sides of the membrane. When liquid is on one side of the membrane, then the direction of flow will be from liquid to vapor. This process is membrane distillation.

In the case of a hydrophilic membrane the liquid water will be transported in the direction of cold to hot. The transport mechanism is not fully understood. It should be noted that the hydrophobic membrane will transport more liquid water than the hydrophilic showing that membrane distillation is stronger than thermal osmosis. When gases are present, membrane distillation will not occur, but thermal osmosis will. The proposed method of will calculate the thermal osmosis transport coefficient along with the thermal osmosis portion of the total flow fluid. The thermal osmosis fluid flow will confirm the magnitude and direction of the fluid flow.

5 Future Research

The first fundamental research is needed is the governing equation for fluid flow across the membrane, the Nernst- Planck equation is used but there are limitations on the equation such as it is an isothermal equation and it is applicable for liquids.

For cases of the total water flow in fuel cells and with electro-osmotic drag, a polynomial fit was required for fluid flow involving gases but when liquids were present a linear fit was applicable. The results do show the electro-osmotic drag coefficient is a function of current density and this relationship needs to be better understood.

The MPL in the fuel cell does impact electro-osmotic drag and back diffusion and the exact mechanism of membrane distillation needs to be incorporated into the water transport equations; this will help understand the MPL even more. Some approach for the fuel cell modeling consisted of using Non-Equilibrium Thermodynamics (NET) with this approach there is a consideration of a thermal gradient capable of driving fluid flow.

The proposed method for extracting the desired fluid drive like electro-osmotic drag, back diffusion and thermal osmosis will determine the transport coefficient at each data point, this would allow to see if the property is a function of either current density, concentration gradient, pressure gradient and/or thermal gradient or the transport property is a constant. The empirical models for determining electro-osmotic drag may have not properly extracted thermal osmosis from the total fluid flow as a result electro-osmotic

drag could be over or under reported with could lead to water management issues in the fuel cells.

When the electro-osmotic coefficient was isolated from the total flow it was noted that the electro-osmotic drag coefficient does change with current density for gases but when liquid is involved on the anode the electro-osmotic drag is constant and this ties to the governing equation used to model fluid flow across the membrane. When the membrane is exposed to gases the hydration state of the membrane properties change is a function of its hydration state but when the membrane is saturated the properties are constant.

There are two main classifications of membrane they are hydrophobic and hydrophilic, it and some of the membrane tested contained hydrophobic and hydrophilic regions, it is not clear which is dominant in instances of thermal osmosis single and two-phase (Membrane distillation) could be present. For instance, in Nafion becomes more hydrophilic as the membrane hydrates, this would result in fluid properties change with hydration state.

The Schroeder Paradox is phenomena where a membrane transport more liquid water compared to water vapor and the proposed solution is membrane distillation/osmotic distillation and a part of the electro-osmotic drag and diffusion models have membrane distillation lumped into either electro-osmotic drag or back diffusion, more information is needed to extract the membrane distillation component from electro-osmotic drag and

back diffusion such as known the vapor pressure difference and the mass transfer coefficient. Hydraulic permeation is showing liquids moves through membrane but if the membrane is hydrophobic membrane distillation will be the primary fluid driver and it will move the water through the membrane as a vapor not liquid, this changes how water is modelled and possibly eliminates the need for D'Arcy law which has been used in the fuel cell.

There are two types of thermal osmosis single and two-phase. The single phase will exist when gases are at two different temperatures, the material of the membrane may impact the direction but there will be no liquid water. The single-phase thermal osmosis would exist when the membrane is hydrophilic. The two-phase thermal osmosis would exist when liquid water is in contact with a hydrophobic material, these scenarios will need to be added to existing models for water transport. Osmotic distillation is a special case of membrane distillation; this will occur when liquid is on one side of the membrane

The phase of the fluid will impact electro-osmotic drag, back diffusion and thermal osmosis and possibility the equation used to model transport water. In instances where water vapor is present electro-osmotic drag coefficient is much lower compared to when liquid water is present. In instances with liquid water present, osmotic distillation and possibly membrane distillation will be lumped into electro-osmotic drag and or back diffusion. The diffusion constant is different for gases, liquids and solid, which could

invalidate some of the assumptions of the Nernst Planck equation and may require a new model to model fluid transport across the fuel cell.

The relationship between thermal osmosis transport coefficient needs to better be understood for hydrophobic and hydrophilic both were treated the same but when the absolute value removed there was different behavior. The first fundamental research is needed is the governing equation for fluid flow across the membrane, the Nernst- Planck equation is used but there are limitations on the equation such as it is an isothermal equation and it is applicable for liquids. For cases of the total water flow in fuel cells and with electro-osmotic drag, a polynomial fit was required for fluid flow involving gases but when liquids were present a linear fit was applicable.

The empirical models for determining electro-osmotic drag may have not properly extracted thermal osmosis from the total fluid flow as a result electro-osmotic drag could be over or under reported with could lead to water management issues in the fuel cells. When the electro-osmotic coefficient was isolated from the total flow it was noted that the electro-osmotic drag coefficient does change with current density for gases but when liquid is involved on the anode the electro-osmotic drag is constant and this ties to the governing equation used to model fluid flow across the membrane. When the membrane is exposed to gases the hydration state of the membrane properties change is a function of its hydration state but when the membrane is saturated the properties are constant.

The relationship between thermal osmosis transport coefficient needs to better be understood for hydrophobic and hydrophilic both were treated the same but when the absolute value removed there was different behavior.

6 Conclusion

When measuring the total water flow across porous media, it is in all cases a single measurement resulting from the summation of all the fluid drivers present, some better known, and some lesser. The objective of the current research is to use the total water flow data and to break it down into its fundamental components without assuming (usually without justification) negligibility of component drivers. The fundamental components consist of the voltage, concentration, thermal and pressure gradients.

Common in the available archival literature is the methodology of forcing data trendlines through the origin that implicitly neglects the possibility of other fluid drivers being present, even if minor. As shown in this research, when this is done it will either overstate or understate that driver and this will lead to lesser prediction of the total water flow, since these well-known and well-cited prior research efforts are the basis for fuel cell modeling.

Conventionally, transport coefficients have been assumed and then subtracted from the total flow to get the other. The reason this is not preferred is because of a great deal of scatter in the electro-osmotic drag, back diffusion and thermal osmosis transport coefficient empirical models, many of which were developed under specific conditions that may not apply to general fuel cell operation over the entire range. The other (even minor) fluid drivers can augment the measured fluid drivers in instances where the other fluid drivers are in the same direction. In cases where the other fluid drive is in the

opposing direction the measured fluid driver will be under stated. The water transport across the membrane will be greater than anticipated, which could result in flooding of the cathode.

The first step in the data analysis in the current research is to consider that other fluid drivers may be present and *not* force the trendline through the origin. In this way, the negligibility of other drivers can be quantified. By coupling the theoretical transport model with empirical data, the transport coefficients can be determined without making empirical model assumptions for any particular driver. With one of the components known from data mining, the other(s) can be determined. With all the components known the composition of the total water flow can be obtained. The fluid drivers can then be compared to one another.

One of the key observations in the data analysis was that there are two domains of thermal osmosis: single- and two-phase. In prior research a good data fit was not achievable for all data. It was observed that data trendlines are different for single- and two-phase data and because of incomplete data sets, conclusions could not be made. Additionally, the current research relied on non-linear data fits to identify minor drivers that come into play only under certain conditions. This approach is important because the membrane properties change with its hydration state. For instance, Nafion becomes more hydrophilic as it hydrates. In the case where the data set calls for a linear trendline, the derivative will be a constant and indicate that the transport property is a constant with

respect to the gradient, this being seen in some of the thermal osmosis experiments with liquids (for example Ren et al [61]).

In the single-phase region, the modes of water transport are electro-osmotic drag, back diffusion and single-phase thermal osmosis. In the two-phase region electro-osmotic drag, back diffusion, single-phase and two-phase thermal osmosis can occur. In addition, there is what has been termed the ‘Schroeder Paradox’ which states that more liquid water will be transported across certain membranes as compared to water vapor. This was termed a paradox because of a lack of explanation at the time, but the current research showed that Membrane Distillation and Osmotic Distillation only need two items: liquid water and a hydrophobic material. The membrane in the fuel cells contains hydrophobic regions while the Microporous Layer is hydrophobic. This is one of the reasons why the two-phase region has an additional fluid driver. Membrane Distillation/Osmotic Distillation also impacts the Microporous Layer (MPL). The MPL will only function when it is wet and it helps move water. When the MPL was added to the cathode when it was wet, it showed that the total water flow was in the direction of cathode to anode. The change in water transport shows an improved back diffusion. And it seems to mask electro-osmotic drag.

Since there is a thermal gradient across the membrane, thermal osmosis (single- and two-phase) will play a role in the water management. The single-phase stage takes place as vapor or liquid but there is no phase change involved. The two-phase thermal osmosis is

membrane distillation/osmotic distillation only when a hydrophobic membrane encounters liquid water. In many experiments, the data trendline was again forced through the origin neglecting other fluid drivers. In some of the prior research, thermal osmosis was only seen above certain temperature differences without an explanation. In the process they have created a contradiction where the trendline was forced through the origin which implies it to be continuous, and the data does not match. When the process proposed in this current work was applied to extract thermal osmosis from the total water flow, it was found that thermal osmosis was not the only fluid driver, and that other drivers were opposing it. The current proposed process can now confirm the direction of thermal osmosis as well as the magnitude, something that has been shown to be problematic (at best) in prior research efforts.

The phase of the water is very important to the fuel cell. When water vapor is present, electro-osmotic drag, back diffusion and single-phase thermal osmosis will be present, and when liquid water is present there will be another fluid driver and that is two-phase thermal osmosis (membrane distillation), this explaining why the data fits are so different in the single- and two-phase regions in prior research.

As far as modeling goes, the Nernst-Planck equation does not consider the impact of thermal osmosis or membrane distillation because it is an isothermal equation, and it was developed primarily for liquids. Overcoming these modeling limitations to better predict and control PEM fuel cells for optimal operation will be the focus of continued research.

REFERENCES

7 REFERENCES

- [1]. http://www.pfrang.de/pageID_2388563.html
- [2]. Fuel Cell Technology for Distribution Generation – An overview by Huang, Z
Zhang, J Jiang
- [3]. Fuel Cell Engine Matthew Mench
- [4]. O.S. Ijaodola, Z. El-Hassan, E. Ogungbemi, F.N. Khatib, T. Wilberforce, Energy
Efficiency Improvements by Investigating the Water Flooding Management on
Proton Exchange Membrane Fuel Cells (PEMFC), Energy 179(2019) 246-267
- [5]. A. Kusoglu and A Weber, New Insight into Perfluorinated Sulfonic Ionmers Chem
Rev 2017 987-1104
- [6]. Weber A.Z. and Newman J., Modeling Transport in Polymer Electrolyte Fuel Cells,
Chemical Review Volume 104 No 10
- [7]. Zawodzinski T.A. Gottsfeld S. The Contact Angle Between Water and Surface of
Perfluorosulphonic Acid Membranes, Journal of Applied Electrochemistry 23 1993-
Short Communication 21, Han 1992
- [8]. Temperature Regulation in a Evaporatively Cooled Proton Exchange Membrane Fuel
Cell Stack, R.H Thring, A Flu, Volume 40, Issue 35 Sept 21st 205 pg 11976-11982
- [9]. Effects of Microporous Layer in Polymer Electrolyte Fuel Cells, ECS 2005 A677-
688
- [10]. Y. Gandomi, M.D. Edundson, F.C. Busdy, M Mench, Water Management in
Polymer Electrolyte Fuel Cells through Asymmetric Thermal and Mass Transport

Engineering of the Microporous Layer (MPL) Journal of Electrochemical Society 163
8 F933-F944

- [11]. Zhou, J, Shukla, S., A Piutz, and Secanell M., Analysis of the Role of the Microporous Layer in Improving Polymer Electrolyte Fuel Cell Performance, *Electrochimica Acta* 366-382
- [12]. Sarker, M Rahman Md, Mojica, F., Mejrazi, S., Wilton, J M Kamp, K, Chung P., (2021) “Experimental and Computational Study of the Microporous Layer and Hydrophobic Treatment in the Gas Diffusion Layer of a Proton Exchange Membrane Fuel Cell”, *Journal of Power Source* 509 230350
- [13]. <https://web.stanford.edu/group/microfluidics/Projects/Archieve?EOPumpsWicks.html>
- [14]. Z. Abdin, CJ Webm E, MacA Gray, PEM Fuel Cell Models and Simulation in MATLAB -Simulink on Physical Parameters, *Energy* 116 (2016) 1131-1144
- [15]. T.E. Springer, T Zawodzinski, S Gottsfeld, Polymer Electrolyte Fuel Cell model, *Journal of Electrochemistry* 1991 138(8) 2334-42
- [16]. M Siemer, T Marquardt, G V Huerta, S Kabelac, Local Entropy Production Rates in a Polymer Electrolyte Membrane Fuel Cell, *J. Non-equilibrium Thermodynamics* 2017; 42(1) 1-30
- [17]. M Bhaiya, Master Thesis, An Open-Source Two-Phase Non-Isothermal Mathematical model of a Polymer Electrolyte Membrane Fuel Cell, Department of Mechanical Engineering, University of Alberta, 2014

- [18]. S. Motupally, A J Becker and JW Weider, Diffusion of Water in Nafion 115 Membranes, Journal of Electrochemical Society 147 (9) 3171-3177 2000
- [19]. S Kim and M. M. Mench, Investigation of temperature driven water transport in polymer electrolyte fuel cell: Thermal osmosis in membrane, Journal of membrane science 328 (113-120 2009)
- [20]. J. Newman, K.E. Thomas-Alyea, Electrochemical Systems, Third Editions
- [21]. Transport Phenomena, R Byron Bird, Warren E. Stewart, Edwin N. Lightfoot
- [22]. D.S. Falcao, V.B Oliveria, CM Rangel, C Pinho, AMFR Pinto, Water Transport through a PEM fuel cell: A one-dimensional model with heat transfer effects, Chemical Engineering Science 64 2009 2216-2225
- [23]. B.S. Pivovar, An Overview of electro-osmosis in fuel cell polymer electrolytes, Polymer 47 (2006) 4194-4202
- [24]. A Kusoglu, A Weber, New Insight into Perfluorinated Sulfonic Acid Ionmers, Chemical Review 2017 117, 987-1104
- [25]. Q. Yan, H. Toghiani, J. Wu, Investigation of Water Transport Through Membrane in a PEM Fuel Cell by Water Balance Experiments, Journals of Power Source 158, 2006 316-325
- [26]. A.Z. Weber, J Newman, Coupled Thermal and Water Management in Polymer Electrolyte Fuel Cells, Journal of Electrochemical Society 2016 153 (12) A2205-A2214

- [27]. R. S. Fu, J. Preston, U Pasogullari, T Shiomi, S. Miyazaki, Y Tabuchi, D Hussey, D Jacobson, Water Transport Across a Polymer Electrolyte Membrane under Thermal Gradient, *Journal of Electrochemical Society* 158 (3) B303 -B312 (2011)
- [28]. Chen, Lei, Chen, Y., Tao, W., (2023) “Schroeder’s Paradox in Proton Exchange Membrane Fuel Cells: A review”, *Renewable and Sustainable Energy Review*, 113050.
- [29]. Ryan O’Hare, Suk-Won Cha, Whitney Colella, Fritz Prinz Fuel Cell Fundamentals
- [30]. Principles of Fuel Cell Xianguo Li
- [31]. Y Cai, J Hu, H Ma, B Yi, H Zhang, Effect of Water Transport Properties on a PEM Fuel Cell Operating with Dry Hydrogen, *Electrochimica Acta* 51 2006 6361-6366
- [32]. T Nguyen, R White, A Water and Heat Management Model for Proton Exchange Membrane Fuel Cells, *Journal of Electrochem Society*, 140 No. 8, August 1993
- [33]. T.E Springer, A Zawodzinski Jr, and S Gottesfeld, Modeling of Batteries and Fuel cells, R.E. White and M. W. Verbrugge and J F Sockel Editors PV 91-10 p 209, The Electrical Chemical Society Softbound Proceeding Series Pennington NJ 1991
- [34]. V.M. Barragan, C Ruiz Bauza, J.P.G Villaluenga, B Seoane, Simultaneous Electroosmotic and Permeation Flows through a Nafion Membrane, 1. Aqueous electrolyte solutions, *Journal of Colloid and Interface Science*, 277 (204) 176-183
- [35]. K. Choi, D Peck, C Soo Kim, Shin, T. Lee, Water Transport in Polymer Membrane for PEMFC, *Journal of Power Sources* 86 (2000) 197-201

- [36]. T. Colinart, A Chenu, S Diderjean, O Lottin, S Besse, Experimental Study of Water Transport Coefficients in Proton Exchange Membrane Fuel Cells, *Journal of Power Sources* 190 (2009) 230-240
- [37]. Doctor of Philosophy, Proton Exchange Membrane Fuel Cells: Water Permeation Through Nafion Membranes, Makoto Adachi 2010 Simon Fraser University
- [38]. X. Ye. C.H. Wang, Measurement of Water Transport Properties through Membrane Electrode Assemblies, *Journal of Electrochemical Society* 154 B676 (2007)
- [39]. H Ito, T Ishikawa, H Ishida, S Someya, T Munkata, Measurement of Net Water Day Coefficient in Polymer Electrolyte Fuel Cells under Cathode- Dry Conditions, *Journal of Electrochemical Society* 166 (15) F1117-F1127 (2019)
- [40]. N. Ge. R. Banerjee, D Muirhead, J Lee, H Liu, P Shrestha, A.K.C. Wong, J Jankovic, M. Tam, D Susac, J Stumper and A Bazylak, Membrane dehydration with increasing current density at high inlet gas relative humidity in polymer electrolyte membrane fuel cells, *Journal of Power Sources* 422 (2019) 163-174
- [41]. D Bezamalinovic, S Strahl, V Roda, A Husar, Water Transport Study in a high temperature proton exchange membrane fuel cell stack, *International Journal of Hydrogen Energy* 39 2014 10627-10640
- [42]. S. Reid, Water Transport in Polymer Electrolyte Fuel Cells: An Exploration of Net Water Drag in Real Time, University of Tennessee Master Thesis 2013
- [43]. K Aotani, S Miyazaki, N Kubo, M Katsuta, An Analysis of the Water Transport Properties of Polymer Electrolyte Membrane, *ECS Transaction* 16(2) 341-352 (2008)

- [44]. Ahmet Kusoglu, and Adam Weber, New Insight into Perfluorinated Sulfonic Ionmers, Chem Rev 2017 987- 1104
- [45]. Fuller, T.F Newman, J. Experimental Determination of the Transport Number of Water in Nafion 117 Membrane. J Electrochem Soc 1992, 139(5),1332-1337
- [46]. Ye, X H Wang, C.Y. Measurement of Water Transport Properties through Membrane-Electrode Assemblies. J. Electrochem Soc 2007,154(7) B676-B682
- [47]. Zawodzinski, T. A. Detouin, C Radzinski, S, Sherman, R.J; Smith, V T; Springer, T.E; Gottsfeld S. Water- Uptake by and Transport through Nafion® 117 Membranes. J. Electrochem Soc 1993,140(4) 1041-1047
- [48]. Ge, S. H. Yi, B.L. Ming, P.W. Experimental Determination of Electro-Osmotic Drag Coefficient in Nafion Membrane for Fuel Cells, J Electrochem Soc2006, 153(8) A1443-A1450
- [49]. Luo, Z. P., Change, Z.Y., Zhang Y X.Li J, Electro- Osmotic Drag Coefficient and Proton Conductivity in Nafion Membrane for PEMFC, Int J Hydrogen Energy 2010, 35 (7), 3120-3124
- [50]. Ise, M, Kreuger, K D Maier, J Electroosmotic Drag in Polymer Electrolyte Membranes: An Electrophoretic NMR Study, Solid State Ionics 1999,125 (104) 213-223
- [51]. Gong, X., Bandis, A, Tao, A Mersi, G; Wang, Y. Inglefield, PT, Jones, A A, Wen WY, Self-Diffusion of Water, Ethanol and Decafluoropentane in Perfluorosulfonate Ionmer by Pulse Field Gradient NMR Polymer 2001, 42 (15) 6485-6492
- [52]. Fuller T F PHD Dissertation, University of California: Berkley CA 1992

- [53]. Hallinan D T, De Angelis MG, Bachetti MG, Sarti GC, Elabd Y, A Non-Fickian Diffusion of Water in Nafion, *Macromolecules* 2010,43 (10),4667-4678
- [54]. Onishi L.M. Prausnitz, J. M. Newman J, Steady-State Diffusion Coefficients for Water in Nafion in the Absence of Inert Gas. *J Electrochem. Soc* 2012, 159 (6) B754-B760
- [55]. Zelsmann HR, Pineri M, Thomas M, Escoubes M, Water Self-Diffusion Coefficient Determination in an Ion Exchange Membrane by Optical Measurement, *J Appl Poly Sci* 1990, 41 (7-8) 1673-1684
- [56]. Ma Z. R., Jiang R. C. Myers, M.E. Thompson, E. L, Gittleman, J Mater C.S., NMR Studies of Proton Transport in Fuel Cell Membranes at Sub-Freezing Conditions., *Chem* 2011, 21 (25) 9302-9311
- [57]. Tsushima S, Teranishi K, Hirai S, Water Diffusion Measurement in Fuel Cell Spe Membrane by NMR, *Energy* 2005, 30(2-4) 235-245
- [58]. Zawodzinski T. A. Neeman M., Sillerud L.O., Gottesfield S., Determination of Water Diffusion Coefficients in Perfluorosulfonate Ionmeric Membranes, *J Phys Chem* 1991, 95 (15) 6040-6044
- [59]. Edmondson C.A. Fontanella JJ, Chung S. H, Greenbaum, S.G., Wnek, G.E. Complex Impedance Studies of S-Sebs Block Polymer Proton-Conducting Membranes, *Electrochem*, 2001, 46 (10-11) 1626-1628
- [60]. Ge S. H., Li X G, Yi B L, Hsing IM, Absorption, Desorption and Transport of Water in Polymer Electrolyte Membrane for Fuel Cell, *J Electrochem Soc* 2005, 152(6), A1149-A1157

- [61]. X. Ren, W Henderson, S Gottesfeld, Electro-Osmotic Drag of Water in Ionomeric Membranes: New Measurement Employing a Direct Methanol Fuel Cells, Journal of Electrochemical Society V144 No.9 Sept 1997
- [62]. P. M Bieshevel, L.E Dykstra Physics of Electrochemical Processes
- [63]. X Ren and S Gottesfeld, Journal of Electrochemical Society, 148(1) A87-A93 (2001)
- [64]. D. Lee, B Hwang, D Lim, H. Chung, S You, y Ku, K Park, Transport of Water Through Polymer Membrane in Proton Exchange Membrane Fuel Cells, Korean Chem Engineering Res Vol 57, No 3 June 2019
- [65]. A Husar, A Higier, H Liu, In Situ measurement of water transport due to different mechanisms in a proton exchange membrane fuel cell, Journal of Power Sources 183 (2008) 240-246
- [66]. Sarker, M., Rahman, Md., Mojica, F., Mejrazi, S., Wilton, J.M., Kamp, K., Chuang P., (2021) “Experimental and Computational Study of the Microporous Layer and Hydrophobic Treatment in the Gas Diffusion Layer of a Proton Exchange Membrane Fuel Cell”, Journal of Power Source 509 230350
- [67]. Zhou, J., Shukla, S., A Putz, M. Secanell, (2018) “Analysis of the role of the Microporous Layer in Improving Polymer Electrolyte Fuel Cell Performance”, Electrochimica Acta 366-382
- [68]. Kim, T., Lee S., Park H. (2010), “A Study of Water Transport as A Function of The Microporous Layer Arrangement”, International Journal of Hydrogen Energy 35 pp 8631-8643

- [69]. A Weber, J Newman, Effects of the Microporous Layer in Polymer Electrolyte Fuel Cells, *Journal of Electrochemical Society* 152 (4) A677-A688 (2005)
- [70]. Y. Gandomi, M. D Edmundson, F.C. Busby, M.M. Mench, Water Management in Polymer Electrolyte Fuel Cells through Asymmetric Thermal and Mass Transport Engineering of the Micro-Porous Layers, *Journal of Electrochemical Society* 163, (8) F933-F944 (2016)
- [71]. H Atiyeh, K Karan, B Peppley, A Phoenix, E Halliop, J Pharoah, Experimental Investigation of the role of the microporous layer on water transport and performance of a PEM fuel cell, *Journal of Power Sources* 170 (2007) 111-121
- [72]. T. C. Yau, M Cimenti, X Bi, J Stumper, Water Transport and Schroeder Paradox in fuel cell membrane electrode assembly, *Journal of Power Sources* 224 (2013) 285-289
- [73]. K Chadha, S Mertemianov, A Thomas, Estimation of the effective water diffusion coefficient in Nafion Membrane by water balance experiment, *Fuel Cells* 2021; 21 139-148
- [74]. Essalhi, M. Kiadeh, N.T., Garchia-Payo, M.C., Khayet, M. 10-Thermo-Osmosis, *Osmosis Engineering* 2021 p279-312, <https://www.sciencedirect.com/science/article/abs/pii/B9780128210161000012?via%3Dihub>)
- [75]. S. Kim, M.M. Mench, Investigation of Temperature-Driven Water Transport in Polymer Electrolyte Fuel Cells: Thermal Osmosis in Membranes, *Journal of Membrane Science* 328 (2009) 113-120

- [76]. S. Kim and M.M. Mench, Investigation of Temperature Driven Water Transport in Polymer Electrolyte Fuel Cells: Phase Change- Induced Flow. Journal of Electrochemical Society 156 (3) B353-B362 (2009)
- [77]. J.P.G Villaluenga, B. Seoane, V.M. Barragan, C Ruiz-Bauza, Thermo-osmosis of mixtures of water and methanol through a Nafion membrane, Journal of Membrane Science 274 (206) 116-122
- [78]. R. S. Fu, J. Preston, U Pasogullari, T Shiomi, S. Miyazaki, Y Tabuchi, D Hussey, D Jacobson, Water Transport Across a Polymer Electrolyte Membrane under Thermal Gradient, Journal of Electrochemical Society 158 (3) B303 -B312 (2011)
- [79]. S. Motupally, A J Becker and J W Weider, Diffusion of Water in Nafion 115 Membranes, Journal of Electrochemical Society 147 (9) 3171-3177 (2000)
- [80]. R. Zaffou, J.S. Yi, H.R. Kunz, J. M Fenton, Temperature-Driven Water Transport Through Membrane Electrode Assembly of Proton Exchange Membrane Fuel Cells, Electrochemical and Solid-State Letters 9 A418-A422 (2006)
- [81]. A. Thomas, G Maranzana, S Didierjean, J Dillet, O Lottin, Thermal Effects on Water Transport in Proton Exchange Membrane Fuel Cells, Fuel Cells, Fuel Cells 12,2012 No.2 212-224.
- [82]. S. Kjelstrup, Thermal osmosis and thermoelectric potential in polymer electrolyte fuel cell material
- [83]. K Bozkurt, L Akyalcin, S. Kjelstrup, The thermal diffusion coefficient of membrane electrode assemblies relevant to polymer electrolyte fuel cells, International Journal of Hydrogen Energy 48 (2023) 1501-1513

- [84]. M Tasaka, T Hirai, R Kiyono, Y Aki, Solvent Transport across cation-exchange membranes under a temperature difference and under an osmotic pressure difference, *Journal of Membrane Science* 71 (1992) 151-159
- [85]. M. Tasaka, T Mizuta, O Sekiguchi, Mass transfer through polymer membranes due to a temperature gradient, *Journal of Membrane Science* 54 (1990) 191-204
- [86]. L D'Ilario, M Canella, Psudothermoosmosis in a Composite Membrane System, *Polymer Journal*, Vol 9 No 3 pp253-260 (1977)
- [87]. M Tasaka, S Abe, S Sugigura, M Nagasawa, Thermoosmosis Through Charged Membranes, *Biophysical Chemistry* 6 (1977) 272-278
- [88]. M Tasaka, M Nagasawa, NonIsothermal Membrane Phenomena Through Charged Membrane, *Journal of Polymer Science Symposium No 49* 3142 (1975)
- [89]. J.I Mengual, F Garcia-Lopez, Thermoosmosis of Water, Methanol and Ethanol through Cellulose Acetate Membrane, *Journal of Colloid and Interface Science*, V125 (21) 1988 667-678
- [90]. N Pagliuca, D G Mita, F.S. Gaeta, Isothermal and Non-Isothermal Water Transport in Porous Membrane. I The Power Balance *Journal of Membrane Science* 14 (1983) 31-57
- [91]. R.P Rastogi, R L Blokhra, R.K Agarwal, Cross-phenomenological Coefficients Part 1 Study on Thermal Osmosis, *Transactions of the Faraday Society* 60 1964 1386-1390
- [92]. M Tasaka, K Kishi, and M Okita, *Journal of Membrane Science* 17 (1984) 149-160

- [93]. M Tasaka, H Futamura, The Effects of Temperature on Thermoosmosis, Journal of Membrane Science, 28 (1986) 183-190
- [94]. R. Kiyono, A Komoto, M Tasaka, T Yamaguchi, T Sata, Membrane Phenomena in Non-Isothermal System Part 2 Effects of Hydrophobicity of Ion-Exchange Groups, Bulletin of the Chemical Society of Japan 70 5/1997 1015-1020
- [95]. M Tasaka, T Mizuta, O Sekiguchi, Mass Transport Through Polymer Membrane Due to a Temperature Gradient, Journal of Membrane Science 54 (1990) 191-204
- [96]. R.P Rastogi, K Singh, Cross-phenomenological Coefficients, Part 5- Thermo-Osmosis of Liquid through Cellophane Membranes, Depart of Chemistry, University of Gorakpur, December 1965
- [97]. F. Bellucci, Temperature Polarization Effects in Thermo-Osmosis, Journal of Membrane Science ,9 (1981) 285-301
- [98]. M Tasaka, T Suzuki, R Kiyono, M Hamada, K Yoshie, Thermoosmosis and Transport Entropy of Water across Poly(4-vinylpyridine/styrene) and Poly (N-vinyl-2-methylimidazole/styrene) Type Membrane in Electrolyte Solutions, Journal Physical Chemistry 1996, 100 16361-16364
- [99]. M.S. Dariel, O Kedem, Thermoosmosis in Semipermeable Membrane, Chemistry Department, Nuclear Research Center, Negev Israel April 28, 1974
- [100]. F.S Gaeta, E Ascolese, U Benicenga, J.M Ortiz de Zarate, N Pagliuca, G Perna, S Rossi and D G Nita, Theories and Experiments on Nonisothermal Matter Transport in Porous Membranes, Journal of Physical Chemistry V96 No 15 1992

- [101]. H Voellmy, P Lauger, Berichte de Bunsen-Gesellschaft fur Physikalsche Chemie70
(2) 1966 165-170
- [102]. Z. Honda, H Komada, D Okamoto, M Kai, Thermoosmotic Behavior of Amino
Groups Containing Membranes in Aqueous Acetic Acid Solutions, Polymer Journal V
43 No 11 pp 771-777
- [103]. A.Z. Weber, J Newman, Coupled Thermal and Water Management in Polymer
Electrolyte Fuel Cells, Journal of Electrochemical Society 153(12) A2205-A2214 2006
- [104]. Y Demirel, Non-Equilibrium Thermodynamics -Transport and Rate Processes in
Physical and Biological Systems.
- [105]. Thermal Osmosis and Thermoelectric Potentials in Polymer Electrolyte Fuel Cell
Materials, Signe Kjelstrup and Tu Delft, D Bedeaux, K Glavatskiy, O Burheim, L
Akyalcin, P Zefaniya
- [106]. N. Ingarra, C.J Kobus, J Maisonneuve, A Method to Account for the Effects of
Electro-Osmotic Drag and Back Diffusion in PEM fuel cells, IMECE 2022
<https://doi.org/10.1115/IMECE2022-96013>
- [107]. K.J Huang, S.J Hwang and W.H Lai, The influence of humidification and
temperature difference between inlet gases on water transport through the membrane
of a proton exchange membrane fuel cell, Journal of Power Sources 2015 284 77-85
- [108]. S.R Bradean H. Haas, K. Eggen, C Richards and T Vrba, Stack Models and
Design for Improving Fuel Cell Startup from freezing temperature ECS Transactions
3(1) 1159-1168 (2006)
- [109]. M Perry, T Patterson, Start and operating of PEMFC stack under sub-freezing
conditions, ASME Fuel Cells 2007-25338 in Proceedings of 5th International

Conference on Fuel Cell Science Engineering and Technology, June 18-20, New York 2007

- [110]. Edmund J. F. Dickinson and Graham Smith, Modelling the Proton-Conductive Membrane in Practical Polymer Electrolyte Membrane Fuel Cell (PEMFC) Simulation: A Review, *Membranes* 2020, 10, 310, doi:10.3390/membranes10110310.
- [111]. Alireza Goshtasbi, A Mathematical Model toward Real-Time Monitoring of Automotive PEM Fuel Cells, *Journal of the Electrochemical Society* 2020 167 02 4518
- [112]. Wei Dai, Haijiang Wang, Ziao-Zi Yuan, Jonathan J. Martin, Daijun Yang, Jinli Qiao, Jianxin Ma, A Review on water balance in the membrane electrode assembly of the proton exchange membrane fuel cells, *International Journal of Hydrogen Energy* 34 2009 9461-9478
- [113]. V.M Barragan and S. Kjelstrup, Thermal Osmosis in Membrane Systems: A Review, *J Non-Equilibrium Thermodynamics* 2017, 42(3) 217-236
- [114]. Onset of Convection in Binary Gas Mixtures: Role of the Dufour Effect, *Physical Review A* Volume 45, Number 6 March 15, 1992, W. Hort, S.J. Linz, M Lucke
- [115]. COMSOL Batteries and Fuel Cell Module , User's Guide 5.4, <https://doc.comsol.com/5.4/doc/com.comsol.help.bfc/BatteriesAndFuelCellsModuleUsersGuide.pdf>

- [116]. N. Ingarra, C.J. Kobus, J Maisonneuve, A Method to Account for the Effects of Thermal Osmosis in PEM fuel Cells, ASME 2022 International Mechanical Engineering Congress and Exposition
- [117]. Electrochemical Systems, John S. Newman 2nd Edition
- [118]. Transport Phenomena, R Byron Bird, Warren E. Stewart, Edwin N. Lightfoot
- [119]. Onset of Convection in Binary Gas Mixtures: Role of the Dufour Effect, Physical Review A Volume 45, Number 6 March 15, 1992, W. Hort, S.J. Linz, M Lucke
- [120]. Numerical Investigation of heat and mass transfer in a Saturated Porous Cavity with Soret and Dufour Effects, KHALED ABDULHUSSEIN JEBEAR AL-FARHANY SCHOOL OF MECHANICAL, AEROSPACE AND CIVIL ENGINEERING
- [121]. Zawodzinski, T., Springer T., Davey J., Valerino J., Gottesfeld S. (1991) Water Transport Properties of Fuel Cell Ionmers, The Electrochemical Society Proceedings of the Symposium Oct 13-18, 1991, Phoenix AZ
- [122]. Ingarra, N., Kobus C.J, Maisonneuve, J, An Explanation for the Schroeder Paraodox in PEM Fuel Cells ASTFE 10th Thermal and Fluids Engineering Conference George Washington University
- [123]. R.A. Johnson, M.H. Nguyen, Understanding Membrane Distillation and Osmotic Distillation, 2017 Wiley and Sons
- [124]. Essalhi, M. and Kayet, M. *Fundamentals of Membrane Distillation*, Principles and Applications, Woodland Publishing Series in Energy, pp. 277-316 (2015).

- [125]. Ingarra, N., Kobus C.J, Maisonneuve, J, Separating the Effect of Thermal Osmosis in PEM fuel Cell Membrane Mixed Mode Dynamics ASTFE 8th Thermal and Fluids Engineering Conference University of Maryland
- [126]. Ingarra, N., Kobus C.J, Maisonneuve, J, On Single- and Two-Phase Thermal Osmosis in PEM Fuel Cell Membrane ASTFE 9th Thermal and Fluids Engineering Conference Oregon State University
- [127]. Alkhudhiri, A., Darwish, N., Hilai, N., (2012), Membrane Distillation: A Comprehensive Review, Desalination 287 pp2-18
- [128]. Ingarra, N., Kobus C.J, Maisonneuve, J, Understanding the Physics of the Microporous Layer (MPL) in PEM Fuel Cells ASTFE 10th Thermal and Fluids Engineering George Washington University
- [129]. Zawodzinski, T.A., Gottesfeld, S, The Contact Angle Between Water and the Surface of Perfluorosulphonic Acid Membranes, Journal of Applied Electrochemistry 23 1993-Short Communication 21, Jan 1992
- [130]. Weber A.Z. and Newman, J. Modeling Transport in Polymer Electrolyte Fuel Cells, Chemical Review Volume 104 Number 10
- [131]. T.A. Zawodzinski, T Springer, J Davy, J Valerio, S. Gottesfeld, Water Transport Properties of Fuel Cell Ionmers, The Electrochemical Society Proceedings of the symposium of Modeling Batteries and Fuel Cells, Oct 13-18, 1991
- [132]. Fundamental of Heat and Mass Transfer Sixth Edition
Incorpera/DeWitt/Bergman/Lavine

- [133]. Park T.H., Caton J.A. An Experimental Investigation of Electro-osmotic Drag Coefficients in Polymer Electrolyte Membrane Fuel Cell, International Journal of Hydrogen Energy 33 (2008) 7513-7520 doi:10.1016/j.ijhydene.2008.09.077
- [134]. S. Kim and M. M Mench, Temperature Gradient Induced Water Transport in Polymer Electrolyte Fuel Cell Membrane, ECS Transaction 13 (28) 10.1149/1.3055409
- [135]. N Ingarra, C. J Kobus, Using Three Variable State Equations to Gain Insight into PEM Fuel Cell Membrane Thermodynamics, ACS Omega Vol 10/Issue 30 Julu 2025

8 Appendix

The primary area of the total water flow research focused on decomposing the total water flow into its electro-osmotic drag and thermal osmosis components. During the data analysis some additional lessons were learned along the way. The lessons learned consisted of limitation on the Nernst-Planck equation, how the Microporous Layer (MPL) functions along with the analysis of thermal osmosis experiments data.

The Nernst-Planck equation was derived from the Stefan-Maxwell equation, and during the derivation process it was assumed that the system is isothermal and neglects any thermal effects. An additional assumption was made; the assumption was made that the solution must be an electrolyte. During the data analysis, it was noticed that there were cases where the total water flow did not follow a linear trendline. This was seen on several occasions, this was noticed when the PEM fuel cell tested was performed with water vapor, but in instances where liquid was on one side of the membrane. It is possible that the Nernst-Planck may not be applicable for the PEM fuel cells cases. There needs to be a reason to explain why there is non-linear behavior for the total water flow in the PEM fuel cell.

In addition, the Nernst-Planck equation, the addition of the MPL does change the behavior of the PEM fuel cell specifically when liquid water is present. When liquid water is present, water is transported back toward the anode and flooding in the cathode

is delayed. This additional mode of water transport is not covered in the Nernst-Planck equation it will be lumped in with back diffusion or electro-osmotic drag; it depends on where the liquid is on the fuel cell. In the case where liquid is on the anode like in a direct methanol fuel cell the direction of the water flow is in the direction of liquid to vapor. In the cases of the PEM fuel cell where liquid water is formed on the cathode and the MPL is present, liquid water will be transported from the cathode to the anode via membrane distillation.

8.1 Current Methods for Analyzing Flow through the Membrane (Nernst Planck)

The Nernst-Planck equation is analogous to the Navier-Stokes equation to the Bernoulli equation, the Navier-Stokes can be simplified to the Bernoulli which states Bernoulli can be derived from Navier-Stokes. The Nernst-Planck equation is derived from the Stefan-Maxwell equation. The Stefan-Maxwell equation is shown in equation 1.[104]

$$\rho_i \frac{\partial v_i}{\partial t} = \rho_i \{v_i \cdot \nabla v_i\} - c_i \nabla T \mu - c_i \nabla P + \rho F - cRT \sum_{j=1}^n \frac{x_i x_j}{D_{ij}} \left(\frac{D_{T,i}}{\rho_i} - \frac{D_{T,j}}{\rho_j} \right) \nabla \ln(T) + \nabla \cdot [2\eta S + \phi(\nabla \cdot v)I] + \frac{cRT}{D_{ij}} \sum_{j=1}^n \frac{x_i x_j}{D_{ij}} (v_j - v_i) \quad (1)$$

The Stefan-Maxwell equation in its original form is applicable to dense gases and liquids. Simplifications are made such as isothermal conditions, constant pressure, and the fluid is a liquid. Additional assumptions are electroneutrality and the addition of forces from an electric field and an activity coefficient of one then the Nernst-Planck equation from

equation 17 and 18 are obtained. [104] It is believed that the Nernst-Planck equation usage is applicable for liquids only. COMSOL has noted “The mass transport of the charge carriers in aqueous systems is normally given by the Nernst-Planck equation” these equations neglect ion-ion interactions, so they are only exact for infinitely dilute solutions.” [115]

“Note that the concentrated electrolyte systems such as those in many batteries use an extended concentration of species flux definition, based on the Maxwell -Stefan set of equations. This will result in a different set of equations to solve for, but the general principles and conclusions will be the same. “

Based on these cases Nernst-Planck would be applicable for liquid but limited to gases. In previous history the alkaline fuel cells contain a liquid electrolyte the PEM fuel cell does not have a liquid electrolyte. The restrictions are note on the NET equations are not know if they are only valid for liquids or vapors.

Ingarra et al [116] stated that the NET equation is not the same as the Nernst Planck equation, the Nernst-Planck equation does not consider the temperature effects likes thermal osmosis. The main fuel cell used before the Proton Exchange Membrane (PEM) was the Alkaline Fuel cell (AFC) this fuel cell did use potassium hydroxide (KOH) has its electrolyte and the Nernst -Planck equation would be applicable here, but the PEM has a solid membrane that required hydration. The Nernst Planck equation may be applicable

for the Alkaline Fuel cell, but it may not be applicable to the PEM fuel cell because of the solid membrane and the presence of water vapor.

8.2 Diffusion Differences between gases and liquid and solids

The PEM fuel cell operates with humidified hydrogen and humidified air, and the membrane is the electrolyte. In the AFC, the electrolyte is liquid potassium hydroxide (KOH), and the fuel cell is provided with hydrogen and oxygen. The diffusion through solids, liquid and gases is different.

Mench [3] had noted that ions are transported three ways, the first one is mass diffusion, the second term is convection, and the last term is migration and putting these terms together obtains the Nernst Planck equation. Mench [3] noted there are differences between solid polymer electrolytes like what is in the PEM fuel cell, the second is liquid electrolytes commonly used in alkaline fuel cells, molten carbon fuel cells and phosphoric acid fuel cells, and gas transport. In the solid polymer membrane, the membrane is composed of hydrophobic and hydrophilic regions, the hydrophobic regions are composed Polytetra-fluorocarbons), and the hydrophilic regions are composed of sulfonic acids groups. With this solid polymer electrolyte, the water content of the membrane will impact its ionic conductivity.

In low hydration states, proton (H^+) ions are dominated by vehicular mechanism or diffusion. In cases of high hydration, a proton hopping or Gotthuss method is used which

will result in a higher conductivity. The ionic conductivity of the membrane depends on the hydration state of the membrane and the temperature of the membrane.

For liquids the ionic conductivity depends on the ion concentration, ion mobility, temperature, ionic radii and ionic charge. The AFC is a fuel cell that uses a liquid electrolyte, and the PEM fuel cell and direct methanol fuel cell uses the membrane as the electrolyte

In cases of gas phase ion transport, diffusion is the dominant mechanism, pressure and temperature play a role. It is noted that the order of magnitude for diffusion coefficients in gases, liquids and solids are greatly different. Diffusions for gases is on the order of magnitude of $0.1 \text{ cm}^2/\text{s}$ and for liquid it is $10^{-5} \text{ cm}^2/\text{s}$, and for solid state diffusion the order of magnitude is $10^{-10} \text{ cm}^2/\text{s}$, and it is a strong function of temperature. Lastly the diffusion of gases in a solid polymer is around $10^{-8} \text{ cm}^2/\text{s}$, this difference in phases will greatly impact which mode of transport will dominate. The phase of water will clearly impact electro-osmotic drag as well as diffusion. The transport of the ions and water will be different for a PEM, AFC and DMFC and this must be taken into consideration, and all three fuel cells are modelled with the same Nernst-Planck and the validity of the equation need to be examined for each of the cases.

8.3 Water Scenarios

There are four scenarios for water transport on the fuel cell, the first one has water vapor on both sides of the membrane, the second case is where there is water vapor at the anode

and liquid water on the cathode, the third scenario is when liquid water at the anode and water vapor at the cathode, the last case is with liquid water on both sides on the membrane. The cathode of the fuel cell will be warmer than the anode. In the cases with liquid water on one side, the direction of the water flow will be from liquid to vapor. When water vapor is present everything will be in single phase. In the cases where liquid water is present, this will be a two-phase flow scenario. In the cases where liquid water is present, the Schroeder Paradox will come into play and additional water transport will come into play.

8.4 Schroeder Paradox

When comparing water transport in the PEM fuel cell membrane, it is expected that water vapor transport should be greater than liquid water transport and this is not the cases in the PEM fuel cell and hence the Schroeder Paradox comes into play. This phenomenon has not been fully understood. The Schroeder Paradox does not come into play with an AFC but does play a role in PEM fuel cells.

Chen et al [28] noted that the Schroeder Paradox refers to a Phenomena that polymers have a different maximum water uptake for liquid and saturated water vapor.

Attempts to explain the Schroeder Paradox through classic thermodynamics, since the membrane transports more liquid water vs water vapor violates the classical thermodynamic principles of thermodynamics. Another issue with confirming Schroeder

Paradox is the experimental error in the temperature and vapor pressure measurement. In some of the experiments their liquid was about 0.1°C cooler than the water vapor.

Zawodzinski et al [121] ran experiments to determine the absorption of water in Nafion as well as the diffusion coefficient and the ionic conductivity. They noted that “*The water content of the membrane equilibrated with water vapor is not the same as the water content with liquid water, has been observed for several polymers/solvent system.*” Zawodzinski et al [121] presented two theories. The first was that Schroeder had experimental difficulties such as temperature gradients from heat of sorption, and difficulty obtaining truly saturated water vapor. The second is that sorption from water vapor phase involves condensation of water on the strongly hydrophobic Teflon-like surface of the polymer. In the EOD experiments, the EOD transport coefficient was significantly higher when the membrane was in contact with liquid water.

Another experiment was performed at variable current density and temperatures by Ren et al. [61] on EOD with Nafion 117 with methanol and water where the anode side of the fuel cell was liquid while the cathode side was vapor. The direction of the water transport would be in the direction of the anode to cathode which would aid electro-osmotic drag. The EOD coefficients vs temperature is shown in Figure 8.4.1. In the direct methanol fuel cell liquid will be on the anode and water vapor is on the cathode. As the temperature increase the vapor pressure increases which will impact membrane distillation/osmotic distillation.

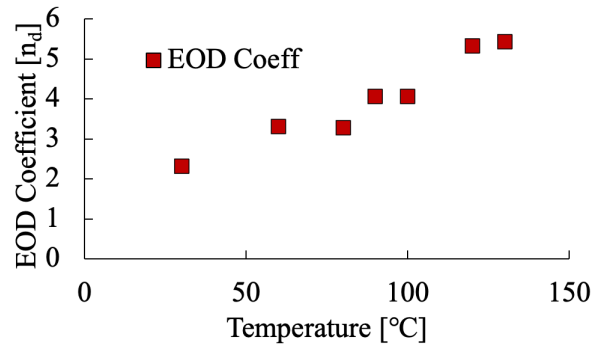


Figure 8.4.1 Electro-osmotic drag in liquid impacted by temperature [61]

Results show that as the temperature increased, the EOD coefficients also increase, this increase will lead to more water transport from the anode to cathode. Ge et al [48] also found that the EOD coefficient was independent of temperature when the membrane was exposed to water vapor, whereas in cases where the membrane was exposed to liquid water the EOD coefficient was dependent on temperature.

To understand the Schroeder paradox, Adachi [37] performed total water flow experiments on water in a fuel cell with liquid water on one side and water vapor on the other side, and with water vapor on both sides. The total water flow versus concentration gradient is shown in Figure 8.4.2 a, and the BD coefficient is shown in Figure 8.4.2b. The curve fit from Figure 8.4.2a is used to compute the back diffusion coefficient in Figure 8.4.2b. The data fit is not forced through the origin; this will account for other fluid drivers present.

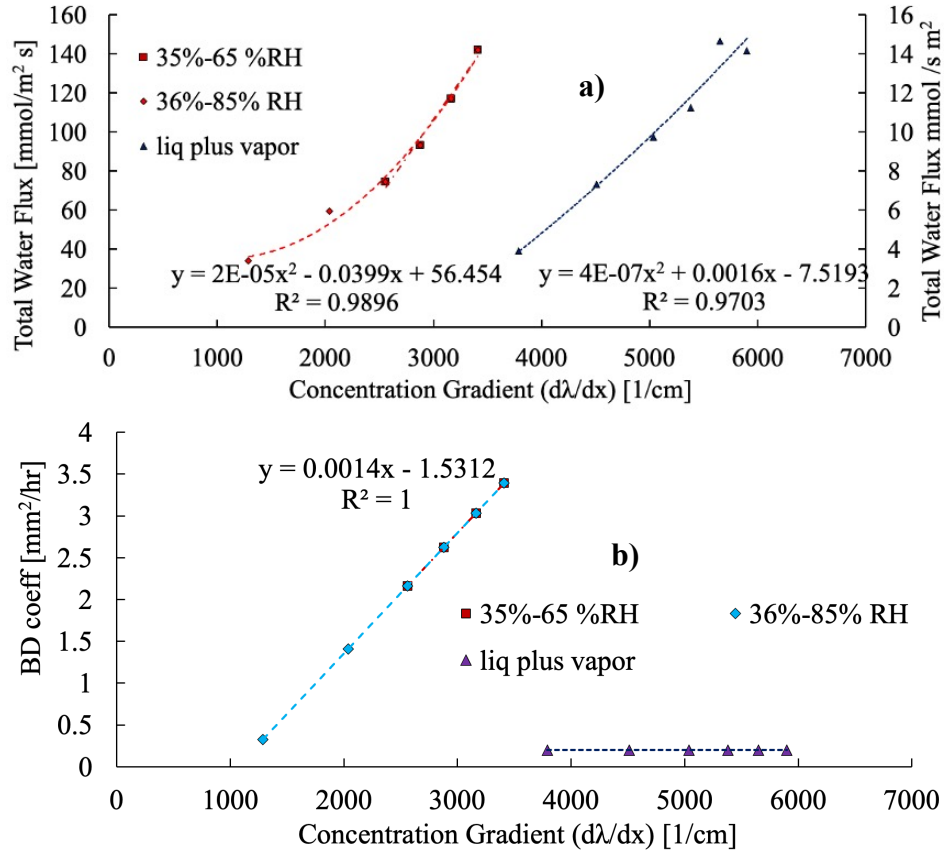


Figure 8.4.2 Total Water Flow Data in Single and Two Phase [37]

In the liquid water/water vapor cases, the total water flow was linear compared to the concentration gradient with a constant BD coefficient. In the case with water vapor on both sides, the behavior is linear only between 35%-65% RH and the computed back diffusion coefficient. Adachi [37] noted that the direction of water flow was from liquid water to water vapor. Also noted was that in the liquid to vapor case, the liquid water experienced an endothermic process from water vaporization. In the cases with vapor on both sides of the membrane, the back diffusion coefficient is changing with the concentration gradient and in the case where liquid water is on one side, the diffusion coefficient is constant.

Yan et al [25] also measured net water flow in a Nafion membrane. The experimental set up consisted of water vapor at the anode and liquid water at the cathode.

For some operating conditions, the total water flow across the membrane of the fuel cell is in the direction of the cathode to anode, while in others it is the opposite direction. In a total water flow experiment performed by Yau et al [72] a fuel cell was run at a constant cell temperature with a fully humidified anode and a variable cathode relative humidity. As the cathode humidity increased the total water was from anode to cathode and was decreased, and when the cathode entered the two-phase region the net water flow was only in the direction of cathode to anode as shown in Figure 8.4.3.

According to the Nernst-Planck equation, the only mode that can move the water from the cathode to the anode is BD. This will occur when the cathode has a higher concentration than the anode. Even with additional pressure on the anode, the water flow is still in the direction of cathode to anode, and the speculation was this was a result of the Schroeder Paradox [72]. It should also be noted that the shape of the curve's changes depending on the single-phase and two-phase region [72].

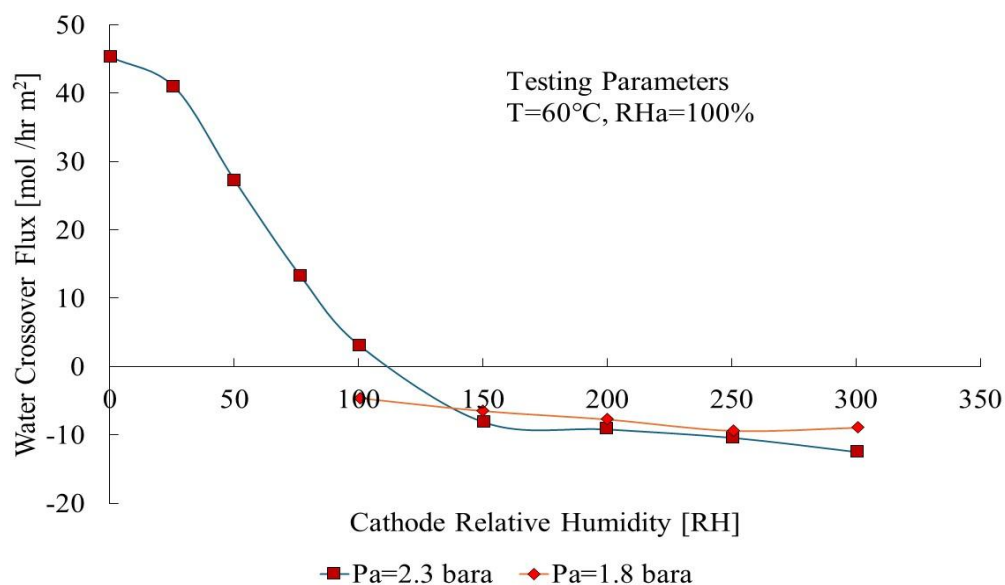


Figure 8.4.3 Total Water Flux at Different Pressures [72]

The total water flow direction was from the cathode to anode (in the direction of liquid water to water vapor). Ingarra et al [122] reviewed Schroeder Paradox and discovered that the Schroeder Paradox is a phenomenon called membrane distillation (MD) or osmotic distillation which is a special case of membrane distillation.

Membrane distillation and osmotic distillation are forms of fluid transport governed by the thermal gradient, in the case of thermal osmosis, it will occur when liquid water is on one side of the membrane and water vapor is on the other side. As a result of these thermal modes of fluid transport, thermal osmosis must be examined further. The experimental data needs to be replotted to where the total water flow is plotted against the concentration gradient and not the cathode relative humidity.

8.4.1 Thermal Osmosis

Thermal osmosis must be further analyzed since the Nernst-Planck equation neglects it. To add thermal osmosis to the Nernst Planck, the magnitude and direction of thermal osmosis needs to be understood, and the effect of the phase of the fluid also needs to be evaluated. During the analysis of thermal osmosis data, the thermal osmosis portion of the total water flow was not extracted which would result in a thermal osmosis coefficient that would have other fluid drivers in it. Tasaka et al [87] has examined thermal osmosis in an oxidized collodion and collodion -sulfonated polystyrene membrane in various concentrations of KCl solutions. The main goal was to understand the pressure driven flow as well as the thermal osmosis fluid flow.

Tasaka et al [87] proposed two methods for determination of thermal osmosis flow, the first one being a direct measurement and the second one an indirect measurement with two experiments, the first experiment consists of thermal hydrostatic pressure measurement and hydraulic permeation data. The combination of the two experiments will yield the thermal osmosis flux. Tasaka et al [87] also plotted the total water volume flux vs temperature gradient as shown in Figure 8.4.1.1 and Figure 8.4.1.2:

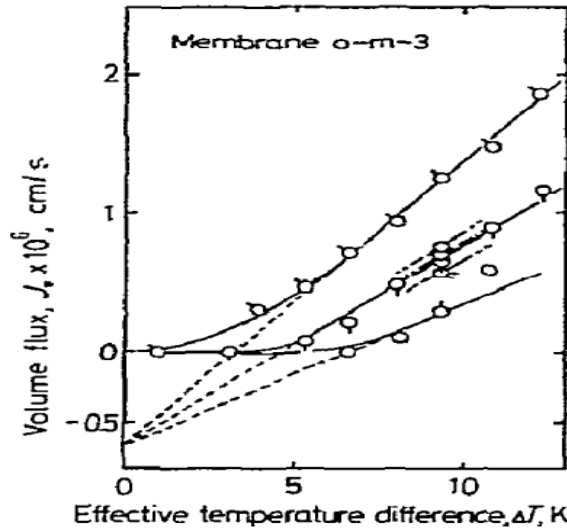


Figure 8.4.1.1 Thermal Osmosis Flux in o-m-3 [87]

There are two distinct trendlines, the first one going through the origin and the second that does not go through the origin, and it had a region of non-linearity. The slope of the trendline is used to compute the thermal osmosis coefficient and determine the direction of thermal osmosis. The positive slope will indicate a cold to hot direction because Tasaka et al [87] had assumed the direction of cold to hot is positive and a negative slope will indicate a hot to cold direction because a positive slope is cold to hot.

The trendline that is forced through the origin assumes the total water flow is all thermal osmosis and there are no other fluid drivers present. In the case where the total water flow is not forced through the origin it assumes that other fluid drivers are present. The total water flow will need to be broken down to determine how much of the fluid flow is thermal osmosis. It is not known which trendline is correct, the data must be analyzed to determine which trendline is correct. The total water flow data needs to be further

examined to determine which trendline is correct. Tasaka et al [87] stated that the direct method was the preferred method for determining the thermal osmosis flux.

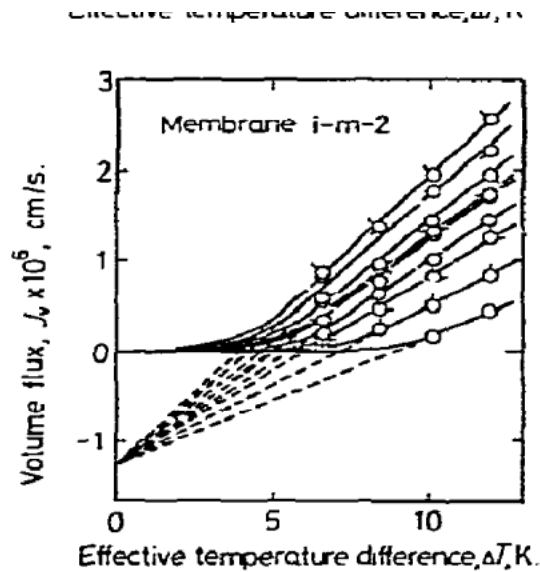
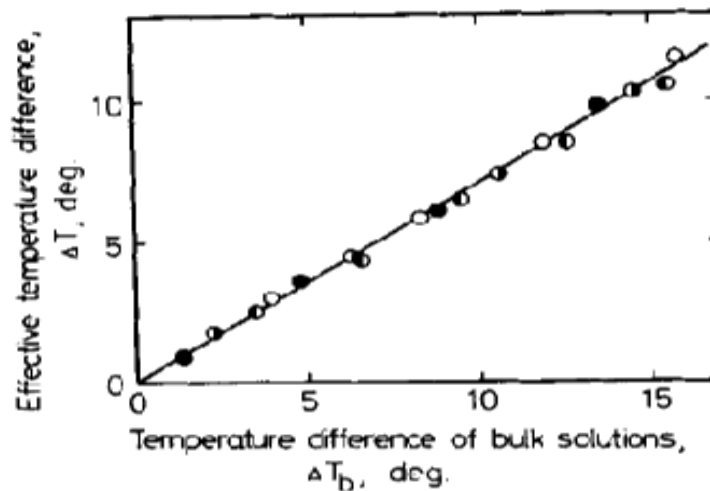


Figure 8.4.1.2 Thermal Osmosis Flux in o-m-3 [87]

It was noted that the thermal osmosis flux was in the direction of the hot side to cold side because of the positive slope of the trendline and the slope of the line was used but, in the Figure 8.4.1.1 and Figure 8.4.1.2 there are two trendlines, one that is forced through the origin and one where the flow was not forced through the origin, it is not known which one was used. Another note thermal osmosis flux was observed only above a finite temperature difference. The data must be further analyzed to determine which trendline is correct. Tasaka et al [88] noted that all graphs converge at a point below the origin, it was concluded that an unknown constant resistance such as a surface tension must be overcome. This data needs to be reprocessed to isolate thermal osmosis from the other unknown fluid driver. It should be noted this driver magnitude and direction must be

determined to know if it is in the same direction of thermal osmosis or opposing thermal osmosis. This is the main reason why the data needs to be reexamined.

Tasaka et al [88] explained thermal osmosis through non-equilibrium thermodynamics, there were two drivers examined, the voltage gradient and thermal gradient. The electrolyte concentration will impact the voltage gradient. Tasaka et al [88] has stated that the thermal membrane potential will impact thermal osmosis. The thermal membrane potential will have an impact effective temperature difference across the membrane as shown in 8.4.1.3:



8.4.1.3 Effective Temperature Difference [88]

The thermal membrane potential will cause a difference between the bulk fluid temperature and the actual temperature across the membrane. The thermal membrane potential varies linearly with the effective temperature difference when the electrolyte solution is not flowing. The membrane potential and thermal osmosis cannot be measured

at the same time a bulk fluid temperature difference is established under the same experimental conditions. Based on the experimental results the relationship between the temperature difference of the bulk solution is not the same as the effective temperature difference. The thermal osmosis experiment consisted of plotting the thermal osmosis flux vs the temperature gradient as shown in Figure 8.4.1.4:

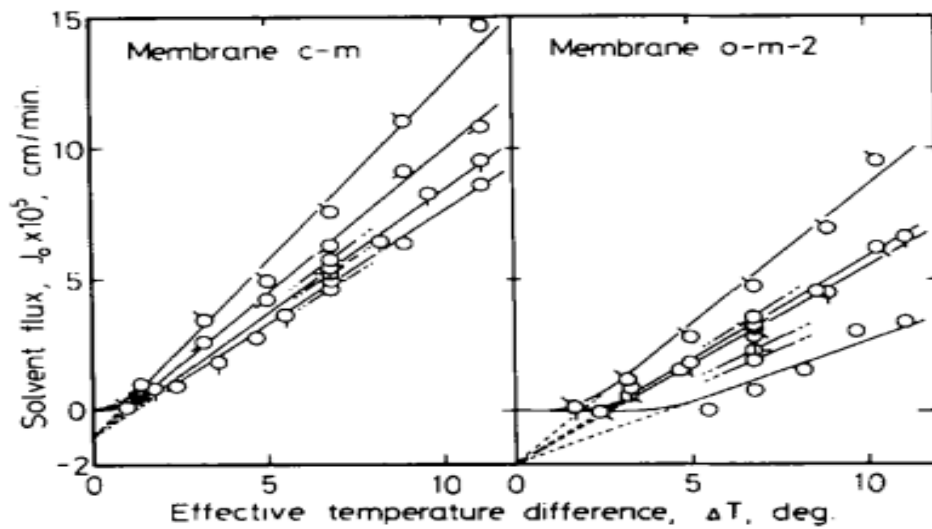


Figure 8.4.1.4 Thermal Osmosis Flux [88]

As in the other cases, there are two data trendlines shown, the first one is forced through the origin and the second trendline is not forced through the origin. In all the cases, the thermal osmosis flow was in the direction of cold to hot, this is determined by the positive slope of the trendline. As before there are two data trendlines, the first one is where the trendline is forced through the origin, the second one is where the flow is not forced through the origin, it is unclear which one was used in the analysis. Only one of the trendlines can be correct. The trendline through the origin assumes that all the total water flow is thermal osmosis, and the other trendline assumes that not all the fluid flow

comes from thermal osmosis. The thermal osmosis portion of the total water flow must be extracted and its contribution to the total water flow must be determined.

Mengual and Garcia-Lopez [89] performed thermal osmosis work with water, methanol and ethanol with a cellulose acetate membrane. There was a mention of thermal polarization effect, this polarization effect does not reflect the true temperature across the membrane. The thermal polarization is also seen in membrane distillation. The thermal osmosis data was reported in tabular form; the first thermal osmosis scenario was with liquid water with three different membranes as shown in Table 8.4-1:

Table 8.4-1 Thermal Osmosis Flux with Liquid Water [89]

Test of Eq. [4] for the Three Membranes and Water							
Membrane no.	t_1 (°C)	t_2 (°C)	t_3 (°C)	$10^6 \times J(T_1 \rightarrow T_2)$ (moles/sec)	$10^6 \times J(T_2 \rightarrow T_3)$ (moles/sec)	$10^6 \times J(T_1 \rightarrow T_3)$ (moles/sec)	$10^6 \times J(T_1 \rightarrow T_2) + J(T_2 \rightarrow T_3) $ (moles/sec)
1	30	35	40	0.30	0.38	0.69	0.68
	30	40	45	0.69	0.44	1.11	1.13
	30	45	50	1.11	0.54	1.68	1.65
	35	40	45	0.38	0.44	0.84	0.82
	35	45	50	0.84	0.54	1.40	1.38
	40	45	50	0.44	0.54	0.98	0.98
2	30	35	40	0.82	0.92	1.79	1.74
	30	40	45	1.79	1.02	2.81	2.81
	30	45	50	2.81	1.22	3.84	4.03
	35	40	45	0.92	1.02	1.91	1.94
	35	45	50	1.91	1.22	3.20	3.13
	40	45	50	1.02	1.22	2.49	2.24
3	30	35	40	1.09	1.28	2.23	2.37
	30	40	45	2.23	1.40	3.74	3.63
	30	45	50	3.74	2.11	5.63	5.85
	35	40	45	1.28	1.40	2.75	2.68
	35	45	50	2.75	2.11	4.86	4.86
	40	45	50	1.40	2.11	3.11	3.51

In all cases the total water flow was in the direction of hot to cold which was different from Tasaka et al [87],[88]. The results reported are the total water flow and not the thermal osmosis portion of the total water flow. The total water flow needs to be plotted to see the total water flow changes with the temperature difference. The thermal osmosis portion of the total water flow needs to be determined.

The model for thermal osmosis is a linear trendline. The direction will be determined based on the sign of the B term. The thermal osmosis coefficient was fit to linear equation as shown in equation 2.

$$J = B \frac{q}{d} \Delta T \quad (2)$$

It is unknown if other fluid drivers were present, and it is not known how these fluid drivers will impact thermal osmosis. The thermos-osmotic permeability was believed to be an Arrhenius style trendline as shown in equation 3.

$$B = B_o e^{(-\frac{E_T}{RT})} \quad (3)$$

The term thermal polarization was also introduced, and thermal polarization is the dissipation of externally applied temperature difference in unstirred liquid layers. The effect underestimates thermal osmosis. The membranes that were examined were

hydrophobic and the water flow was always in the direction of hot to cold. The thermal osmosis data needs to be examined to make sure only thermal osmosis fluid flow is extracted from the total water flow.

Paglicua et al [90] studied water transport through non-selective membrane, the research is aimed to compare water flux from hydraulic pressure to thermal osmotic flux. The goal was to determine transport coefficients such as hydraulic permeability, thermos-osmosis permeability, and activation energy. All experiments were conducted with liquid water. In all cases, the temperature driven water flow was in the direction of the hot side to cold side, in the isothermal cases the water flow was in the direction of higher to lower pressure. The first case examined was water flux with differential pressure and constant temperatures as shown in Figure 8.4.1.5:

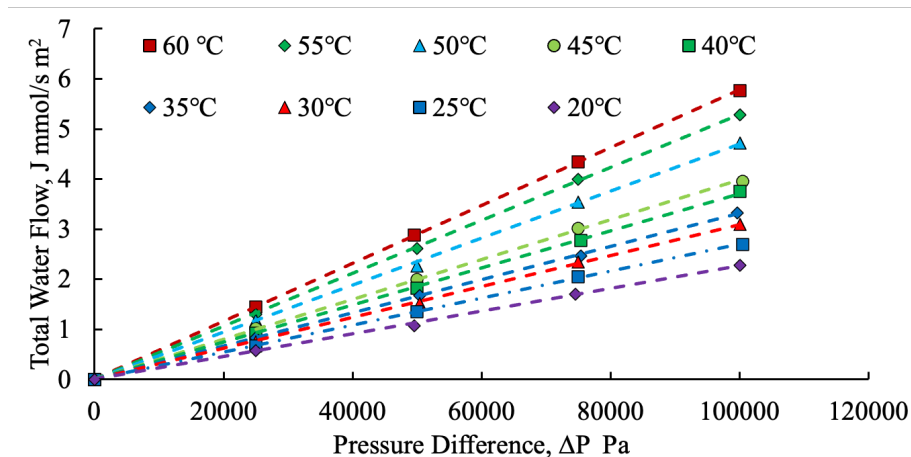


Figure 8.4.1.5 Pressure Driven Flow [90]

The total water flow was fitting to a linear trendline that is forced through the origin, which also assumes that no other fluid drivers are present, and all the fluid flow is from

the pressure. The pressure driven water flow was also forced through the origin assuming that no other fluid drivers were present. It is not known if other fluid drivers were present. It is also not known if the other fluid driver is a major fluid driver or if it is neglectable. The pressure driven flow was modelled with equation 4.

$$J_W = A_1 \Delta P \quad (4)$$

The total water flow needs to be examined, and the pressure component of the total water flow needs to be extracted from the total water flow. The transport coefficient is plotted against different temperatures like in an Arrhenius plot to obtain isothermal permeation about different temperatures as shown in Figure 8.4.1.6:

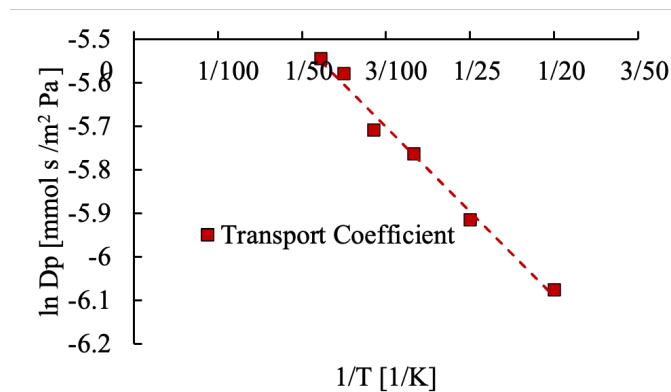


Figure 8.4.1.6 Determination of Activation Energy [89]

The pressure-based transport coefficient is changing with temperature indicating it is a function of temperature. The plot shown in Figure 8.4.1.6 was used to determine the

activation energy required. The slope of the line can be used to compute the activation energy by using equation 5.

$$\ln(A_T) = \ln(A_o) + \frac{-E_a}{RT} \quad (5)$$

A trendline is obtained such can be used to obtain the activation energy and the coefficients. Experimental data needs to be used to find the activation energy as well as the thermal osmosis coefficient. The next experiment considered temperature driven flow as shown in Figure 8.4.1.7:

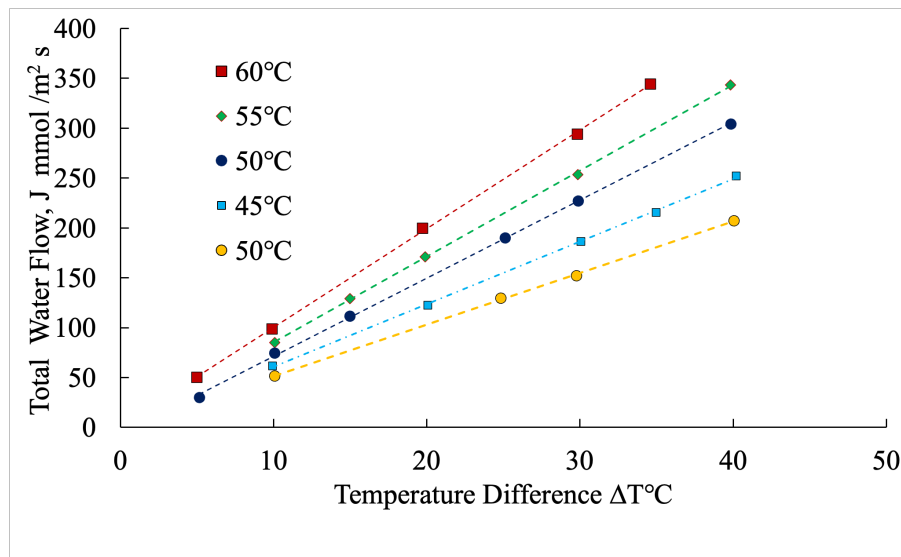


Figure 8.4.1.7 Thermal Osmosis Flow [90]

The total water flow was fitted to a linear trendline that is forced through the origin, this assumes that no other fluid drivers are present. The same process as in the pressure driven flow was repeated, the slope of the lines was used to determine the thermal osmosis transport coefficient at each temperature. The direction of the thermal osmosis fluid flow

is in the direction of hot to cold based on the slope of the trendline being positive. The thermal osmosis data must be reexamined to determine the contribution of thermal osmosis to the total water flow.

The formula for computing thermal osmosis is shown in equation 6. The trendline was also forced through the origin like in the pressure case, it is not known if other fluid drivers are present, this assumes that all the total water flow is thermal osmosis.

$$J_w = B_1 \Delta T \quad (6)$$

The Arrhenius behavior is assumed again, and the thermal osmosis coefficients are plotted against temperature as shown in Figure 8.4.1.7. There is also another term that is introduced, and the new term is a heat of transport Q^* , the heat of transport is related to the change in pressure with respect to temperature as shown in equation 7.

$$\frac{B_1}{A_1} = \frac{\Delta p}{\Delta T} = \frac{Q^*}{VT} \quad (7)$$

To understand thermal osmosis, the activation energy can be determined along with the heat of transport, these terms may help understand the direction of thermal osmosis.

The plot of the thermal osmosis transport coefficient is plotted over the inverse of the absolute temperature as shown in Figure 8.4.1.8:

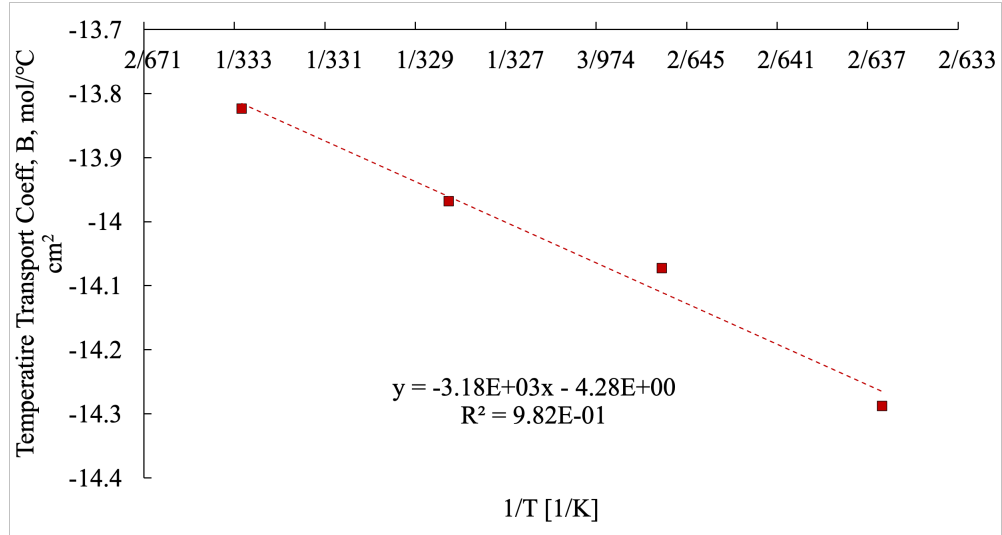


Figure 8.4.1.8 Determination of Activation Energy [89]

The heat of transport will influence the direction of thermal osmosis, if the heat of transport is positive energy is required, and if the heat of transport is negative energy will be released. The whole analysis of activation energy and thermal osmosis will need to be reexamined with the trendlines not forced through the origin to obtain the true thermal osmosis.

Rastogi et al [91] used non-equilibrium thermodynamics to understand thermal osmosis in porous media, they chose cellophane membrane. The non-equilibrium thermodynamics equation for water flux is shown in equation 8.

$$J_w = -L_{11} \frac{v}{T} \Delta P + L_{12} \frac{\Delta T}{T^2} \quad (8)$$

The total water flux is plotted against the temperature gradient, and it is shown in Figure 8.4.1.9. The total water flow data was fit to a linear trendline. The slope of the trendline will determine the direction of thermal osmosis.

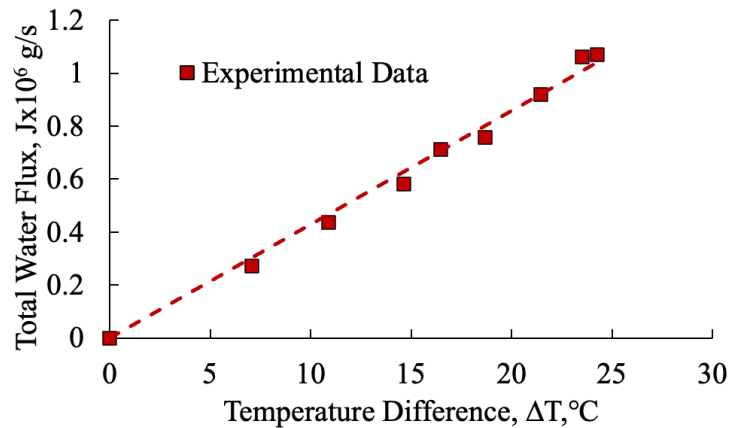


Figure 8.4.1.9 Thermal Osmosis Water Flux [91]

The total water flow data was fitting to a linear trendline that is forced through the origin, and this assumes that no other fluid drivers are present. This also assumes all measured fluid flow is from thermal osmosis. The slope of the trendline is used to compute the thermal osmosis coefficient and the positive slope is indicating that total water flow is in the direction of hot to cold.

As in the other cases, when the data trendline was forced through the origin, this assumes no other fluid drivers are present but equation 8 states there is a pressure and temperature gradient component. The data needs to be further examined to see if the other fluid drivers are substantial or neglectable. The total water flow needs to be broken down to obtain the thermal osmosis component of the total water flow.

Another factor that could influence thermal osmosis are the types of ions present. There are cation and anions, and some membranes are ion selective and other membrane are not. Tasaka et al [92] have also examined thermos-osmosis with anion-exchange membranes, as shown in Figure 8.4.1.10 and Figure 8.4.1.11:

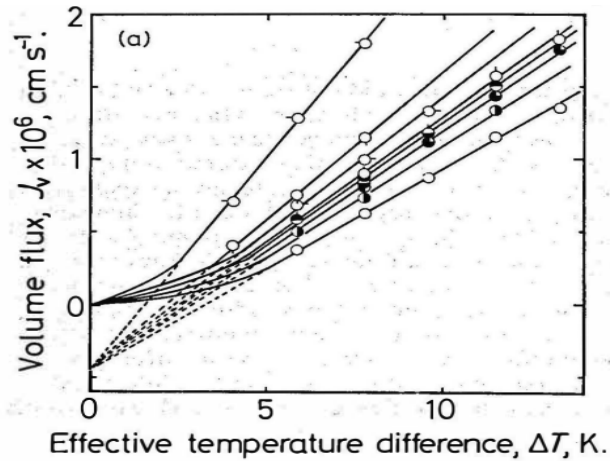


Figure 8.4.1.10 Thermal Osmosis Water Flux [92]

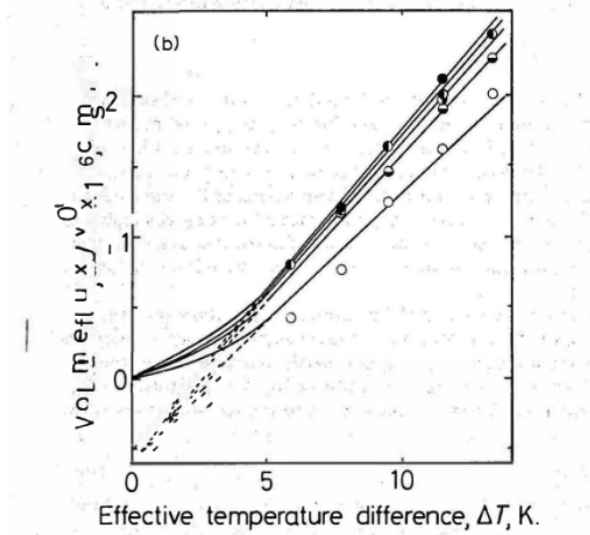


Figure 8.4.1.11 Thermal Osmosis Water Flux [92]

The total water flow data was fitting to two trendlines, the first data trendline is forced through the origin, and the second one is not forced through the origin. The positive slope indicates that the direction of thermal osmosis is cold to hot, and the slope of the trendline is used to compute the thermal osmosis. By forcing the trendline through the origin it assumes that all the fluid flow is thermal osmosis, in the case where the trendline is not forced through the origin other fluids drivers are present. It is not known if the other fluid driver is a major driver or if it is neglectable. For the thermal osmosis flux Tasaka et al [92] used equation 9.

$$J_w = -D\Delta T \quad (9)$$

It is assumed that Tasaka et al [92] forced the trendline data through the origin, this needs to be examined further to see if the assumption was valid. Tasaka et al [92] also noted that thermoosmosis was observed only about a finite temperature difference, it was theorized that an unknown contact resistance such as interfacial tension must be overcome for thermal osmosis to be observed therefore a temperature difference of 5K was needed to exceed the threshold. If this is true, then the data trendline cannot be forced through the origin because thermal osmosis would be continuous from no temperature difference to infinity, but thermal osmosis flow was seen above 5K this is contradicted by forcing the data trendline through the origin. Another explanation is that there are other fluid drivers present such as back diffusion or the osmotic flow; the question is how this will impact the true thermal osmosis. With the second trendline not

forced through the origin, the thermal osmosis portion of the total water flow needs to be examined, and the thermal osmosis portion of the total water flow needs to be obtained.

Kiyono et al [94] conducted thermal osmosis experiment with hydrophobic membranes, in their finding the flow decreased toward the hot side as alkyl groups were added making the membrane more hydrophobic. Transport energy and entropy were calculated based on experimental data. The total water flow through the membrane had two components, the pressure gradient and thermal gradient components as shown in equation 10:

$$-J_V = D^*[\Delta s T_m \ln(\Delta T) - v \Delta \pi] \quad (10)$$

It is believed that the entropy difference will change the sign of the thermal osmosis term. If the entropy change is positive the direction will be cold to hot, and if the entropy changes negative then the direction will be hot to cold. If no temperature difference is present, then equation 10 becomes equation 11.

$$-J_V = D^*[L_p \Delta \pi] \quad (11)$$

In the case where there is no osmotic pressure present then equation 10 simplifies to equation 12. The thermal osmosis fluid flow will follow the natural log of the temperature difference.

$$-J_v = D^e \ln (\Delta T) \quad (12)$$

Kiyono et al [94] has plotted the total water flow vs natural log of temperature difference as shown in Figure 8.4.1.12. The thermal osmosis portion of the total water flow was not extracted from the total water flow.

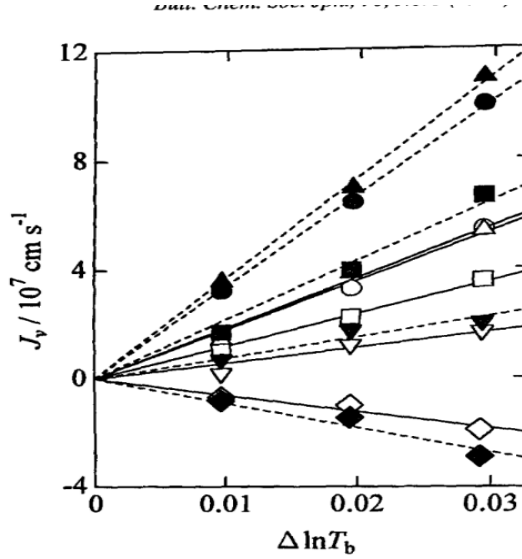


Figure 8.4.1.12 Thermal Osmosis Water Flux [94]

The data trendline is forced through the origin which provides two issues, the first one is the natural log of zero, and forcing through the origin assumes no other fluid drivers are present. The natural log of zero is negative infinity and the thermal osmosis coefficient would be infinite at this point, but the thermal osmosis flux could be zero at this point just by the temperature difference across the membrane.

The slope of the trendline is used to compute the thermal osmosis transport coefficient and the positive slope indicates the direction of the thermal osmosis is hot to cold and a

negative slope indicates the thermal osmosis flow is hot to cold. This case only shows one trendline and it is forced through the origin.

Kiyono et al [94] ran another thermal osmosis experiment with a different membrane material as shown in Figure 8.4.1.13, and as before the total water flow is forced through the origin which also causes the same two issues with the previous experiment.

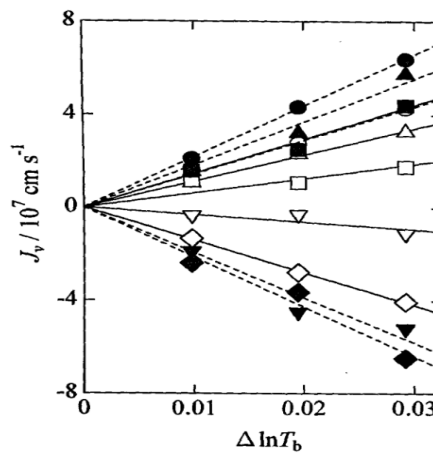


Figure 8.4.1.13 Thermal Osmosis Water Flux [94]

As in the other case, the data trendline is forced through the origin, this causes two issues, the first one is that the natural log of zero is negative infinity and the second issue is that the total water flow is equal to the thermal osmosis water flow. The total water flow trendline must not be forced through the origin to eliminate the natural log of zero, and this will account for other fluid drivers.

Kiyono et al [94] conducted two other experiments that were run with osmotic pressure difference as shown in Figure 8.4.1.14 and Figure 8.4.1.15. The osmotic pressure data

could have other fluid drivers with the data and the results that were reported were the total fluid flow across the membrane.

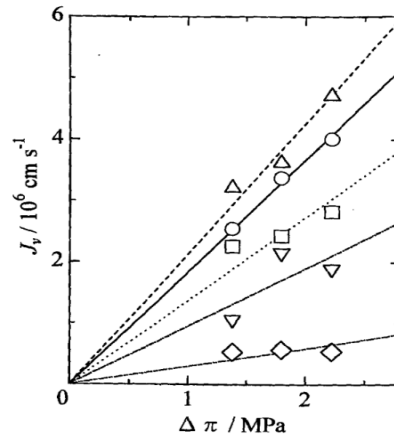


Figure 8.4.1.14 Osmotic Water Flux [94]

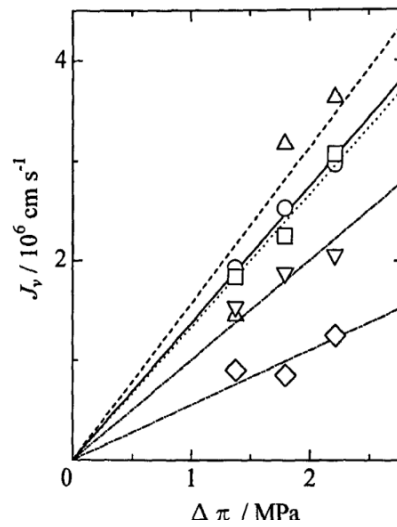


Figure 8.4.1.15 Osmotic Water Flux [94]

The data trendlines in all the cases were forced through the origin assuming no other fluid driver is present, and it also assumes all the fluid flow is from the osmotic pressure difference. All the osmotic pressure data trendlines are linear trendlines that are forced

through the origin. The use of the linear trendline fit for the osmotic pressure data needs to be examined further because the data looks non-linear.

As in the thermal osmosis cases, the total water flow in the osmotic flux was forced this origin and this assumes that no other fluid drivers are present. The current trendline assumes all the fluid flow is from osmotic pressure. The data must be reanalyzed to see if the other fluid driver plays a major role in the total water flow and this is done by breaking down the total water flow into its components and determining the strength of each fluid driver.

Tasaka et al [95] examined thermal osmosis for hydrophobic and hydrophilic material, their theory was for hydrophobic material that thermal osmosis flux will be in the direction of hot to cold and for cases of hydrophilic material the direction of thermal osmosis will be in the cold to hot direction. The theory was that the difference between the free fluid and the fluid in the membrane will dictate the direction of thermal osmosis. This is the main reason why hydrophobic membrane move fluid in the hot to cold and for hydrophilic material was moved from cold to hot. Tasaka et al [95] had also membrane distillation seen in porous poly(tetrafluoroethylene) membranes which is the same direction of normal distillation. The objective of the experiments is to validate the direction of thermal osmosis.

The thermal osmosis trendline data is forcing the trendlines to the origin, this assumes that no other fluid drivers are present, this assumes that thermal osmosis is continuous

from zero to infinity but Tasaka et al [95] had mentioned that thermal osmosis was seen above a finite temperature difference. The experimental data must be examined further where the data trendline is not forced through the origin, and total water flow must be broken down into its fundamental drivers to see if the other fluid driver is substantial or neglectable.

The second thermal osmosis experiment was conducted with a Neosepta membrane, the water flux across the membrane was plotted against the temperature difference of the bulk solution as shown in Figure 8.4.1.16:

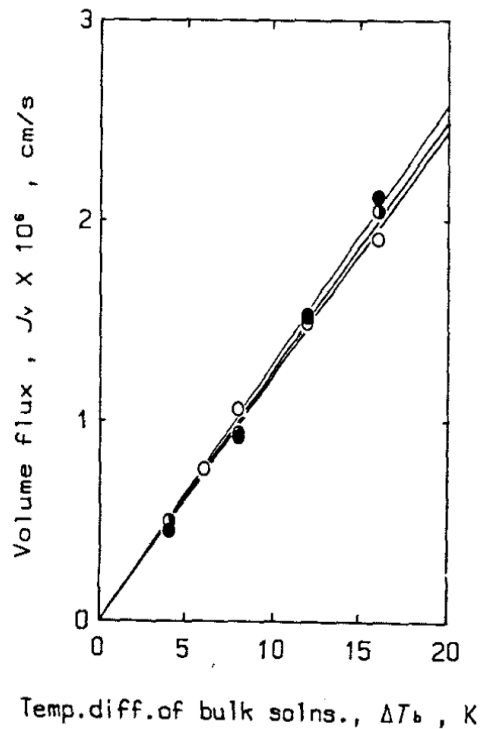


Figure 8.4.1.16 Thermal Osmosis Flux [95]

In the case of the thermal osmosis flow through the Neosepta membrane, the data trendline was only forced through the origin and there was not two trendlines. The slope of the trendline is used to compute the thermal osmosis transport coefficient and the direction of the thermal osmosis is cold to hot. By forcing the trendline through the origin it assumes that all the fluid flow is temperature driven flow. The total fluid flow needs to be further examined to see if the other fluid drivers are substantial or neglectable.

Tasaka et al [95] also conducted thermal osmosis experiments with Fluoropore as shown in Figure 8.4.1.17. As in the other cases the total water flow was reported and not just the thermal osmosis portion of the total water flow.

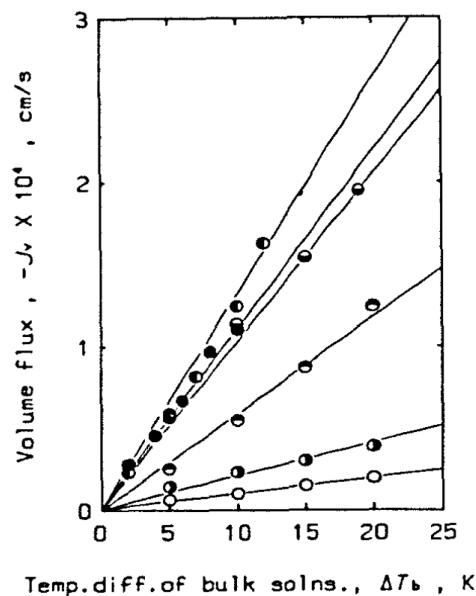


Figure 8.4.1.17 Thermal Osmosis Flux [95]

The total water flow trendline was also forced through the origin, assuming other no other fluid drivers are present. The slope of the trendline is used to compute the thermal

osmosis transport coefficient and the positive slope indicates that the direction of temperature driven flow was in the direction of cold to hot.

In the cases when the data trendline was only forced through the origin, it assumes all the fluid water is from thermal osmosis and no other fluid drivers are present. By not forcing the data trendline through the origin it will capture other fluid drivers present. There was not a scenario where the trendline was not forced through the origin. To better understand thermal osmosis, the total water flow needs to be broken down, and the thermal osmosis portion of the total water flow needs to be obtained. The other fluid drivers are unknown, so it is not known if they are neglectable or if they are major fluid drivers. Tasaka et al [95] also conducted thermal osmosis experiment with Fluoropore with different mean temperature as shown in Figure 8.4.1.18. The total water flow across the membrane was measured and reported. The total water flow data trendline was forced through the origin and this assumes no other fluid drivers are present and all the fluid flow was thermal osmosis. The magnitude and the direction of the other fluid driver are not known, and it must be determined to know if the assumptions made are valid. The thermal osmosis portion of the total water flow needs to be obtained also.

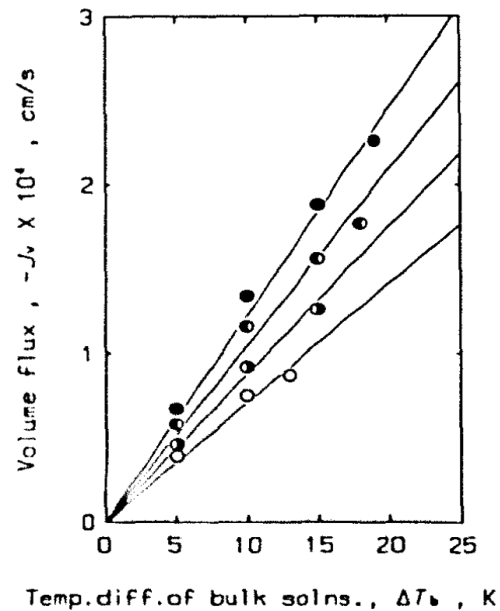


Figure 8.4.1.18 Thermal Osmosis Flux [95]

The total water flow was fitting to a linear trendline forced through the origin. The positive slope indicates that the direction of thermal osmosis is cold to hot, the slope is also used to compute the thermal osmosis transport coefficient. The data needs to be reevaluated, and the thermal osmosis portion of the total water flow needs to be examined to see if other fluid drivers are present and if they are substantial or neglectable.

Tasaka et al [95] also examined thermal osmosis with HiPore membrane as shown in Figure 8.4.1.19. As in the other cases, the total water flow was reported and not the just the thermal osmosis portion of the total water flow.

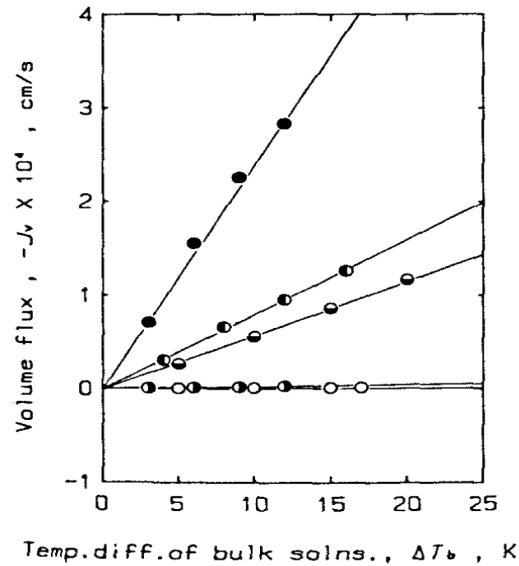


Figure 8.4.1.19 Thermal Osmosis Flux [95]

The slope of the trendline is used to compute the thermal osmosis coefficient, and the positive slope indicate the direction of the temperature driven flow is cold to hot. The thermal osmosis portion of the total water flow needs to be extracted from the total flow.

In the case the total fluid flow was forced through the origin, this assumes that all the fluid flow is from thermal osmosis and no other fluid drivers are present. It is not known if the other fluid drivers play a major role or if the fluid flow is neglectable. The total water flow data needs to be reexamined. Tasaka et al [87] to determine the thermal osmosis portion of the total water flow. Tasaka et al [95] ran thermal osmosis experiments with Yumicron membrane, as shown in Figure 8.4.1.20:

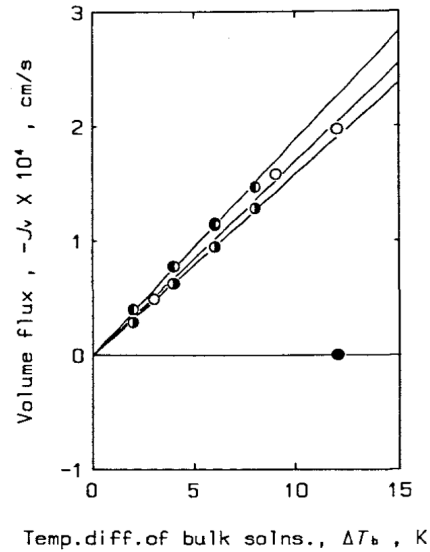


Figure 8.4.1.20 Thermal Osmosis Flux [95]

The total water flow across the membrane which consists of thermal osmosis and another fluid drivers. The slope of the trendline indicates the temperature driven flow is in the direction of cold to hot. As before the total water flow trendline data was forced through the origin, this assumes all the fluid flow is from the thermal osmosis and there could be other fluid drivers present, and it is not known if they are neglectable. The total water flow data needs to be broken down to determine how much of the total water flow originates from thermal osmosis.

Rastogi and Singh [96] examined thermoosmosis of methanol (CH_3OH) and water in a cellophane membrane. Their theory was only the pressure gradient and temperature gradient were the only fluid drivers as shown in equation 13.

$$J_{total} = L_{11} \left(\frac{-v\Delta P}{T} \right) + L_{12} \left(\frac{-\Delta T}{T^2} \right) \quad (13)$$

There is a relation between the transport coefficients, pressure, temperature and heat transport as shown in equation 14. The coefficient relationship can give us the heat of transport, and the heat of transport will influence the direction of thermal osmosis.

$$\left(\frac{\Delta P}{\Delta T} \right) = \frac{-L_{12}}{L_{11}vT} = -\frac{Q^*}{vT} \quad (14)$$

The change in the pressure with the respect temperature is related to the pressure and temperature coefficient and the heat of transport. The heat of transport could influence the direction of thermos-osmosis. The total water flux was plotted against the temperature difference as shown in Figure 8.4.1.21:

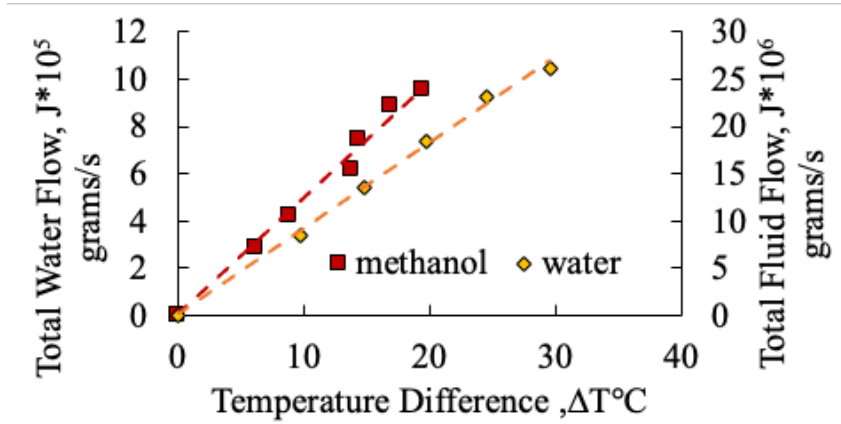


Figure 8.4.1.21 Thermal Osmosis Flux [96]

The trendline data was forced through the origin for the methanol and water.

The slope of the trendline is used to compute the thermal osmosis coefficient and the positive slope indicates the direction is hot to cold. By forcing the trendline through the origin it assumes that all the fluid flow is from thermal osmosis. The magnitude and direction of the other fluid driver is not known, and it must be determined along with the thermal osmosis portion of the total water flow.

The same experiment was done with a constant temperature and a variable pressure gradient across the membrane; the objective was to get the pressure and temperature transport coefficients to obtain the heat of transport as shown in equation 14.

The pressure driven flow flowed from a higher pressure to a lower pressure. The fluid transport data is shown in Figure 8.4.1.22:

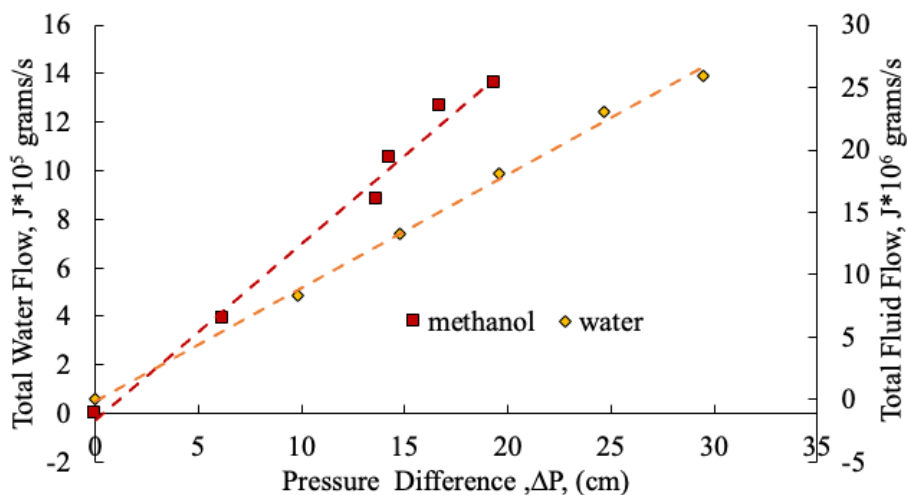


Figure 8.4.1.22 Pressure Driven Fluid Flux [96]

The pressure-driven water flow trendline was forced through the origin assuming no other fluid drivers were present. By forcing the data trendline through the origin it assumes no other fluid drivers are present and all the fluid flow is from the pressure gradient. The total water needs to be broken down into its fundamental fluid drivers. Rastogi and Singh [96] have noted that the heat of transport is a positive number, and this indicates energy is required to activate thermal osmosis.

Bellucci [97] has studied thermal osmosis in cellophane. The theory of thermos-polarization is introduced. Thermal polarization refers to the difference between the bulk temperature gradient and the actual temperature gradient across the membrane. In the bulk temperature difference includes the thermal boundary layer on both sides of the membrane and this reduces the effective temperature difference driving thermal osmosis.

The actual vs bulk temperature differences depend on the membrane thermal conductivity as well as the heat transfer coefficients. The water flux across the membrane is governed by the pressure thermal gradient as shown in equation 15.

$$J_W = A \frac{\Delta P}{\delta} + B \frac{\Delta T_m}{\delta} \quad (15)$$

When the pressure driven flow and temperature driven flow oppose one another there will be no fluid flow across the membrane. If the mass flux is set equal to zero and the pressure driven flow and temperature driven flow terms are set equal, a relationship

between the pressure term, thermal term and the transport coefficients can be obtained.

The relationship between the pressure term, temperature term and the transport coefficients are shown in equation 16.

$$\frac{\Delta P}{\Delta T} = -\frac{B}{A} = -\frac{Q}{vT} \quad (16)$$

By obtaining the transport coefficients, the heat of transport can be obtained. The heat of transport will influence the direction of thermal osmosis. It is good to understand if the value is positive or negative.

Bellucci [97] performed one experiment with a temperature difference, to understand thermal osmosis. The total water flow was reported, and the thermal osmosis portion of the total water flow was not isolated. The temperature driven fluid flow is plotted in Figure 8.4.1.23:

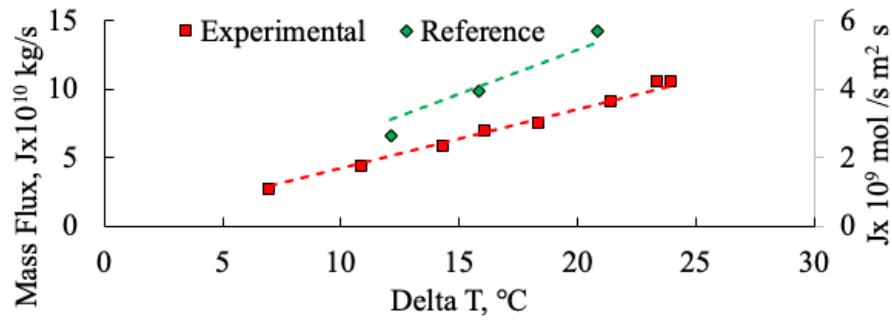


Figure 8.4.1.23 Temperature Driven Fluid Flux [97]

Like other researchers the data trendline was forced through the origin, this will neglect other fluid drivers that are present. By forcing the trendline through the origin it is assumed that all the fluid flow is from thermal osmosis. The total water flow needs to be reanalyzed by breaking down into its fundamental fluid drivers. One of the theories is that the heat of transport will influence the direction of thermal osmosis. The heat of transport is a function of temperature as shown in equation 17.

$$Q^* = Q_0^* e^{\left(\frac{-E_a}{RT}\right)} \quad (17)$$

Based on equation, the behavior of the heat of transport follows the Arrhenius behavior. To better understand heat of transport, additional experiments at different temperatures are needed.

Tasaka et al [98] theorized that thermal osmosis flux across the membrane is induced by a thermal gradient. The magnitude and direction of the thermo-osmosis depend on the membrane properties and the electrolyte. The entropy difference between the water inside the membrane and the free water will determine the direction. Thermal osmosis water flux can be expressed in terms on the temperature gradient as shown in equation 18.

$$-J_v = D^e \Delta(\ln T) = D \Delta T \quad (18)$$

The thermal osmosis transport coefficient can be expressed in terms of entropy difference as shown in equation 19.

$$D = D^*(\Delta s) \quad (19)$$

The flux of fluid from the pressure gradient is shown in equation 20.

$$-J_v = L_p \Delta \pi \quad (20)$$

Tasaka et al [98] coupled the pressure coefficient is coupled to the thermal osmosis coefficient as shown in equation 21.

$$L_p = -v_o D^* \quad (21)$$

The entropy difference can be coupled with pressure transport coefficient and the temperature transport coefficient as shown in equation 22.

$$\Delta s = \frac{v_o D}{L_p} \quad (22)$$

Tasaka et al [98] has noted that for hydrophobic material fluid flow is in the hot to cold direction just in distillation, this is due to the interface of water near the hydrophobic

structure. The water near the hydrophobic structure reassembles gas phase. There are indications of the phase change of water. There is no phase change around hydrophilic material. Water in the hydrophobic membrane is unstable, and the entropy difference is positive. In the case with a cation exchange membrane that thermal osmosis changes with the counter-ions. In the case of the anion-exchange membrane thermal osmosis appears from cold to hot.

Tasaka et al [98] stated that there are two fluid drivers for moving fluid, one of them is the through a temperature difference and the other fluid driver is the pressure gradient. To obtain the thermal osmosis transport coefficient, the temperature difference across the membrane is varied and the volume transport across the membrane is measured. To obtain the pressure driven flow, the temperature difference is fixed the pressure across the membrane is varied and the volume flux is measured. Tasaka et al [98] ran osmotic pressure experiments as well as thermal osmosis experiments. The First experiment was with SA-14 membrane. The thermal osmosis experiment was conducted with an SA-14 membrane, and the results are shown Figure 8.4.1.24. The total water flow was reported and not the thermal osmosis portion of the total water flow was not reported.

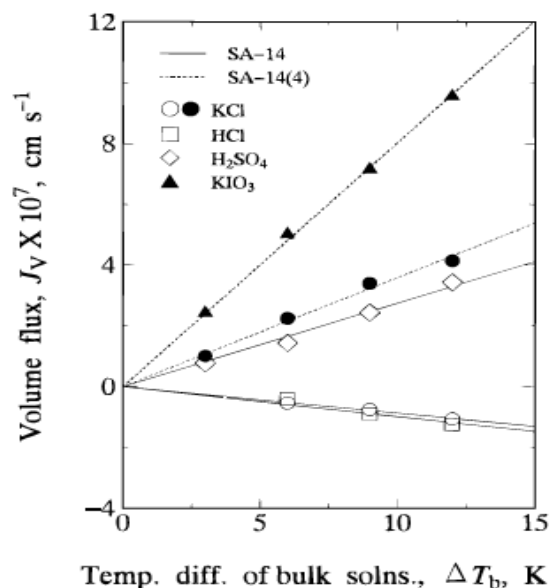


Figure 1. Dependence of thermoosmotic volume flux, J_v , on the temperature difference of bulk solutions, ΔT_b , for membrane SA-14 in KCl, HCl, and H₂SO₄ solutions and for membrane SA-14(4) in KCl and KIO₃ solutions.

Figure 8.4.1.24 Temperature Driven Fluid Flux [98]

The data is fit to a linear trend line, and it is forced through the origin. The positive slope denotes temperature driven flux in the cold to hot direction, and a negative flux is a temperature driven flux in the hot to cold direction. The data trendline was forced through the origin, this assumes that all the flow from the experiment was thermal osmosis. It is not known if the other fluid driver is substantial or neglectable, the total water needs to be broken down into its fundamental drivers, and these drivers must be assessed as either a major driver or minor driver. Tasaka et al [98] also ran an isothermal experiment with an osmotic pressure difference across the membrane, in this case the fluid flow across the membrane was measured against the pressure gradient as shown in Figure 8.4.1.25:

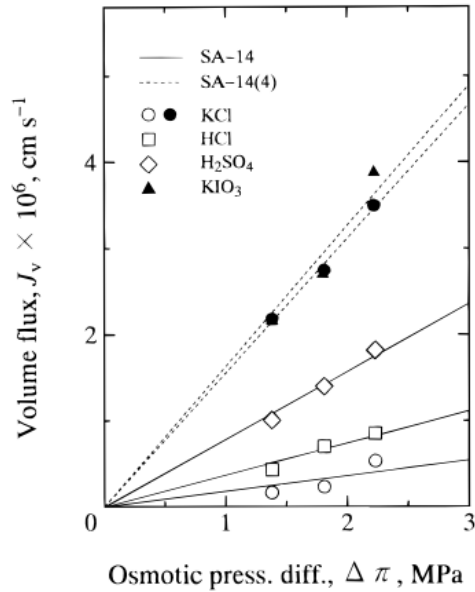


Figure 8.4.1.25 Pressure Driven Fluid Flux [98]

The positive slope of the line is indicating the direction flow is from a higher pressure to lower pressure. The pressure driven water flow trendline data is forced through the origin just like the thermal osmosis, this assumes no other fluid drivers are present, and all the fluid flow across the membrane is driven by the pressure gradient. It is not known if the other fluid drivers are major drivers or if they are neglectable. It is also not known if the osmotic drag flow should vary linearly with the pressure difference. Tasaka et al [98] performed thermal osmosis experiments with SA-15 membrane as shown in Figure 8.4.1.26:

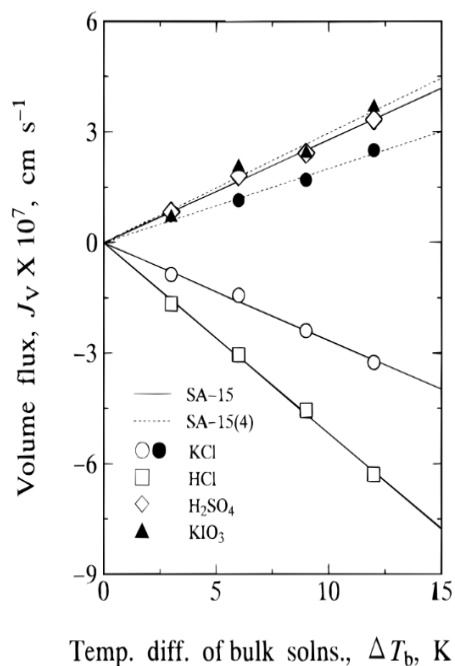


Figure 8.4.1.26 Temperature Driven Fluid Flux [98]

By forcing the trendline through the origin this assumes all the fluid flow is thermal osmosis and all the fluid flow is from thermal osmosis. The positive slope indicates the temperature driven flow is in the direction of cold to hot, and the negative slope is indicating the opposite. The total water flow needs to be analyzed to determine how much of the total water flow is thermal osmosis. Tasaka et al [98] also conducted an osmotic pressure experiment with SA-15 membrane as shown in Figure 8.4.1.27:

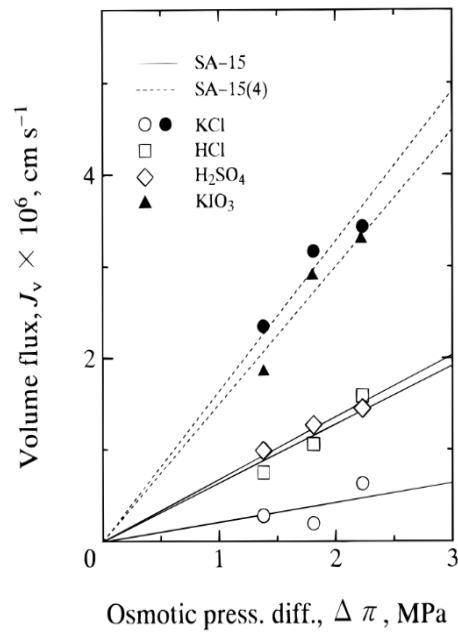


Figure 8.4.1.27 Pressure Driven Fluid Flux [98]

The total water flow trendline was fit to a linear trendline that is forced through the origin. The assumption being the current trendline is that all the total water flow is from osmotic pressure, there could other fluid drivers present. It is not known if the other fluid drivers are neglectable or if they are major contributors. The total water flow needs to be broken down its fundamental fluid drivers, and each fluid driver must be evaluated.

Daniel and Kedem [99] performed thermal osmosis experiments with semipermeable membranes, specifically measuring thermal osmotic flow with cellulose acetate membranes. Daniel and Kedem [99] reported that there are two drivers for the water flux, the first one is the thermal gradient and the second is the pressure gradient as shown in equation 23.

$$J_v = L_d[(\Delta p - \Delta \pi) + \frac{Q^*}{VT} \Delta T] \quad (23)$$

The thermal osmosis experiment was performed with liquid water and the temperature difference across the membrane ranged from 10°C to 50°C. The volume flux was plotted against the temperature difference as shown in Figure 8.4.1.28:

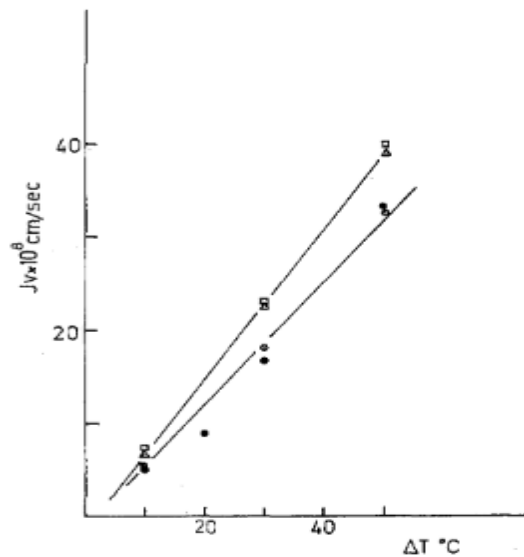


Figure 8.4.1.28 Thermal Osmosis Flux [99]

The slope of the trendline is positive indicating that the temperature driven fluid flow is in the hot to cold direction. The slope of the trendline is used to compute the thermal osmosis transport coefficient. The trendline seems to go through the origin, it is not clear if the data was forced through the origin, it assumes that all of fluid flow is from thermal osmosis, other fluid drivers could be present, and the other fluid drivers needs to be quantified. It is not known if the other fluid drivers are neglectable or major contributors.

There was a second experiment where the temperature gradient was fixed, and the salt concentration was varied as shown in Figure 8.4.1.29. In this case the thermal osmosis would be fixed due to the fixed thermal gradient, and the back diffusion would be changing.

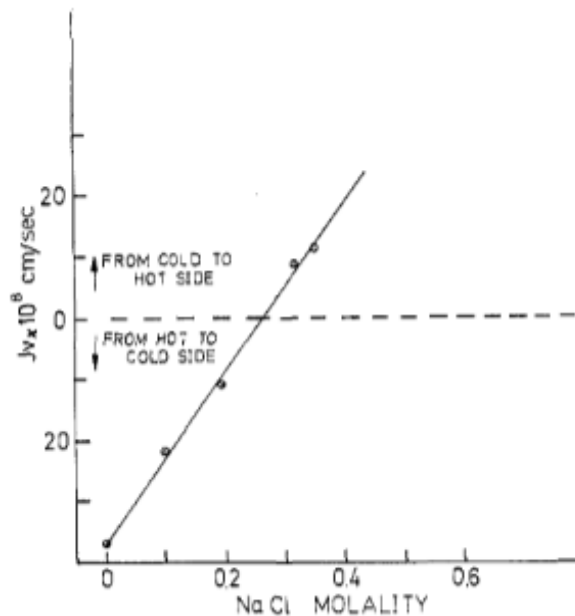


Figure 8.4.1.29 Impact of Salt Concentration of Water Flow [99]

In this case of variable salt concentration, the water flow changes direction based on the salt concentration. The total water flow is composed of the fluid flow driven by the salt difference concentration and thermal osmosis. The total water flow needs to be decomposed into its thermal osmosis and concentration driven fluid flow.

Gaeta et al [100] also examined thermal osmosis in porous media specifically hydrophobic they noted a phase change of water in the process and introduced membrane distillation. Membrane distillation is the process of at which liquid water evaporates on

the hot side and pass through the membrane condenses on the cold side. Gaeta et al [100] purposed three theories for water transport across porous media, the first driver is due to thermal excitation to the porous media, the second assumed entropy balanced transport and the third is distillation in vapor filled pores that will occur in hydrophobic material. Two of the three can apply to both hydrophobic and hydrophilic membranes, the other case is specific to hydrophobic material and to liquids that cannot penetrate them. Capillary evaporation theory is explained by an evaporation process at the warmer side and condensation on the colder side and the liquid passes through the membrane as a vapor. This will also occur if liquid is on one side and vapor is on the other side. When the membrane loses hydrophobicity, a variable percentage of the pores of the membrane can be liquid filled, and part of the membrane will be liquid filled, and the other part can permeate vapor.

Gaeta et al [100] has purposed a hybrid model for liquid transport. In membrane distillation the vapor pressure difference drives the fluid flow across the membrane. The equation for membrane distillation is expressed in equation 24.

$$J_V = \beta e^{-\frac{L}{RT}\Delta T} \quad (24)$$

Gaeta et al [100] also conducted non-isothermal water-based experiments with hydrophobic membranes as shown in Figure 8.4.1.30:

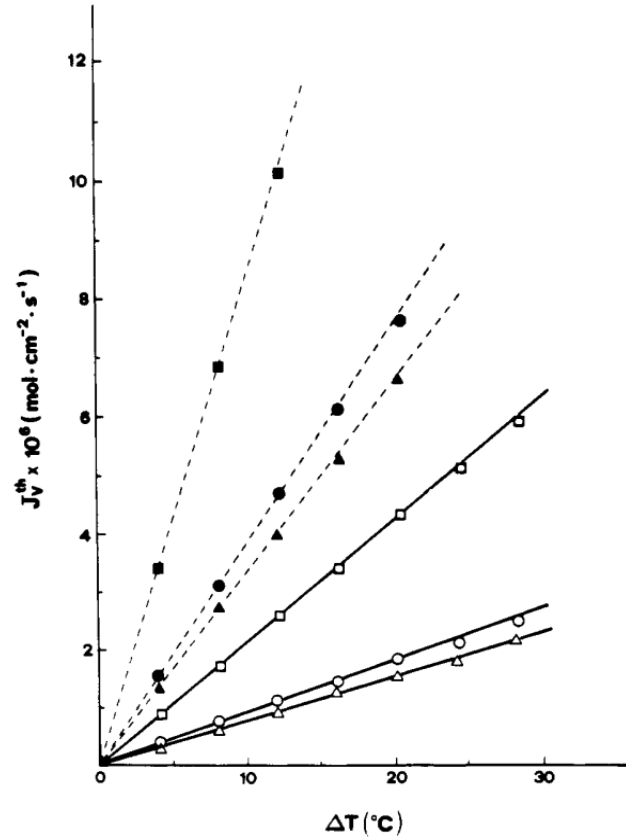


Figure 8.4.1.30 Non-Isothermal Fluid Flow [100]

The slope of the trendlines is positive indicating that the thermal osmosis is in the hot to cold direction. The slope of the trendline is used to compute the thermal osmosis coefficient. By forcing the trendline through the origin it assumes that all the fluid flow is from thermal osmosis, other fluid drivers could be present and the other fluid drivers needs to be quantified. The total water needs to be decomposed into its fundamental drivers, and each driver needs to be evaluated, and its portion of the total water flow needs to be computed.

Vollellmy and Lauger [101] stated when a membrane separates two liquid media at different temperatures, there will be heat of transport and mass transfer takes place. Thermal osmosis in these experiments was observed from the cold side to hot side; the materials used in the experiment are polystyrene and toluene. When salts were introduced, the behavior changed, and the flow reversed at 38°C. Vollellmy and Lauger [101] stated that there are two drivers of fluid flow, pressure difference and temperature difference as shown in equation 25.

$$J_V = L_{VT} \frac{\Delta T}{L} - L_{VP} \frac{\Delta P}{L} \quad (25)$$

The pressure and water transport coefficients are related to one another as shown in equation 26.

$$\frac{\Delta P}{\Delta T} = - \frac{L_{VT}}{L_{VP}} \quad (26)$$

There is also a coupling of pressure difference and temperature difference to heat of transport as shown in equation 27.

$$\frac{\Delta P}{\Delta T} = - \frac{Q^*}{VT} \quad (27)$$

Vollellmy and Lauger [101] plotted fluid flow vs temperature gradient as shown in Figure 8.4.1.31:

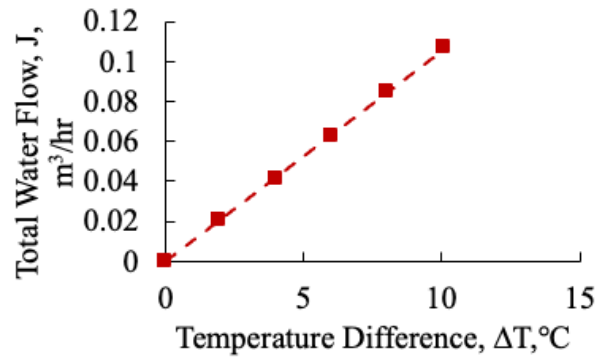


Figure 8.4.1.31 Non-Isothermal Fluid Flow [100]

The slope of the trendline will provide the thermal osmosis coefficient. The slope of the trendline is positive. By forcing the trendline through the origin, it assumes that all the total water is from thermal osmosis flow and neglects other fluids drivers. fluid flow from thermal osmosis and does not account for other fluid drivers. The total water needs to be broken down into its primary fluid driver components, and the thermal osmosis portion of the total water flow needs to be determined.

Honda et al [102] conducted thermal osmosis experiments with diethylamino-polystyrene (DEA-PSt) membranes with acetic acid and water. Honda et al [102] found that the water flow does change direction pending on the material selected. For the polystyrene membranes without the amino groups the flow was from the hot side to cold side. The silicone-based membrane was also flowing in the hot to cold direction. The polystyrene membrane, the water flux was in the cold to hot direction. Honda et al [102] stated that three variables can move water across the membrane, the variables are

pressure, temperature and concentration gradient as shown in equation 28. The pressure, concentration and thermal gradient can move fluids.

$$J_v = -\frac{A_x}{l} [L_{11}\Delta P + L_{12}\Delta C + L_{13}\Delta T] \quad (28)$$

The total water flow was plotted against the thermal gradient as shown in Figure 8.4.1.33.

The thermal osmosis portion of the total water flow was not extracted, instead it was assumed that all the fluid flow is from thermal osmosis.

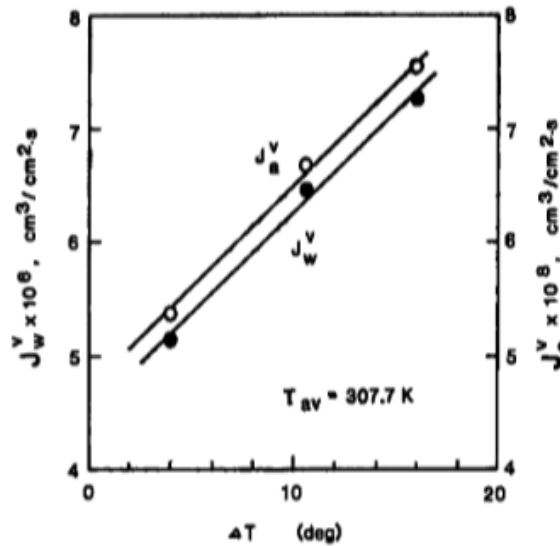


Figure 8.4.1.32 Non-Isothermal Fluid Flow [102]

The model used to fit the trendline is shown in equation 29.

$$J_W = L_{PW} \left[\frac{RT}{v_w} \left(\frac{\Delta C_w}{C_w} + \frac{l_{12}}{l_{11}} \frac{\Delta C_a}{C_a} \right) + \frac{\Delta H_w + \frac{l_{12}}{l_{11}} \Delta H_a + \frac{l_{13}}{l_{11}} \Delta T}{v_w T} \Delta T \right] \quad (29)$$

The concentration gradient and thermal gradient are contained in the equation 64 which indicates the flow will not go through the origin. Thermal osmosis is not the only fluid driver present; the total water flow needs to be decomposed it primary drivers. The thermal osmosis portion of the total water needs to be determined. It is not known if the thermal osmosis portion of the fluid flow is a major or minor fluid driver. The concentration change with temperature is also examined in Figure 8.4.1.34:

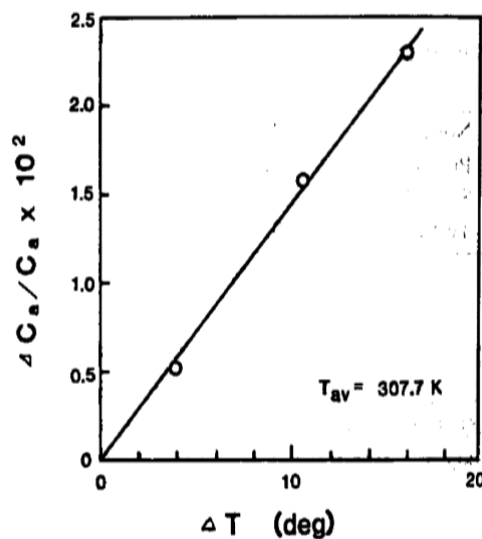


Figure 8.4.1.32 Concentration change by thermal gradient [102]

This is one of the few cases where the flow was not forced through the origin and this considers the impact of the concentration gradient. The temperature difference across the membrane will influence the concentration gradient and this is one of the secondary effects from the concentration and thermal gradient.

8.5 Thermal Osmosis Analysis

Tasaka et al [87] examine the change in pressure with respect to temperature to understand thermal osmosis, the change in pressure with respect to temperature is linked to the heat of transport. Tasaka et al [87] had initially plotted the trendline through the origin, the first step was to replot the data and find the best fit, the best fit determined was an exponential fit as shown in Figure 3.71, the trendlines do not go through the origin.

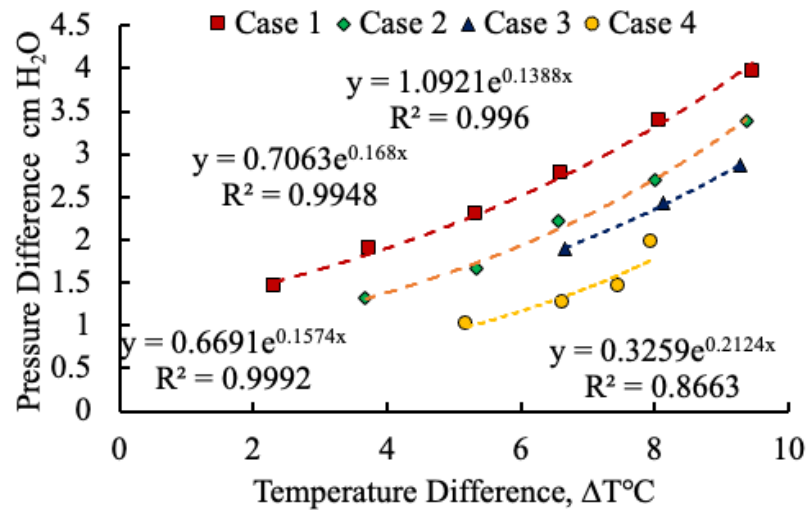


Figure 8.5.1 Pressure and Temperature relationship [87]

The relation of pressure and temperature is an exponential. The pressure and temperature relationship was forced through the origin and when the data was examined it is clearly does not go through the origin, the trend line indicates it is exponential much like the vapor pressure of water. This was not a good assumption and must be examined further.

The next step involves examining the total water flow data, as before there were two plots, once were the trendline was forced through the origin and the second case where

the data was not, the original data will be plotted both ways and examined to see which way is correct, only one is correct because the slopes will not be the same. It is possible to get a linear fit that is forced through the origin, the correlation is a good fit, but the data looks skewed. The slope of the line is positive indicating that thermal osmosis is in the assumed direction. The next plot is of the thermal osmosis where the data is not forced through the origin as shown in Figure 8.5.2:

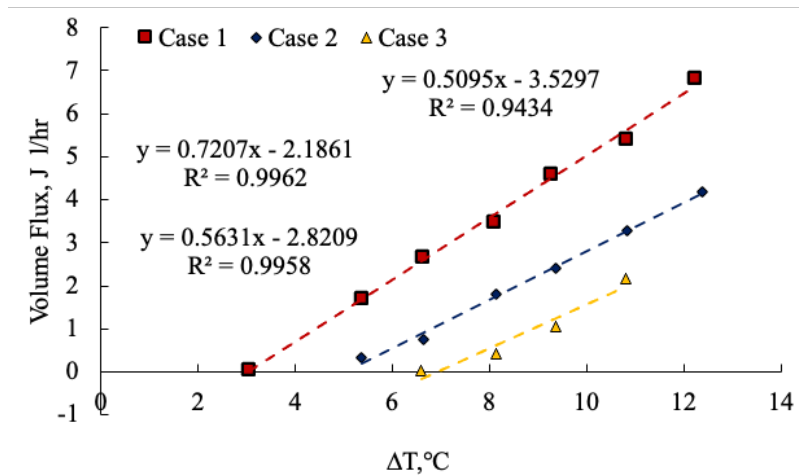


Figure 8.5.2 Thermal Osmosis water flow Not Forced Through the Origin [87]

The direction of the thermal osmosis does not change when the data is refit, the new trendline is less skewed compared to the case where the data is forced through the origin, in all case the constant from the data fit is of the opposite sign of the slope, indicating that the other fluid driver is opposing thermal osmosis. Based on the new fit it appears that other fluid drivers are present.

Tasaka et al [87] had also plotted thermal osmosis data two different ways, the first one where the trendline is forced through the origin and the second where the data was not

forced through the origin, one of the these has to be correct, both cannot be correct. The fit of the data forced through the origin is shown in Figure 3.74. The total water flow was fit to a linear trendline, that was forced through origin, this assumes that all the water flow is from thermal osmosis. The trendlines do go a good fit, and the data was fit to a linear trendline. The direction of thermal osmosis is in the assumed direction. The next step is to examine how a linear fit when the data not forced through the origin as shown in Figure 8.5.3:

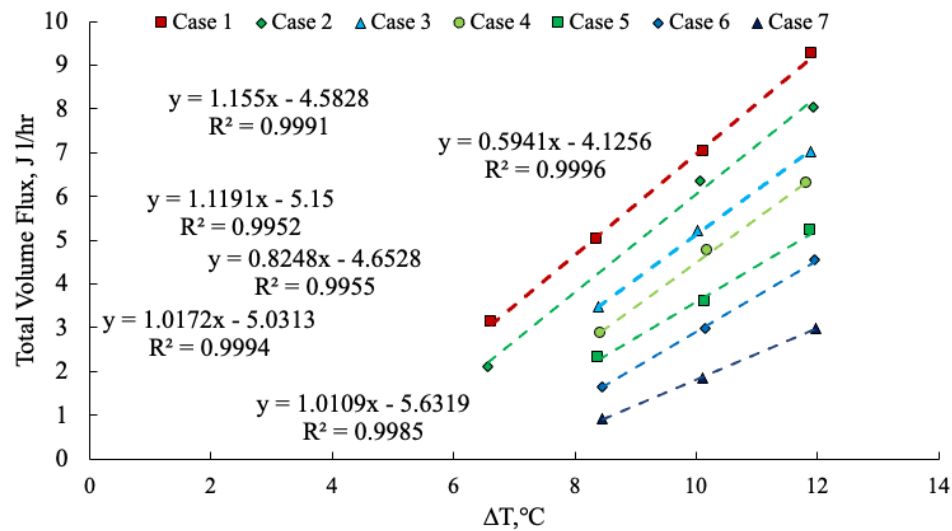


Figure 8.5.3 Thermal Osmosis water flow Forced Through the Origin [87]

The total water flow is fitted to a linear trendline that is not forced through the origin, this assumes that some fluid flow is from thermal osmosis and there are other fluid drivers present. The current method assumes that all of the fluid flow is thermal osmosis. The linear trendline not forced through the origin does provide a better fit compared to the other data fit. The direction of thermal osmosis does not change but there is a constant

from the linear trendline and this constant in all the cases is in the opposite direction of thermal osmosis indicating that thermal osmosis must work against the other fluid driver. The thermal osmosis portion of the total water needs to be extracted along with the thermal osmosis transport coefficient.

Mengual et al [89] had conducted thermal osmosis experiments with liquid water, methanol and ethanol, since their data was given in a table format it is not known what method was type of trendline was used to obtained insight on thermal osmosis.

The thermal osmosis data is plotted where the data was not forced through the origin.

The first data plot consisted of water three different membranes as shown in Figure 8.5.4:

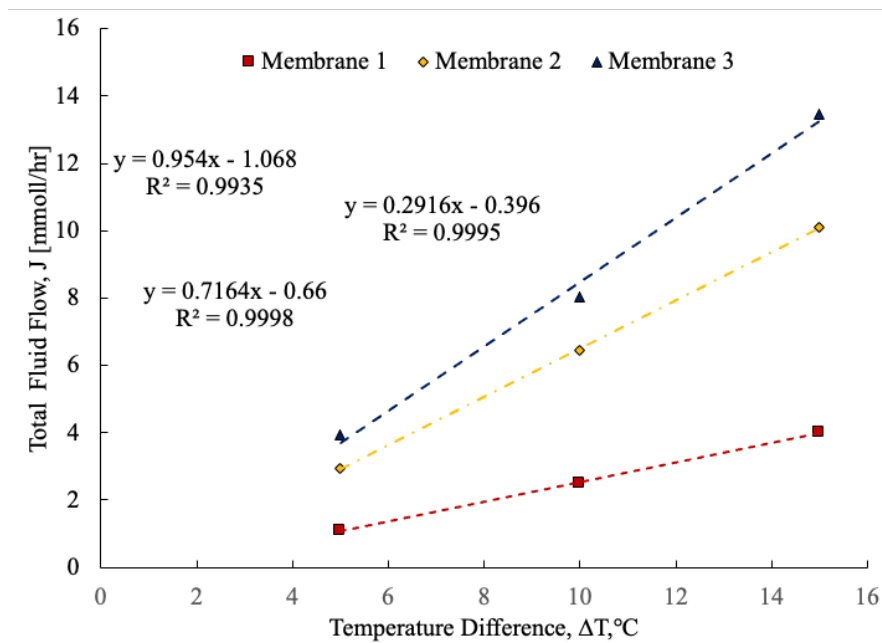


Figure 8.5.4 Thermal Osmosis water flow Not Forced Through the Origin [89]

The total water flow is fitting to a linear trendline where the trendline is not forced through the origin, this assumes that a portion of the total water flow is thermal osmosis. The temperature driven water was in the direction of hot to cold, and the correlation with the data is good, and in all cases the constant from the data trendline is in the opposite direction of thermal osmosis and thermal osmosis must work against this fluid driver. Thermal osmosis was also conducted with methanol on the same membrane

The total water flow is fitting to a linear trendline where the trendline is not forced through the origin, this assumes that a portion of the total water flow is thermal osmosis. The thermal osmosis was in the direction of hot to cold and the new data fit did change the slope, and a constant was generated for the trendline. The constant is the opposite sign of the thermal osmosis indicating it is opposing thermal osmosis. Based on the constant there are other fluid drivers present in the experiment. All the cases need to have the thermal osmosis portion extracted from the total water flow along with thermal osmosis transport coefficient.

Pagliuca et al [90] performed thermal osmosis experiments with liquid water and hydrophobic membranes, the first experiment was performed with only the pressure difference across the membrane, and the initial data was forced through the origin, the data was replotted to see if any other fluid drivers were present. The plot is shown in Figure 8.5.5:

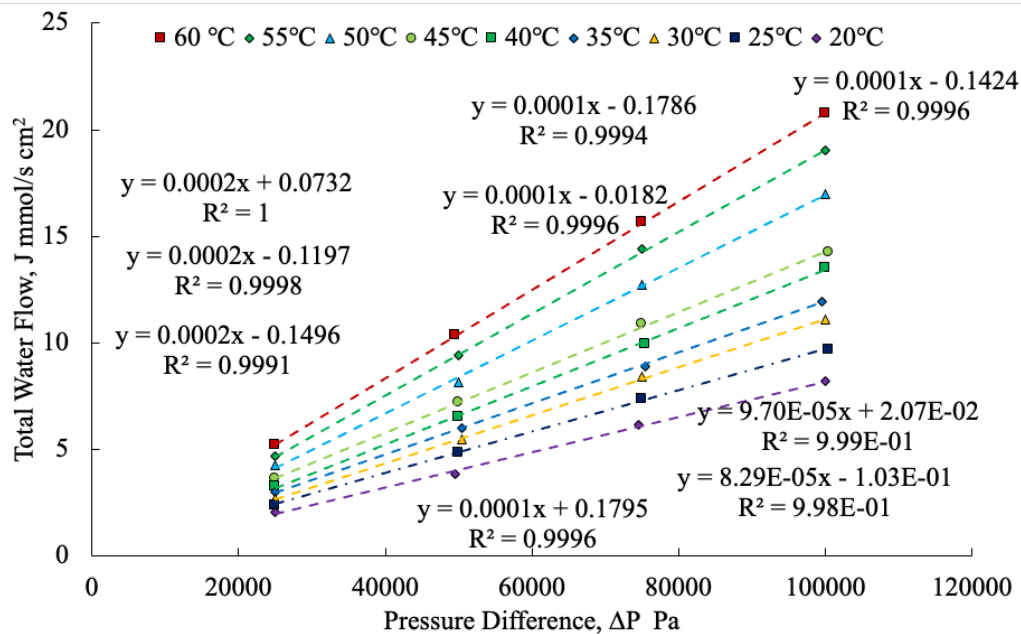


Figure 8.5.5 Isothermal Water flow with Pressure Difference [90]

The data can be fit to a linear trendline where it is not forced through the origin. The fluid flow is in the direction of the pressure gradient and there is a constant which implies another fluid driver is present. Pagliuca et al [90] also performed experiments under non-isothermal conditions like in the isothermal case, the trendline data was forced through the origin, this is neglecting other fluid drivers present, to test for other fluid drivers the data is fit to a new trendline where the data is not forced through the origin as shown in Figure 8.5.6:

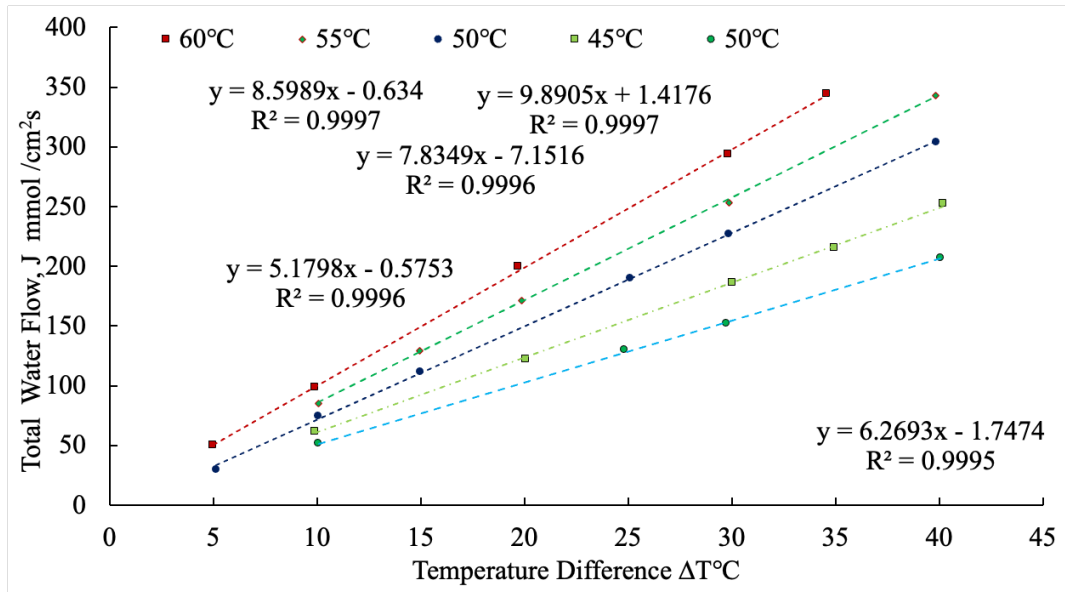


Figure 8.5.6 Non-Isothermal Water flow [90]

A linear trendline is obtained and the slope of the trendlines are positive indicating that the thermal osmosis fluid flow is in the direction of hot to cold. There is a constant obtained for the data fit indicating that other fluid drivers are present.

Rastogi et al [91] performed thermal osmosis experiments with liquid water, originally their trendline data is forced through the origin assuming no other fluid drivers are present. The thermal osmosis data is refitted to a linear trendline to see if other fluid drivers are present as shown in Figure 8.5.7:

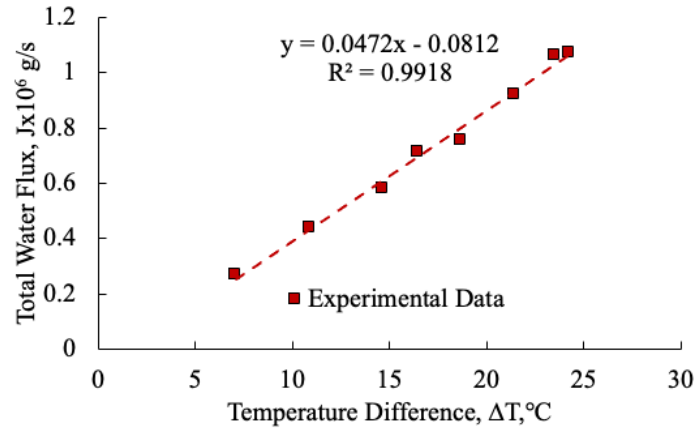


Figure 8.5.7 Non-Isothermal Water flow [91]

The total water flow data is fitted to a linear trending that is not forced through the origin. The constant from the trendline fit indicates that thermal osmosis is not the only fluid driver present. The slope of the trendline is positive indicating thermal osmosis is in the hot to cold direction. The water flow data was fit to a linear trendline, and the slope is positive indicating that the temperature driven flow is in the hot to cold direction. The constant from the trendline is in the opposite direction of thermal osmosis and thermal osmosis must work against the other fluid driver. The thermal osmosis portion of the total water flow needs to be extracted as well as the thermal osmosis transport coefficient.

Tasaka et al [92] also examined thermal osmosis for anion membranes as before there are two trendlines that are shown the first one is where the water flow is forced through the origin and the second case where the data is not forced through the origin. Both cannot be correct, and the data is examined two ways the first being where the trendline was forced through the origin and the second one where the trendline was not forced through the

origin. The first data plot is shown in Figure 3.82. The experimental data is forced to a linear trendline which assumes that all the total water flow is thermal osmosis. A good data fit is obtained for the case where the data was not forced through the origin. The direction of fluid flow was in the hot to cold direction and the thermal osmosis experiments was conducted temperature differences above 5 K. The same data is reprocessed where the data is not forced through the origin as shown in 8.5.8:

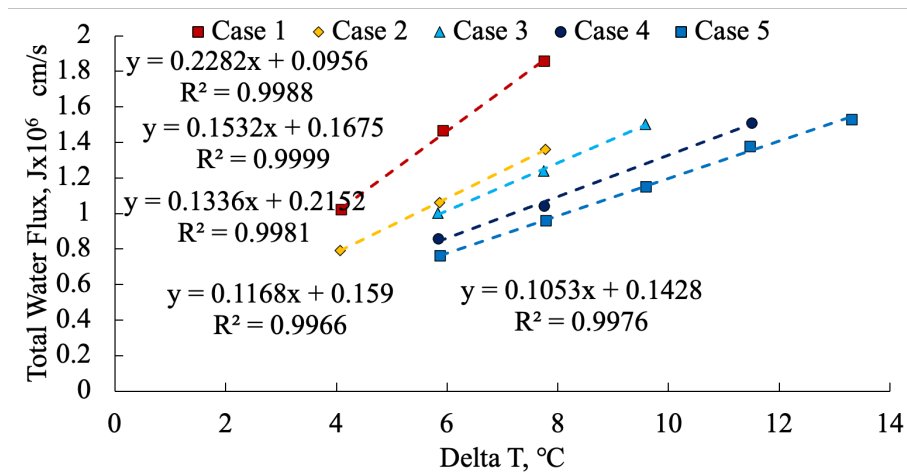


Figure 8.5.8 Non-Isothermal Water flow not forced through the origin [92]

The experimental data is fit to a linear trendline that is not forced through the origin, this considers that thermal osmosis is a portion of the total water flow. The trendline for the cases where the trendline is not forced through the origin does have a better data fit due to the constant. The direction of thermal osmosis does not change, the constant from the trendline fit is the same sign as the thermal osmosis coefficient so the other fluid driver is in the same direction as thermal osmosis. Another fluid driver is working with thermal osmosis which would overstate thermal osmosis. The thermal osmosis portion of the total

water needs to be extracted from the total water flow along with the thermal osmosis transport coefficient.

Tasaka et al had also run another thermos-osmosis experiment where there were two trendlines shown, the first one forced through the origin and the second one where the data was not forced through the origin, both cannot be correct, and they are examined to see which one is correct. A good data fit is obtained for the total water flow data, and the direction of the temperature driven water flow is in the direction of hot to cold. This assumes that no other fluid drives are present, to check to see if other drivers are present the total water flow is replotted and the trendline is not forced through the origin as shown in Figure 8.5.9:

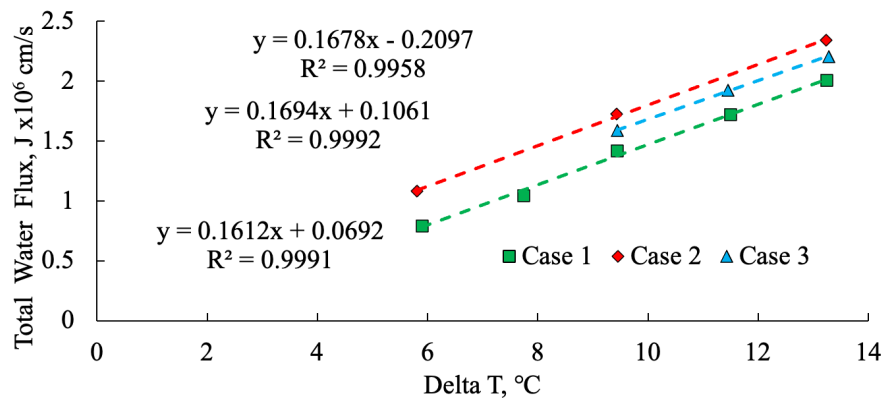


Figure 8.5.9 Non-Isothermal Water flow not forced through the origin [92]

The data was fitted to a linear trendline that is not forced through the origin, it assumes that thermal osmosis is a portion of the total water flow. The data fits were good also; there is a constant because of the linear trendline fit which implies that other fluid drivers are present in the experiment. The second trendline fit also implies that not all the fluid

flow is thermal osmosis. The thermal osmosis portion of the total water flow needs to be obtained along with the thermal osmosis transport coefficient.

Kiyono et al [94] also examined thermal osmosis but plotted thermal osmosis with respect to natural log (ln) of temperature and forced the trendline through the origin.

The concern is that the natural log of zero is negative infinity and this is not achievable.

The data is replotted to where it is not forced through the origin as shown in Figure 8.5.10:

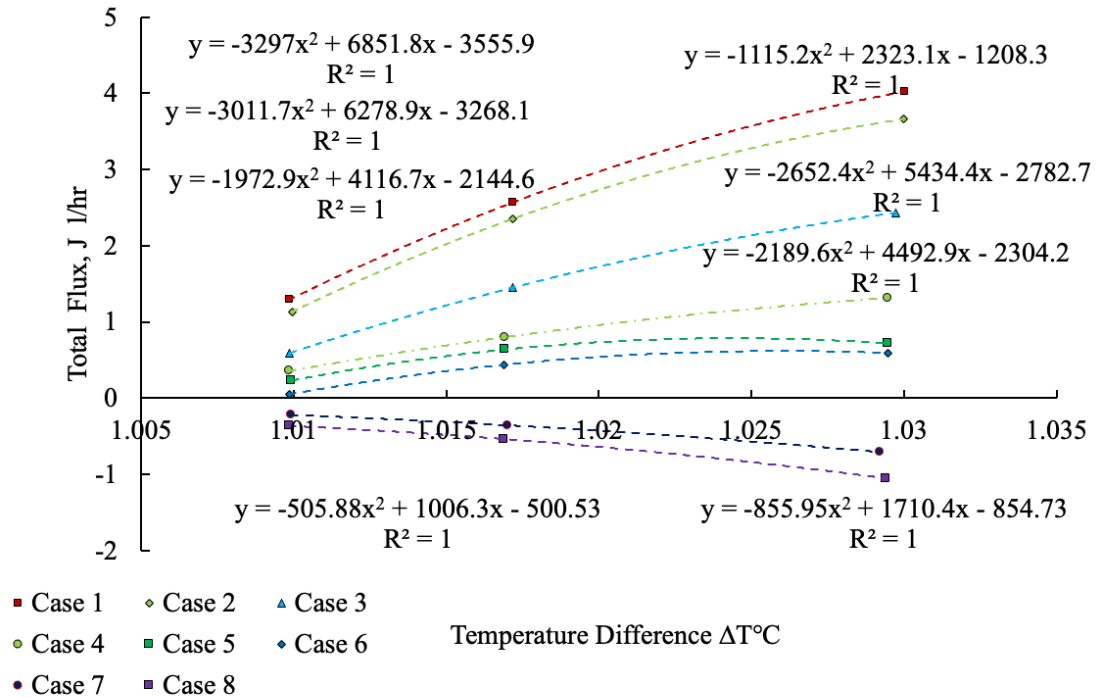


Figure 8.5.10 Non-Isothermal Water flow not forced through the origin [94]

The data was replotted the experimental data was fit to a polynomial fit, the trendline does not go through the origin, this is the result of other fluid drivers present. The total

water flow data is replotted to a polynomial, and the data is not forced through the origin. The thermal osmosis portion of the total water flow needs to be extracted along with the thermal osmosis transport coefficient. Kiyono et al [94] did not only study thermal osmosis, Kiyono et al [94] also experimented with osmotic pressure like in the thermal osmosis experiments the total water flow was forced through the origin which would neglect other fluid drivers. The osmotic pressure data is replotted to see if the trendline can go through the origin, the replotted data is shown in 8.5.11:

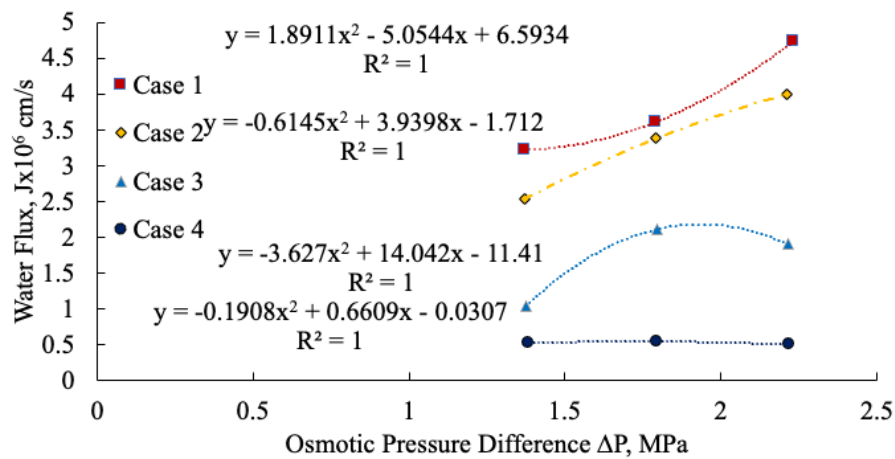


Figure 8.5.11 Osmotic Fluid Flow Not Forced Through Origin [94]

The total water flow was replotted to a polynomial fit to where the trendline is not forced through the origin which indicates that other fluids drivers are present. The osmotic flux needs to be extracted from the total water flow along with the osmotic pressure transport coefficient. In both cases the trendline could not be forced through the origin, each trendline is either a linear line with a constant or a polynomial at no point does it go through the origin this could be the result of other fluid drivers present. The assumption of a linear trendline through the origin is not a good assumption.

Tasaka et al [95] also used Neosepta membrane for thermal osmosis and the original data was forced through the origin. It is believed that other fluid drivers are present in the experiments. The experimental data is fitted to a trendline that is forced through the origin, this assumes that all the fluid flow is thermal osmosis. There is a good correlation between the data and the trendline so this data fits, but the data fit of where the trendline is not forced through the origin is shown in 8.5.12:

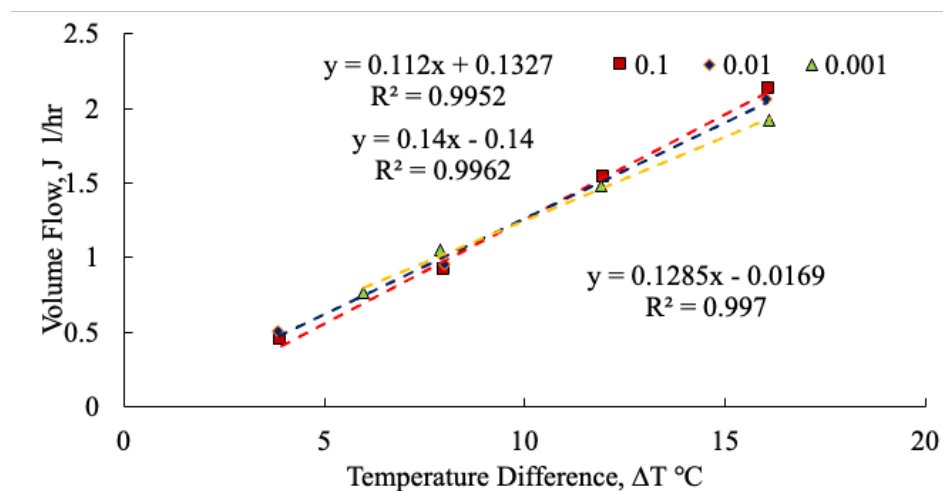


Figure 8.5.12 Water flow forced through the origin [95]

The total water flow data is fitted to a linear trendline that is not forced through the origin, this assumes that thermal osmosis is a portion of the total water flow. The second trendline does also provide good correlation between the data and the curve fit, the insight gained is that this assumes that other fluid drivers are present in the experiment. The second trendline is assumed to be the correct one because other cases have had other fluid drivers present. The fluid flow across the membrane is so small accuracy is needed,

and the results need to make sure only thermal osmosis is isolated from the total water flow.

Tasaka et al [95] had also performed thermal osmosis work with Fluoropore membranes and Tasaka et al [95] only shown a trendline that go through the origin assuming no other fluid drivers are present. The experimental data is plotted two ways, the original way and the second way where the trendline is not forced through the origin. The total water flow data was fit to a linear trendline that is forced through the origin, this assumes that all the total water flow is from thermal osmosis. The original trendline does provide good correlation with the data but it assumes no other fluid drivers are present. The next step is to examine how the data fit would be if the trendline was not forced through the origin as shown in Figure 8.5.13:

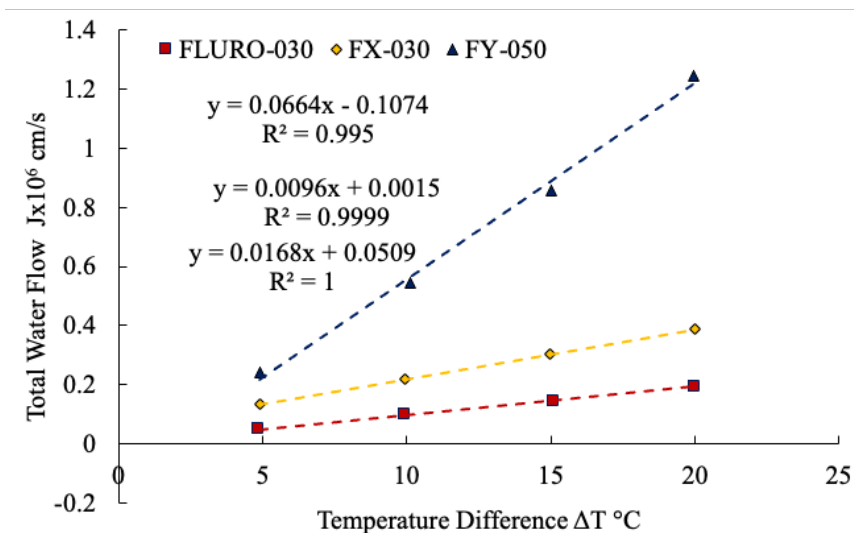


Figure 8.5.13 Water flow not forced through the origin [95]

The experimental data is refitted to a linear trendline that is not forced through the origin, this assumes that a portion of the total water flow is thermal osmosis. The correlation of the data of the proposed trendline equal to the original fit, there is a constant from the linear trendline it is small, but it is denoting that not all the flow is thermal osmosis. In two of the cases the slope of the trendline is the same sign as the constant from the trendline which indicates that the other fluid driver is in the same direction of thermal osmosis. In the remaining case, the constant is of the opposite side of the slope of the trendline indicating that thermal osmosis is moving in the opposite direction of the other fluid driver.

Tasaka et al [95] also performed thermal osmosis with Fluoropore at different temperatures at various temperatures. The experimental data is fitted to a trendline that is forced through the origin, this assumes that the total water flow is thermal osmosis. The original method does provide a good fit for this case, and the second method is evaluated in Figure 8.5.14:

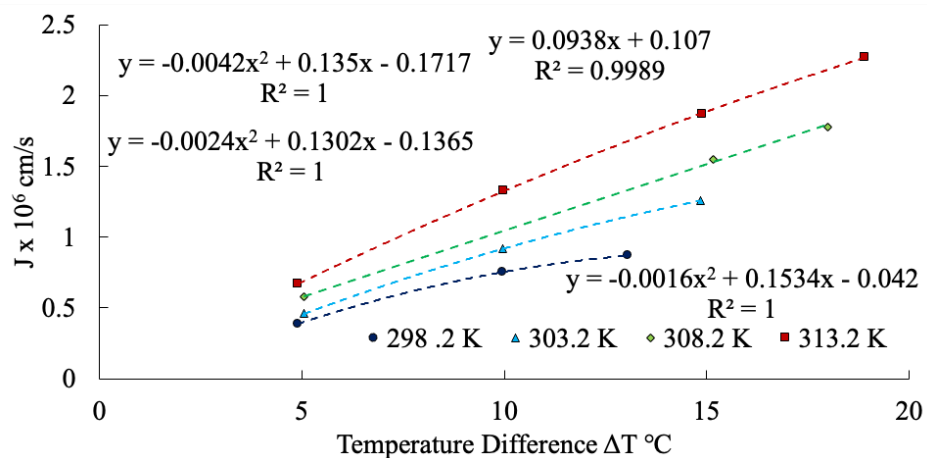


Figure 8.5.14 Water flow not forced through the origin [95]

The data is refitted to either a linear fit or a polynomial fit, this assumes that thermal osmosis is one of the fluid drivers in the total water flow. The fit for the proposed method does provide good correlation also, one case required a fit to polynomial and the other cases were fit to a linear trendline. The constants indicate that other fluid drivers are present. In two of the three cases the second data fit is equivalent to the original fit and once case it is worst, but the proposed method would account for fluid flow if there was no thermal gradient present. In the cases where the data trendline is forced through the origin, it is assumed that the total water flow across membrane is all thermal osmosis or pressure osmosis. When the total water flow data is not forced through the origin, thermal osmosis or the pressure-based flow is a portion of the total fluid flow, the desired effect needs to be determined.

Rastogi et al [96] had performed thermal osmosis testing as well as pressure gradient testing with Du Pont 600 cellophane membrane with water and methanol. The thermal osmosis data is replotted to wear the trendline is not forced through the origin, this only considers thermal osmosis is the only fluid driver present. The same data is replotted to where the trendline is not forced through the origin, the new plot is shown in Figure 8.5.15:

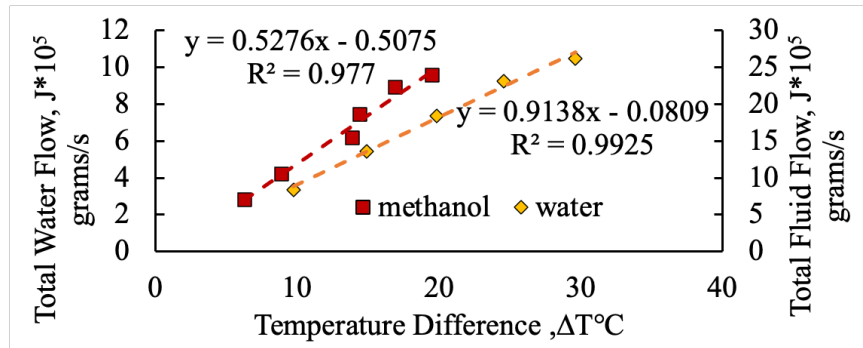


Figure 8.5.15 Water flow not forced through the origin [96]

The new trendline is as good as the original data and it also permits fluid flow through the membrane if there is no temperature difference. According to the new data there is a fluid driver working against thermal osmosis. Rastogi et al [96] had also examine pressure driven flow also and as before the trendline was forced through the origin. The case of where the trendline is not forced through the origin is shown in Figure 8.5.16:

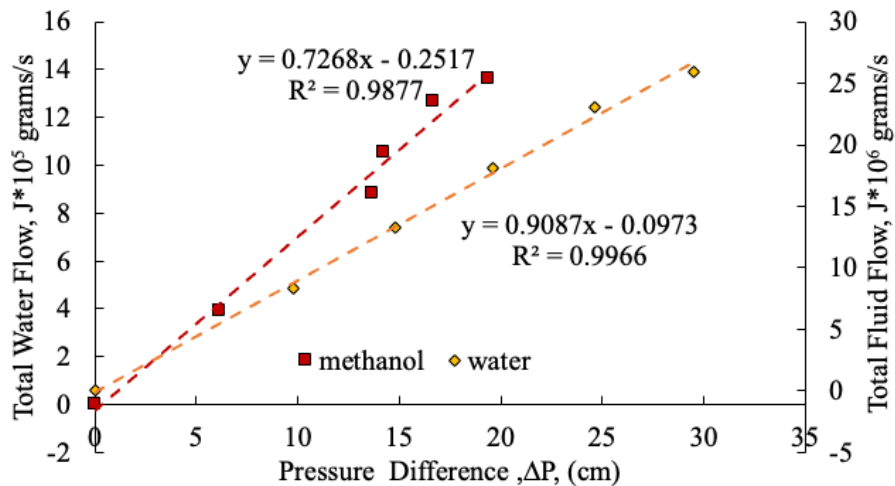


Figure 8.5.16 Water not forced through the origin [96]

The proposed correlation is not as good as the other correlation but allows other fluid drivers to be present. In summary, by not forcing the trendline data through the origin, it assumes that there are other fluid drivers present, the thermal and pressure component need to be extracted. Bellucci et al [97] performed thermal osmosis experiments to understand thermal polarization. The experiment consisted of a cellophane membrane and water. The same data is replotted to where the trendline is not forced through the origin as shown in Figure 8.5.17:

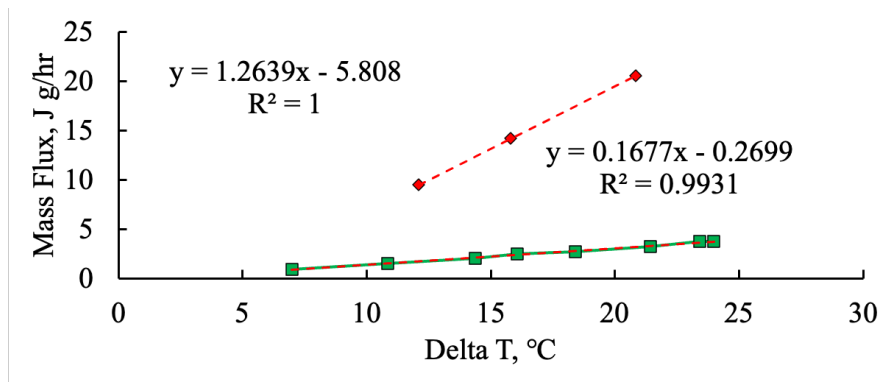


Figure 8.5.17 Water Flow not forced through the origin [97]

The second correlation is just as good but with the new constant obtained. The constant obtained is in the opposite direction of thermal osmosis. In both cases the temperature driven water flow was in the direction of hot to cold. Tasaka et al [98] has examined different ions in a SA-14 and SA-15 membranes, there was an examination the pressure driven flow and temperature driven flow. In both experiments, the data trendlines were both forced through the origin, assuming no other fluid drivers are present. This assumption needs to be examined to see if it valid. The experimental data is refitted to trendline that does not go through the origin as shown in Figure 8.5.18:

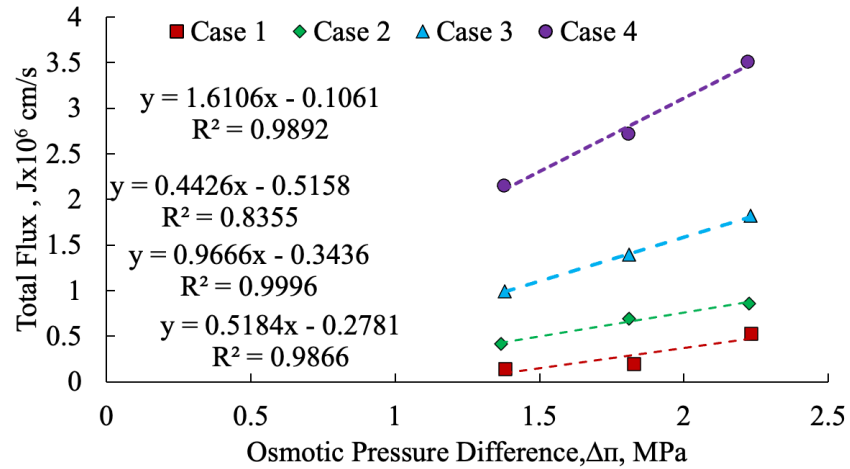


Figure 8.5.18 Water not forced through the origin [98]

The data is processed to where the trendline is not forced through the data as shown in Figure 8.5.19. The new fit is a linear trendline and the correlation is good, the other fluid drivers will be lumped into the constant, and the variable will contact thermal osmosis.

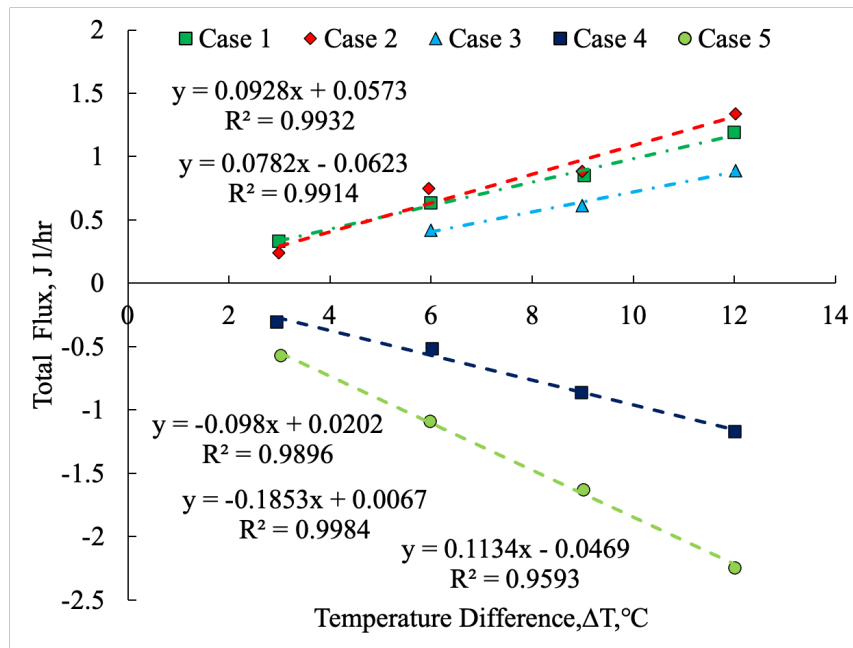


Figure 8.5.19 Water not forced through the origin [98]

The linear trendline does indicate that other fluid drives are present, in the cases where the slope is the positive the assumed direction if correct, and if the sign of the slope is negative then the thermal osmosis flow is in the opposite direction. The total water flow needs to be broken down to extract thermal osmosis from the total water flow.

Dariel et al [99] examined thermal osmosis with and forced the linear trendline data. The data trendline assumes that all the flow is from thermal osmosis. The data was replotted to, and the data was not forced through the origin as shown in Figure 8.5.20. The data trendline does go through the data point and the constant is of the opposite sign of the slope indicating that the other fluid driver is opposing thermal osmosis.

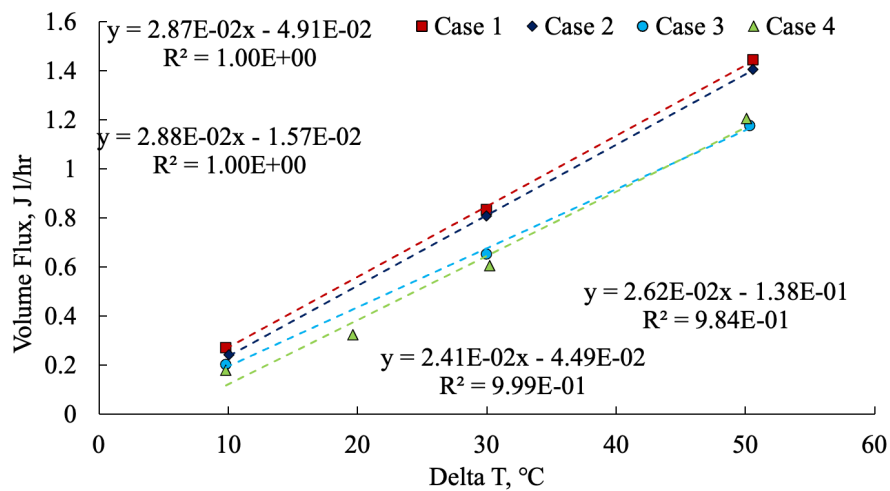


Figure 8.5.20 Water Flow not forced through the origin [99]

The proposed method provides equivalent correlation to the original. The insight gained shows that there is a fluid driver that is opposing thermal osmosis. Dariel et al [99] also

had examined the impact of the concentration of ions, the concentration of ions does change direction of fluid flow. This case is not forced through the origin as shown in Figure 8.5.21:

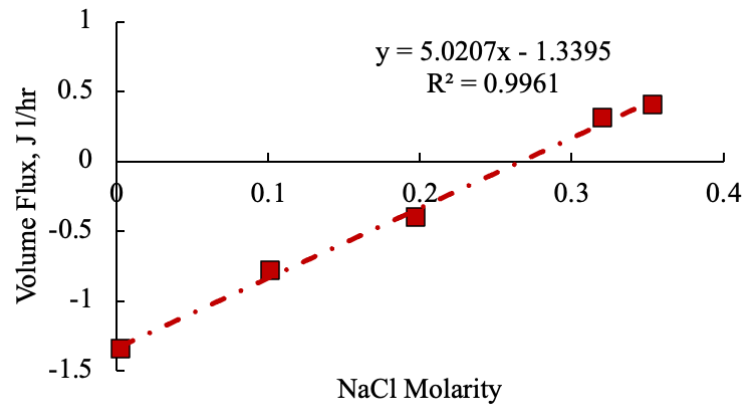


Figure 8.5.21 Concentration impact of fluid flow [99]

Gaeta et al [100] had also examined thermal osmosis with liquid water also different membranes to understand thermal osmosis, their experiments concluded that the direction of the temperature driven flow was in the direction of hot to cold and the trendline through their data was forced through the origin, The data is replotted to compare the fit of a linear trendline that is not forced through the origin as shown in Figure 8.5.22:

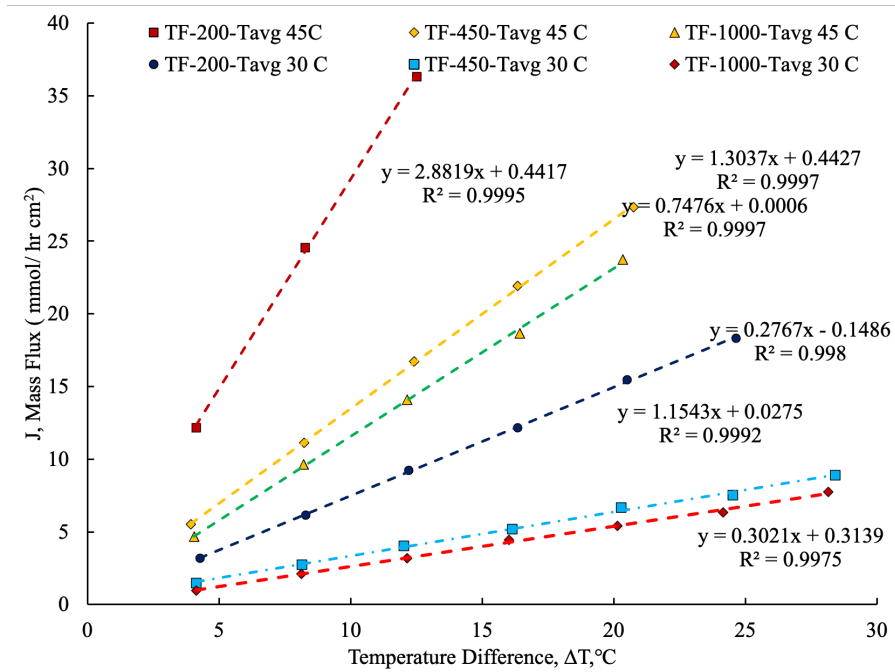


Figure 8.5.22 Temperature Driven Flow Not Forced Through the Origin [100]

The proposed data fit is equivalent to the original data fit but the proposed data fit assumes that other fluid drivers are present in the system. The other fluid driver is in the same direction of thermal osmosis.

Vollellmy and Lauger [101] also examined thermal osmosis on their experiment the temperature driven flow was plotted against the thermal gradient, and the data fit was forced through the origin. The next step is to replot the data but not force it through the origin as shown in Figure 8.5.23:

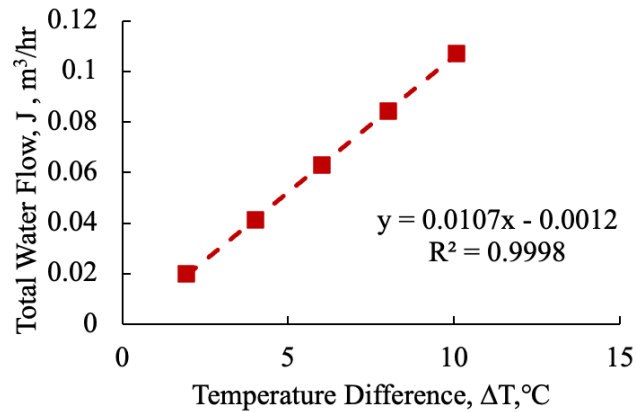


Figure 8.5.23 Temperature Driven Flow Not Forced Through the Origin [101]

Both correlations are good correlations, but the proposed one assumes that other fluid drivers are present. With the new correlation the thermal osmosis needs data needs to be extracted from the total water flow. The strength of the other fluid driver needs to be determined. Honda et al [102] original plot did not extrapolate data to the origin Their theory was that the Soret effect impacts thermal osmosis. The forcing through the origin does not go through all the data points. This kind of trend was seen when multiple fluid drivers are present, they will need to be reexamined. The data is then refitted to a trendline to where the data is not forced through the origin as shown in Figure 8.5.24. The new data fit does provide a better fit where it goes through all data points.

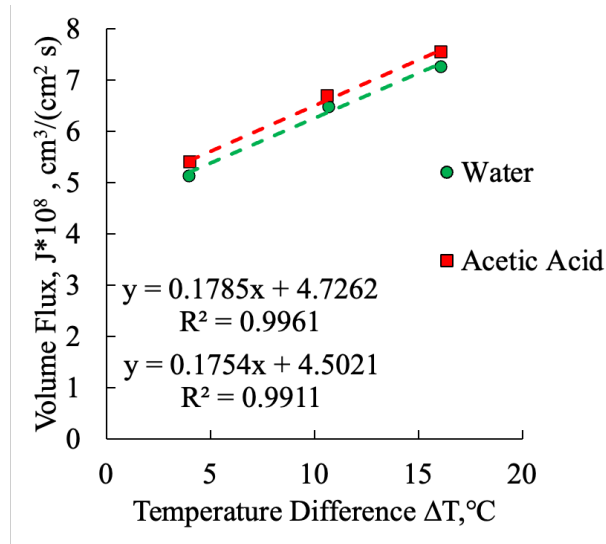


Figure 8.64 Temperature Driven Flow Not Forced Through the Origin [102]

The proposed data fit is better in this case, the correlation is better mainly because of other fluid drivers present, in this experiment it is believed that the Soret effect is impacting the results.

In summary when the trendline is forced through the origin, it is assumed or implied that all the fluid flow is from the fluid driver. When the trendline is not forced through the origin, it assumes that other fluid drivers are present, and the thermal osmosis portion of the total flow needs be extracted along with the transport coefficient.

8.5.1 Membrane Distillation

Membrane Distillation (MD) was introduced in the 1960's-1970's when several patents appeared. One of the applications that uses membrane distillation is desalination. One of the early challenges of membrane distillation was that there was limited availability of

hydrophobic materials. Membrane Distillation requires liquid water and a hydrophobic membrane. The liquid water will evaporate and pass through the membrane as a vapor and then condense as shown in Figure 8.5.1.1. This set up assumes that liquid is on both sides of the hydrophobic membrane.

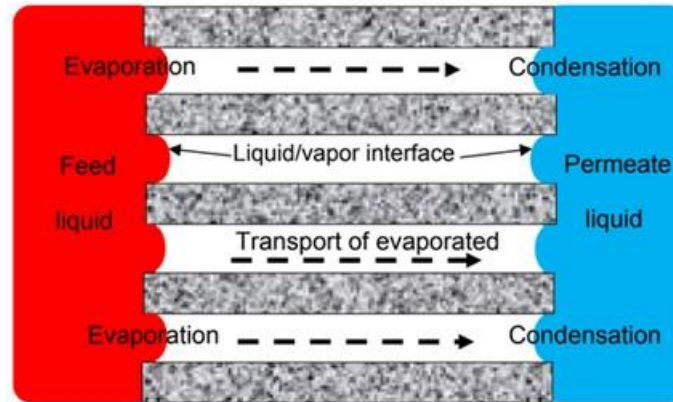


Figure 8.5.1.1 Membrane Distillation Process [124]

Kim and Mench [76] originally mentioned that PCI flow occurred with hydrophobic porous media, specifically when PTFE and microporous layer (MPL) were introduced and their direction of water flow was in the direction of hot to cold.

Ingarra et al [125][126] had noted that the PCI flow is membrane distillation, in membrane distillation shown in Figure 3.127 has evaporation on the hot side of the porous media and the water is transported through the membrane as a vapor and it condensed on the cold side. The Nafion membrane does have hydrophobic and hydrophilic regions. Both Phase Change Induced Flow (PCI) and Membrane distillation

are transporting water the same way. Membrane distillation is driven by vapor pressure difference as shown in Equation 30 [124][127]:

$$J = C_m \frac{dP}{dx} \quad (30)$$

Where J is the mass flux, C_m is a membrane coefficient, and $\frac{dP}{dx}$ is the pressure difference across membrane. The chain rule can be applied to the pressure difference term as shown in equation 31. The temperature difference will introduce a vapor pressure difference.

$$\frac{dP}{dx} = \frac{dP}{dT} \frac{dT}{dx} \quad (31)$$

The new term of dp/dT can also be simplified by using Clausis-Clapeyron equation and related to enthalpy and temperature [127]:

$$\frac{dp}{dT} = \frac{\Delta H_v}{RT^2} \quad (32)$$

The change in pressure versus temperature terms do have the heat of vaporization term in the numerator. This heat of vaporization must be overcome to begin MD [127]. By combining equation 32 and 31 into 30, the mass flux is:

$$J = C_m \frac{\Delta H_v}{RT^2} \frac{dT}{dx} \quad (33)$$

The heat of vaporization requires energy for the process to start; this heat needs to be overcome to start membrane distillation. If the fluid is heated then the temperature of the fluid will remain constant, if it is not heated the liquid temperature will drop to evaporate the vapor. Kim and Mench [76] also stated that PCI is driven by vapor pressure difference just like in membrane distillation. Membrane distillation is not covered in the Nernst-Planck equation. Membrane distillation also has different configurations, there is direct contact (DC), Vacuum membrane distillation, air gap membrane distillation and liquid gap membrane distillation and these configurations are shown in Figure 8.5.1.2:

MD configuration	Scheme of MD variant	Scheme of membrane pore	Heat and mass transfer resistances ^a
Direct contact membrane distillation (DCMD)			
Vacuum membrane distillation (VMD)			
Air gap membrane distillation (AGMD)			
Liquid gap membrane distillation (LGMD)			

Figure 8.5.1.2 Different Membrane Distillation Configurations [124]

The configuration that matches the fuel cell is the direct contact membrane distillation.

There are two phenomena that occur during the membrane distillation the phenomena are concentration polarization and thermal polarization. In the concentration polarization there is a concentration change on one side of the membrane when water evaporates, when this occurs this region of increase solutes concentration and this is referred to as concentration polarization as shown in Figure 8.5.1.3. The evaporation of the liquid will increase the concentration at membrane.

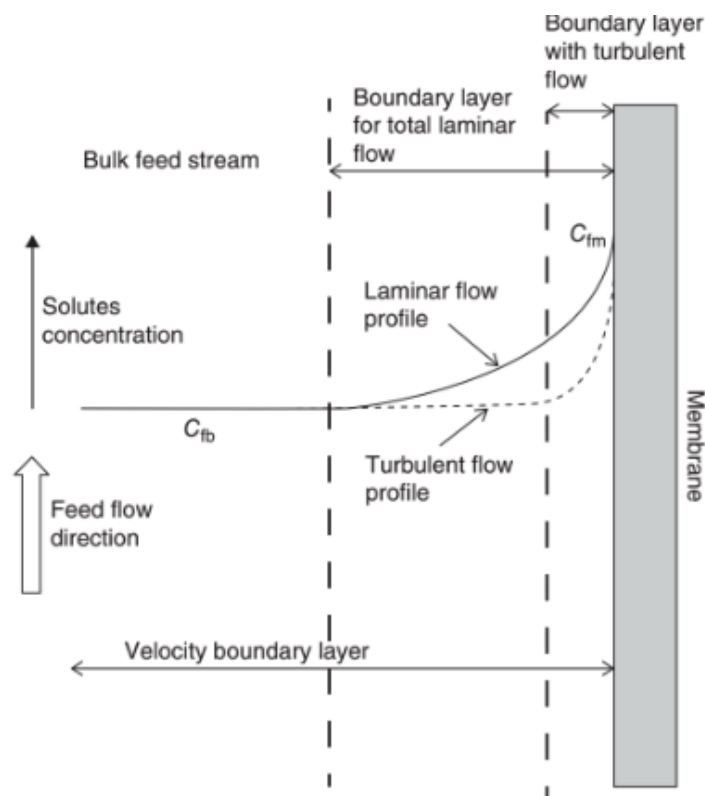


Figure 2.1 Feed-side concentration polarization profile in MD for laminar and turbulent flow. C_{fm} , solutes concentration at the feed-membrane interface; C_{fb} , solutes concentration in the bulk feed stream.

Figure 8.5.1.3 Concentration Boundary Layer [124]

The definition of the concentration polarization coefficient is shown in equation 34. The concentration boundary layer is like the thermal boundary layer. This indicates that the velocity and thermal boundary layer impacts the phenomena.

$$\theta_c = \frac{\theta_{fm}}{\theta_{fb}} \quad (34)$$

The concentration boundary layer does lie within the velocity boundary layer, and this would be true under certain fluid flows, this would explain why the hydrogen flow and air flow impacts the total water flow. Temperature Polarization is the region of decreased temperature adjacent to the feed -membrane interface and the region of increased temperature adjacent to the membrane. This phenomenon is defined on both sides of the membrane by the temperature polarization boundary layers. Temperature polarization provides heat transfer resistance by reducing the effective temperature across the membrane. The temperature polarization boundary layers lie within the velocity boundary layer. The thermal polarization boundary layer is reduced under turbulent conditions. The schematic of the thermal boundary layer is shown in Figure 8.5.1.4:

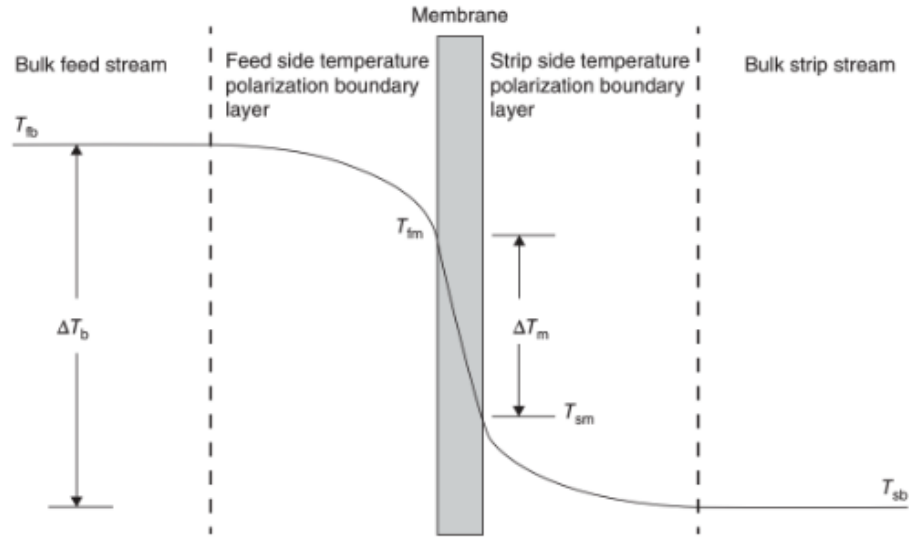


Figure 2.2 Temperature polarization profile in DCMD. ΔT_m , interfacial temperature gradient; ΔT_b , bulk stream temperature gradient; T_{fm} , feed-membrane interfacial temperature; T_{sm} , membrane-strip interfacial temperature; T_{fb} , bulk feed temperature; T_{sb} , bulk strip temperature.

Figure 8.5.1.4 Thermal Boundary Layer [124]

The evaporate on the hot side will lower the temperature at the membrane and this will lower the temperature across the membrane. In Tasaka et al thermal osmosis experiment that was an attempt to calculate the actual temperature difference across the membrane. The thermal polarization equation is shown in equation 35.

$$\theta_t = \frac{T_{fb} - T_{fm}}{T_{fb} - T_{sb}} \quad (35)$$

In Tasaka et al [88] thermal osmosis experiment that was an attempt to convert the bulk solution temperature, a sample of Tasaka et al [88] temperature relationship. In the process of membrane distillation, the temperature difference across the membrane creates

a difference in vapor pressure. Membrane Distillation can also occur at isothermal conditions; this is called osmotic distillation. Osmotic distillation will occur when a membrane is separating a liquid and vapor at a constant temperature. There are three dimensionless numbers that are related the dimensionless numbers are the Prandtl number, Schmidt number and the Lewis number. The Prandtl is fluid property that relates the viscous and thermal boundary layer as shown in equation 36.[132]

$$Pr^n = \frac{\delta_v}{\delta_T} = \frac{\nu}{\alpha} \quad (36)$$

The type of fluid will impact the Prandtl number. The Prandtl number is a function of the fluid properties. The second number is the Schmidt number which relates the viscosity to diffusion and the concentration boundary layer to the viscous boundary layer as shown in equation 37.[132]

$$Sc^n = \frac{\delta_v}{\delta_c} = \frac{\nu}{D} \quad (37)$$

The Lewis number relates mass diffusivity to thermal diffusivity as well as the concentration boundary layer to the thermal boundary layer as shown in equation 38.[132]

$$Le^n = \frac{\delta_T}{\delta_c} = \frac{\alpha}{D} = \frac{Sc}{Pr} \quad (38)$$

The Lewis number is different for liquid and gasses. With the Prandtl, Schmidt and Lewis number all coupled together this indicates that mass flux, fluid will impact membrane distillation. The fluid velocity will impact the viscous boundary layer which will impact the concentration gradient and thermal gradient across the membrane. The relationship between the Lewis, Schmidt and Prandtl number indicates that the mass flow of air and hydrogen will impact the water transport and polarization effects of the fuel cell. The Lewis, Schmidt, and Prandtl are impacted by the fluid velocity which will also explain the hydrogen flow and air flow impacted the total water flow.

8.5.2 Osmotic Distillation

As mentioned, osmotic distillation is a special case of membrane distillation, in this case the system is at isothermal conditions as a result, temperatures of the fluid will change because of evaporation and condensation of water. Osmotic distillation will occur with liquid on one side of the membrane and vapor is on the other side.

Adachi [37] performed net water flow experiments on water in a fuel cell with liquid water on one side and water vapor on the other side, and with water vapor on both sides. The net water flow versus concentration gradient is shown in Figure 3.14.3a. In the scenario with liquid on one side of the membrane and vapor on the other side, the movement of water flow was in the direction of liquid to vapor side, the vapor can pass through the membrane, but the liquid water cannot freely move through the membrane and for it to move through the hydrophobic portion of the membrane the water must

evaporate to pass through the membrane, mainly the vapor pressure difference will drive the water flow in the direction from the liquid side to vapor side. Adachi [37] noted that when the experiment was performed with liquid water on side and water vapor was on the other side the liquid was about 1°C cooler than the vapor

Yan et al [25] had done total water flow experiments with liquid water on one side of the membrane and humidified hydrogen, like Adachi [37] the direction of water flow was in the direction of liquid to vapor. This is a result of osmotic distillation. Like membrane distillation concentration polarization and temperature polarization will occur also, because the evaporation of water on the liquid side and condensation on the other side of the membrane.

8.6 Microporous Layer (MPL)

In the fuel cell there is an optional component that can be placed into the fuel cell and this component is the Microporous Layer (MPL). The MPL can be placed either in the anode or the cathode or both the anode and the cathode. The transport mechanism of the MPL is not fully understood. It is believed that the water management of the fuel cell is improved by adding the MPL.

Sarker et al [66] noted that the impact of (polytetrafluoroethylene) PTFE and MPL on fuel cells operating conditions is not fully understood and required additional information. With uncertainty in the electro-osmotic drag and back diffusion coefficient

models makes it more difficult to understand the MPL in the fuel cell. Sarker et al [66] noted that the addition of the MPL has an impact on the fuel cell operating in wet conditions. In some prior research, as current density increased, the net water flow changed direction. In other cases (pending on MPL configuration) the direction remained in one-direction only and was not impacted by the current density. One common theme is that the MPL only functions in wet conditions and does not provide function in dry environments [67]. Zhou et al [67] noted that the MPL needs to be hydrophobic, and when the fuel cell is dry the MPL does not impact the performance and water management. They noted that when the cell is wet, there is two-phase water flow.

Kim et al [68] tested a 25 cm² to investigate water transport through the fuel cell with different Microporous Layer configurations. Electrochemical Impedance Spectroscopy (EIS) was used to measure cell resistance and water balance was used to measure net water drag coefficient to explain the impact of the Microporous Layer. Kim et al [68] tested the cell configurations, the first one was the baseline without an MPL, the second one was with a cathode only MPL and the last one consisted of both an anode and cathode MPL. These configurations were also tested at three different relative humidities. The first scenario total water transfer coefficient is shown in Figure 8.6.1.

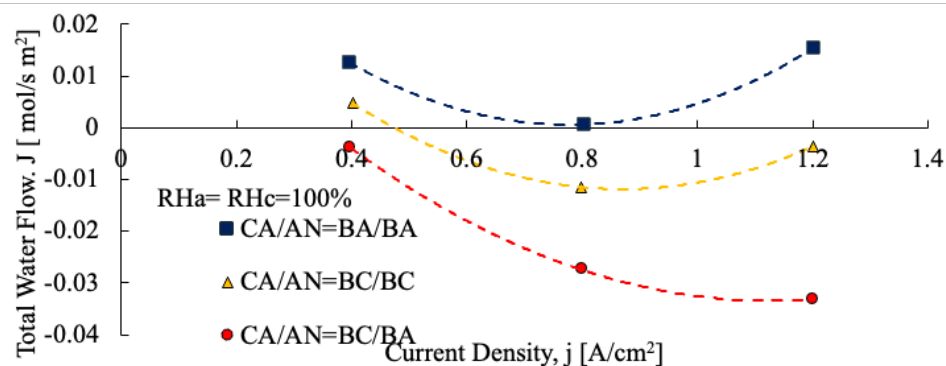


Figure 8.6.1 Total Water Transfer Coefficient with 100% RH Inlet Conditions [68]

The total water flow across the membrane was reported as the total water transfer coefficient and it does not show how the total water flow changes with current density. When the fuel cell did not have an MPL, the total water flow stayed positive even with both sides fully humidified, this indicates that electro-osmotic drag exceeds back diffusion. This case can be referred to as the baseline. The scenario with the cathode only MPL had the total water flow in the direction of cathode to anode at all current densities. In this case back diffusion exceeds electro-osmotic drag. The MPL has added a transport mechanism pushing the water flow toward the anode. The case without the MPL had the direction anode to cathode, the MPL is adding an additional model of water transport.

When the MPL was added to the anode and cathode, the total water flow started off positive and became negative. This indicates electro-osmotic drag exceeds back diffusion at low current densities but as current density increases the total water flow becomes negative. A scenario with only an anode MPL only was not examined. The fuel cell generates water on the cathode proportional to the current density, and there is a

point where liquid water is formed on the cathode. This is scenario will have a wet microporous layer. A microporous layer will have different performance in a dry fuel cell compared to a wet fuel cell.

The data water reported as the total water transfer coefficient and not the total water flow. The total water flow in all was not broken down into the electro-osmotic drag and back diffusion components, and as a result the electro-osmotic drag and back diffusion coefficient at each data point. It is also noted that largest total water transfer coefficient occurred when the membrane when only the cathode MPL is present. It appears that the MPL does add a new mode of water transport that occurs when the MPL is exposed to liquid water. Kim et al [68] also repeated the same test with different inlet condition, in this case the anode relative humidity was set to 100% and the cathode relative humidity was set to 70%, the results are shown in Figure 8.6.2:

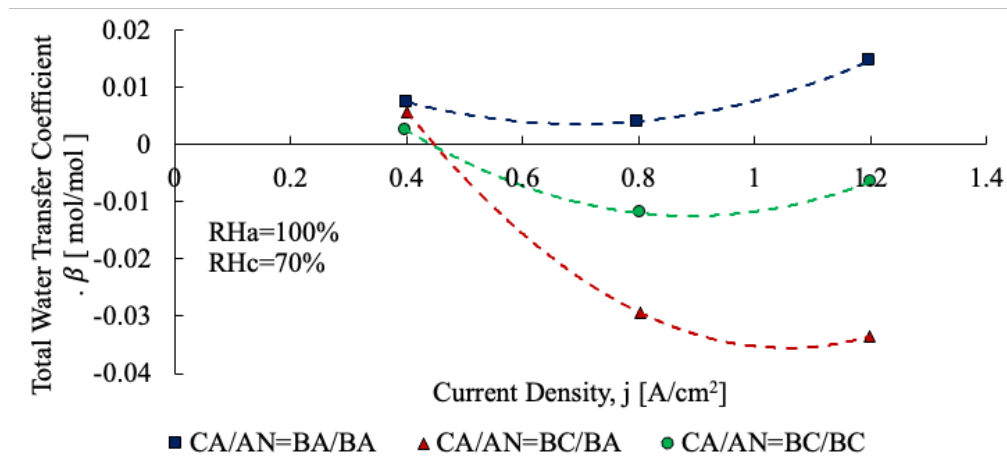


Figure 8.6.2 Total Water Transfer Coefficient with 100% and 70% RH Inlet Conditions [68]

The total water flow was reported as the total water transfer coefficient and not the total water flow. The case where there is no MPL, the total water flow is in the direction of anode to cathode. The electro-osmotic drag portion of the total water flow exceeds back diffusion. This case is the base line case. When the cathode MPL is added to the fuel cell, the total water flow started off positive at lower current density and became negative at higher current density. The cathode relative humidity is at 70%, and there is a point where liquid water is formed when the air becomes over saturated. The MPL changes once it is in the wet environment. When the anode MPL is added the total water flow starts off positive at lower current density and becomes negative at higher current densities. When liquid water is present, the MPL is considered wet. More data points are needed to find the exact transition point where liquid water is formed. It is not possible to fully understand which portion of the total water flow is electro-osmotic drag and which portion is back diffusion. The total water flow needs to be broken down into its component, but the current empirical coefficient models cannot be used. A method is needed to determine the electro-osmotic drag and back diffusion without assuming a transport coefficient.

Kim et al [68] stated that the MPL manages water by controlling the transport and distribution, as a result the membrane is hydrated, and oxygen transport resistance is lowered. Kim et al [68] stated that the MPL creates a capillary barrier to liquid water at the interface forcing liquid to water to be transported in the direction of cathode to anode, this is due to higher hydraulic pressure. The MPL also improves the removal of liquid

water preventing excessive water accumulation at the cathode. This improved water transport will reduce the risk of flooding. To gain further insight the total water flow must be examined and not the total water transfer coefficient.

Weber and Newman [69] also ran experiments attempting to understand how the micro-porous layer functions in the fuel cell, Weber and Newman [69] ran three configurations, one fuel cell with no MPL, a second fuel cell with a cathode MPL and the third fuel cell with both an anode and cathode MPL. The inlet relative humidity of the anode and cathode was set to 100 %. The total water flow across the membrane was reported as the total water transfer coefficient as shown in Figure 8.6.3:

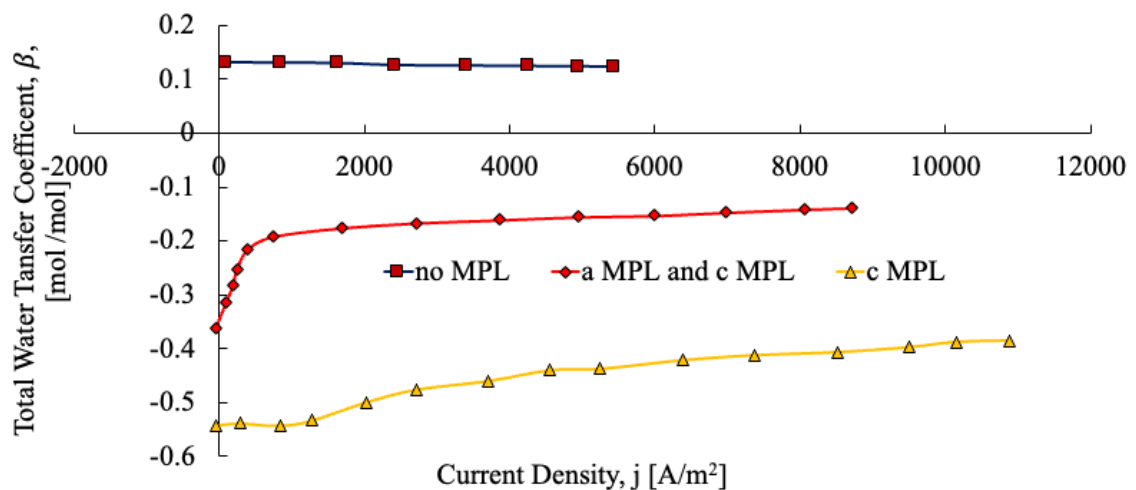


Figure 8.6.3 Total Water Transfer Coefficient with 100% and 100% RH Inlet Conditions [69]

The results were in the total water transfer coefficient and results need to be converted to total water flow. The total water flow was in the direction of anode to cathode without the MPL present, and this indicates that electro-osmotic drag exceeds back diffusion. When

the cathode MPL was introduced, the total water flow becomes negative direction changes to cathode to anode, this is evidence that back diffusion exceeds electro-osmotic drag the same occurred when the fuel cell had both cathode and anode MPL. Weber and Newman [69] theorized that the MPL acts as a valve pushing water to the anode and improving oxygen transport.

The MPL increases liquid pressure due to the lower permeability of the MPL and moves the water to the anode, by designing the MPL, it can help with membrane hydration.

The water transport from the MPL is not fully understood without understanding the electro-osmotic drag and back diffusion. It appears that the MPL does add an additional mode of water transport, but the MPL responds differently when the MPL is wet compared to being dry. This experiment only looks at a wet MPL. As in the Kim et al [68] the total water transfer coefficient provides insight, but the total water flow needs to be analyzed.

Gandomi et al [70] believed that the MPL can be engineered to control the total water flow across the membrane of the fuel cell. The total water transfer coefficient was reported for all experiments, and the fuel cells active area is 5 cm². Gandomi et al [70] examined different MPL configurations as well wet and dry fuel cell operation. The first scenario was tested with a MPL with the different inlet conditions. The total water transfer coefficient is shown in Figure 8.6.4:

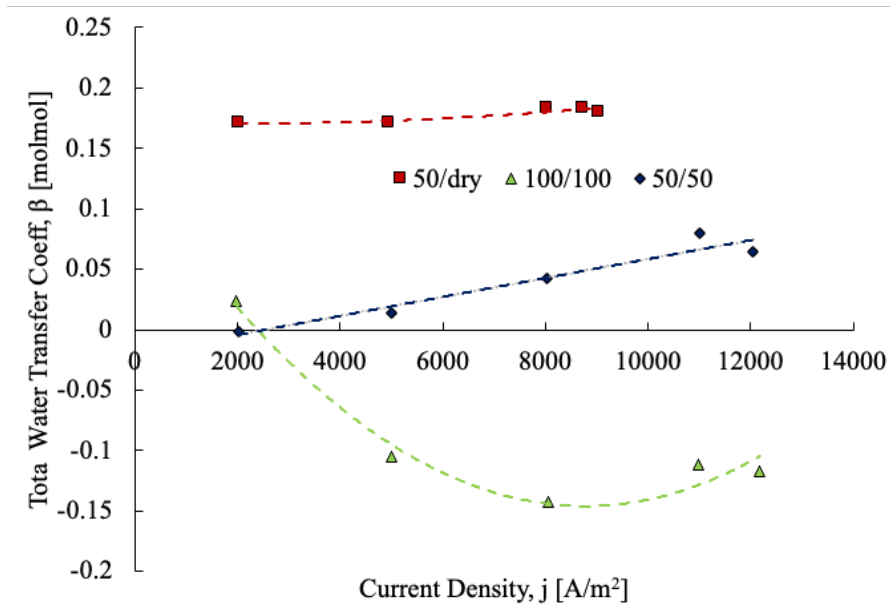


Figure 8.6.4 Total Water Transfer Coefficient with MPL 1 Conditions [70]

The total water flow was reported as the total water transfer coefficient and not the total water flow, it is not known how the total water flow changes with current density. When the fuel cell had a partially humidified anode and a dry cathode, the total water flow was positive indicating that electro-osmotic drag exceeds back diffusion. When the anode and cathode were at the same relative humidity the total water flow stayed positive for all current density but the total water across the membrane is less than the case when the cathode is dry. In this case the electro-osmotic drag exceeds back diffusion.

When both sides of the fuel cells are fully humidified the total water flow starts up positive but as the current density increase the flow reverses and back diffusion exceeds electro-osmotic drag.

When the anode was partially humidified and the cathode is dry, the total water flow across the membrane is positive, indicating electro-osmotic drag exceeds back diffusion. When the cathode relative humidity is increased the total water flow starts off positive and becomes negative at larger current density, and in the case where the anode and cathode were fully humidified the total water flow is negative for all current densities. For the dry conditions the total water flux was toward the cathode and in the 50%/50% case the flow started toward the cathode but when the current density increased, the flow direction changed but in the 100%/100% case the total water flux was always in the direction of cathode to anode.

Gandomi et al [70] had noted that the thermal resistance of the MPL can be tuned to lower phase change induced flow (PCI) from out of the cathode, and preventing the anode from drying out. Gandomi et al [70] noted the PTFE content influences the water material especially on the cathode and the MPL acts as a barrier to push water from the cathode. It was also noted that for wet operating conditions, the MPL lowers mass transport resistance of water and factors removal of water from the anode but in dry conditions the MPL needs to have a lower thermal resistance to reduce PCI flow and increase the back flux of water to the anode.

Gandomi et al [70] did not break down the total water flow into its electro-osmotic drag or back diffusion components and no insight into electro-osmotic drag and back diffusion can be obtained. The data reported was in terms of the total water transfer coefficient.

The total water flow needs to be analyzed to see what portion of the electro-osmotic drag and what portion is back diffusion. In addition to the decomposition of the total water flow, the impact of the MPL needs to be understood. The total water flow across the membrane needs to be understood to gain insight into electro-osmotic drag, back diffusion. Electro-osmotic drag and back diffusion need to be better understood to understand how water is transported by the MPL.

Atiyeh et al [71] attempted to understand performance and water transport in a PEM fuel cell with and without the microporous layer at various inlet relative humidity. Fuel cells were built with and without the MPL. The MPL configurations consisted of cathode only MPL, anode only MPL and MPL on both the anode and cathode. The MPL did keep the fuel cell in the ohmic region longer and delayed when the mass transport losses started. Only the total water transfer coefficient across the membrane has been recorded as shown in Figure 8.6.5:

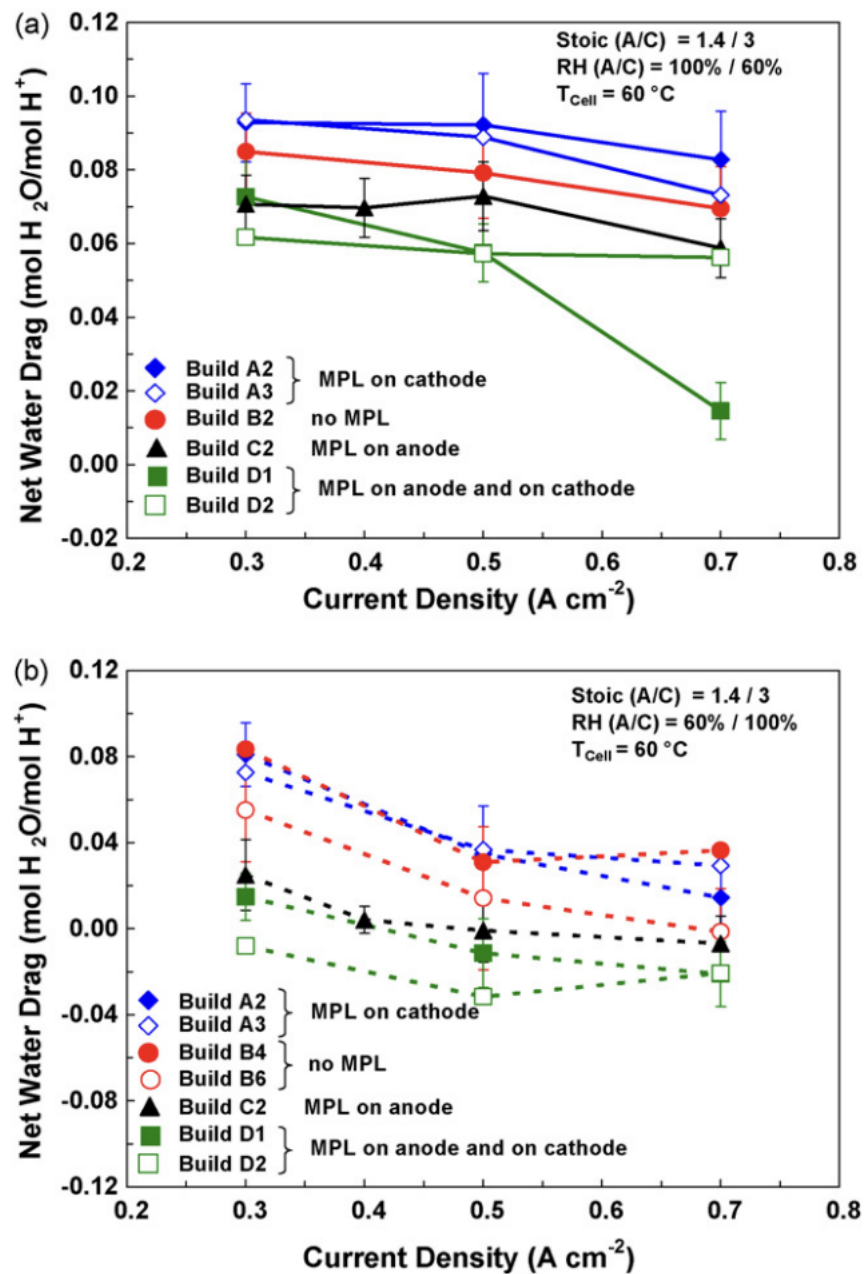


Figure 8.6.5 Total Water Transfer Coefficient with Different Fuel Cell Configurations [71]

Fuel cell configurations consisted of fuel cells without any MPL, fuel cells with a cathode MPL only and with fuel cells that had an anode and cathode MPL. The MPL

configuration does impact the total water flow. The MPL is adding a model of water transport, and it is being lumped in with back diffusion. In the first case the anode was fully humidified and the cathode water partially humidified. The data only indicates the direction of the total water flow, and the data needs to be converted into the total water flux to understand the electro-osmotic drag, back diffusion and mechanism of transport behind the MPL. The total water transport coefficient was reported and the impact to electro-osmotic drag and back diffusion coefficient was not reported. The total water flow needs to be obtained to calculate the electro-osmotic drag and back diffusion portions of the total water flow without assuming an electro-osmotic drag coefficient.

Yau et al [72] attempted to understand the Schroeder Paradox and MPL in total water flow experiments. The first step of the experiment was to understand the Schroeder Paradox and how water vapor and liquid water are impacted by concentration gradient. In the first experiment the cathode inlet relative humidity was varied from 0% to over 100%. The cathode air was oversaturated to produce liquid water and the total water flow across the membrane was reported as shown in Figure 8.6.6:

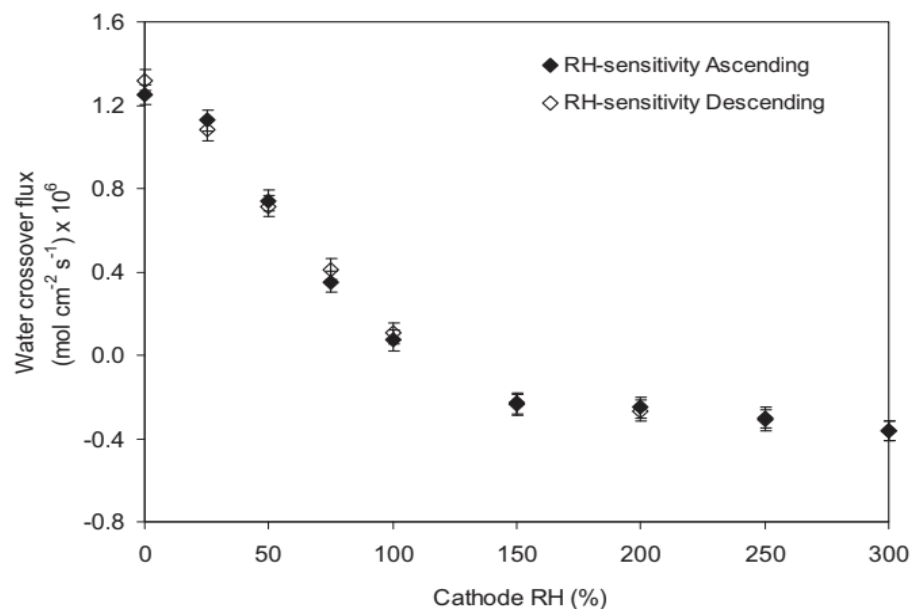


Figure 8.6.6 Total Water Transfer at Different Cathode RH [72]

The total water flow was reported, and the data will not need to be converted. As the relative humidity of the cathode increased, the water flux was increasing, when the cathode relative humidity was over 100% the direction of water reversed. There were two issues with the data, the first one was not plotted against the concentration gradient, and the second issue is that the fluid flow was not separated into its components. It is possible that other fluid drivers are present, and the data needs to be further analyzed.

The same experiment was repeated in this case a pressure component added. Even at the pressures the direction of the total water was not changed. The data does not reflect a concentration gradient only a cathode relative humidity. The total water flux was changing as the cathode relative humidity is increasing, when the cathode relative humidity is over 100%, the total water flow reverses. The total water flow trendlines are

different between the single- and two-phase region. The total water flow also needs to be broken down into its fundamental fluid drivers.

Lastly the MPL was examined, in this case the cathode relative humidity was 100%, and the anode relative humidity is 75%. In both cases and the total water flow was always in the direction of cathode to anode as shown in Figure 8.6.7:

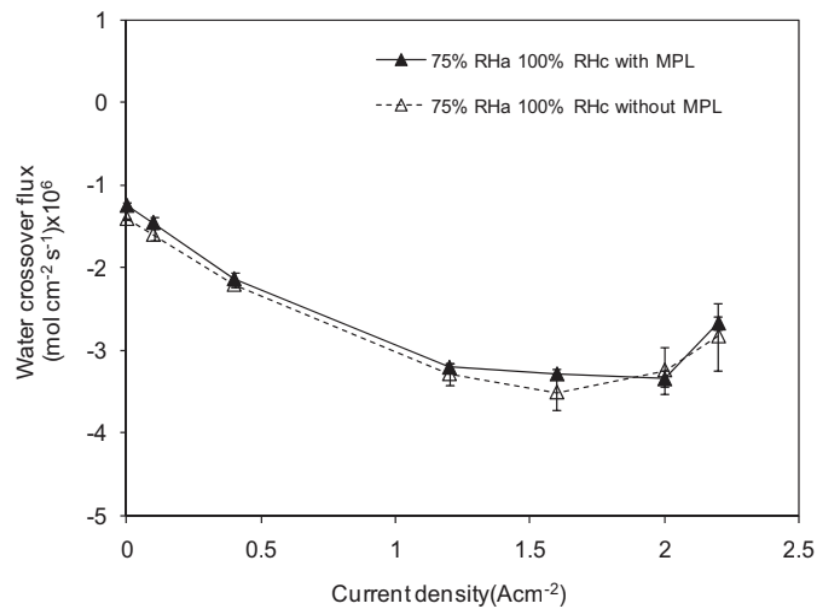


Figure 8.6.7 Total Water Transfer at various current density [72]

The total water flow across the membrane in both cases shows the total water flow was in the direction of cathode to anode. The data can be fit to a polynomial fit, and the data does not fit a linear trendline. In all the cases the water flow was not broken down into its fundamental components. The total water flow needs to be examined further to see how much of the total water flow was in the direction of electro-osmotic drag and back diffusion.

8.7 Microporous Layer (MPL)

In the PEM fuel cell, the membrane, catalysts layer and gas diffusion layers are required, the microporous layer is an optional component that has an influence of the fuel cell.

There has been research on which MPL configuration and what material work best for fuel cell performance, and how the MPL functions in dry and wet environments. One common theme is that the MPL only functions in wet conditions and does not provide function in dry environments [11] Zhou et al [11] noted that the MPL needs to be hydrophobic, and when the fuel cell is dry the MPL does not impact the performance and water management. They noted that when the cell is wet, there is two-phase water flow.

Kim et al [68] had reported the total water transfer coefficient and to compute the electro-osmotic drag and back diffusion coefficient, the total water flux needs computed with the current density and the total water flux for the fully humidified fuel cell is shown in

Figure 8.7.1:

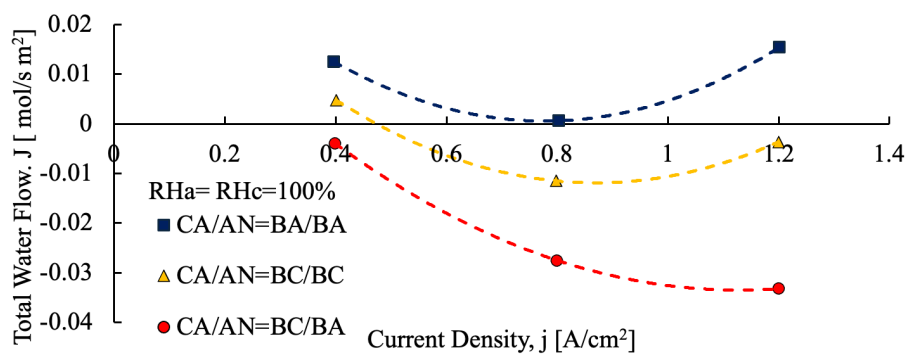


Figure 8.7.1 Total Water Flux the Membrane with MPL [68]

When the MPL is added to the cathode, all the total water flow is in the direction cathode to anode. In the case where both the cathode and anode MPL were added, the flow started off anode to cathode and at higher current densities the direction reversed, lastly the case with no MPL the flow stayed positive, and all the flow was in the direction of anode to cathode. In the second case examined by Kim et al [68] examined the cathode with a different relative humidity, as before the total water transfer coefficient has been reported and this needs to be converted to the total water flux. The total water flux is shown in Figure 8.7.2. The total water flow across the membrane is not linear in all cases.

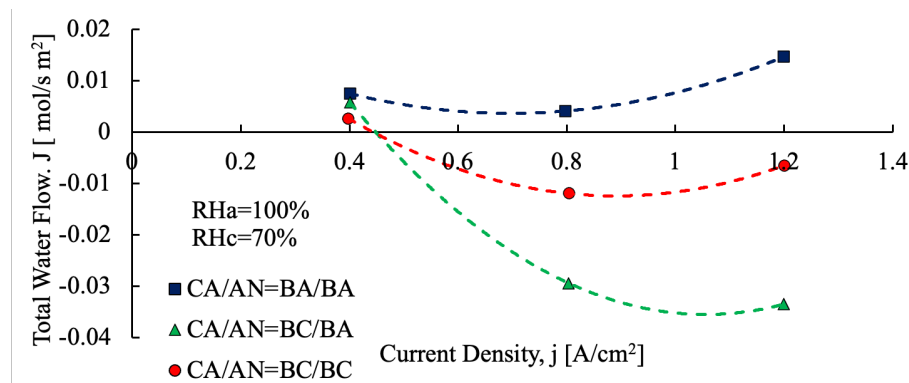


Figure 8.7.2 Total Water Flux the Membrane with MPL [68]

In the case with no microporous layers, the total water flow was in the direction of anode to cathode. When the cathode MPL was added, the flow started of anode to cathode, and it reversed. In the last case where the anode and cathode had a MPL the water flow across the membrane was positive then became negative. As the current density increases, the water generation at the cathode increases, which increases the probably of liquid water at the cathode. The last case Kim et al [68] examined was where the anode

was fully humidified and the cathode was only partially humidified as shown in Figure 8.7.3:

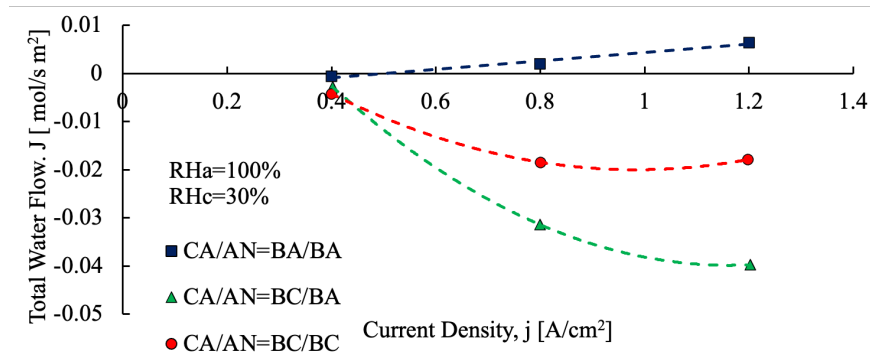


Figure 8.7.3 Total Water Flux the Membrane with MPL [68]

As in the other two cases, the case of no MPL has the total water flow in the direction of anode to cathode, and in the case where there is only the cathode MPL, the total water flow is in the direction of cathode to anode. Lastly in the case where the anode and cathode MPL are present the water flow was in the direction of cathode to anode.

Weber et al [69] performed work with the MPL on a fuel cell and examined a scenario where both the anode and cathode were fully humidified. When comparing the fuel cells confirmation it was done with only the total water transfer coefficient, the total water transfer coefficient needs to be used to obtain the total water transfer across the membrane. The total water flow across the membrane as shown in Figure 8.7.4:

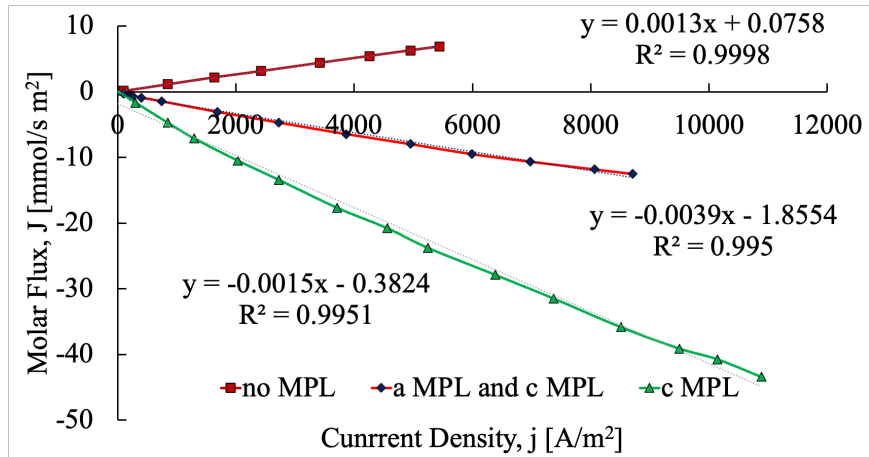


Figure 8.7.4 Total Water Flux the Membrane with and without MPL [69]

In the case with no MPL the total water flow was in the direction of anode to cathode, when the cathode MPL was added the total water flow reversed and when the MPL was on both sides the water flow across the membrane was in the direction of cathode to anode. The total water flow across the membrane was linear in all cases.

Gandomi et al [70] tested different configurations as well as different MPL configurations. In all cases the total water transfer coefficient was reported in all cases. The first case examined had the same MPL on the cathode and anode but ran the experiment with different inlet conditions as shown in Figure 8.7.5:

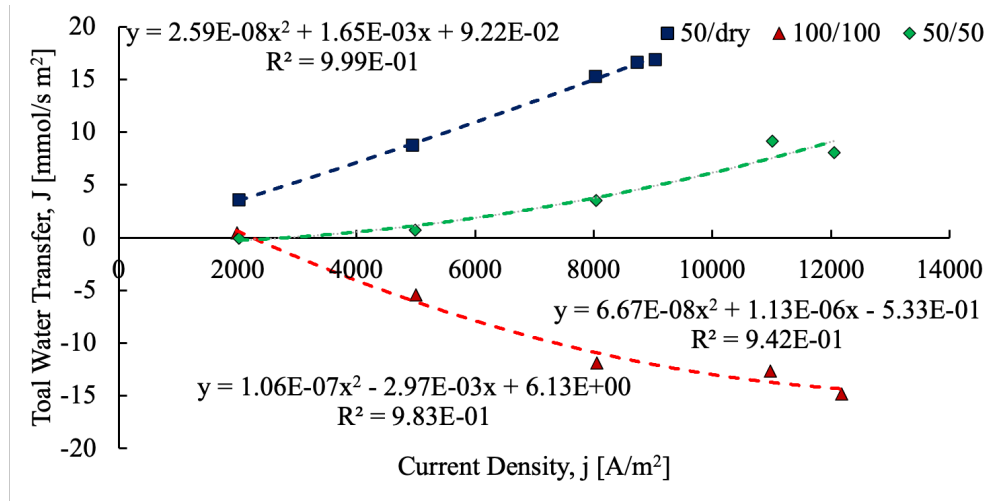


Figure 8.7.5 Total Water Flux the Membrane with MPL [70]

In the case where the cathode was dry, the total water flow stayed in the direction of cathode to anode, in the cases where the anode and cathode were partially humidified the direction of water flow was in the direction of anode to cathode, in the last case where both sides were humidified the total water flow was in the direction of cathode to anode.

Gandomi et al also noted that a phase change does occur with the addition of the MPL.

As in the other cases the case that the cathode dry have the water flow in the direction of anode to cathode, and in the case where the cathode partially humidified the total water started positive and became negative, and in the last case all the water flow was in the direction of cathode to anode (negative total water flow).

Atiyeh et al [71] also examined the impact of the MPL in the fuel cells, like others the total water transfer coefficient was reported, the first step is to convert the total water transfer coefficient to total water flux as shown in Figure 8.7.6:

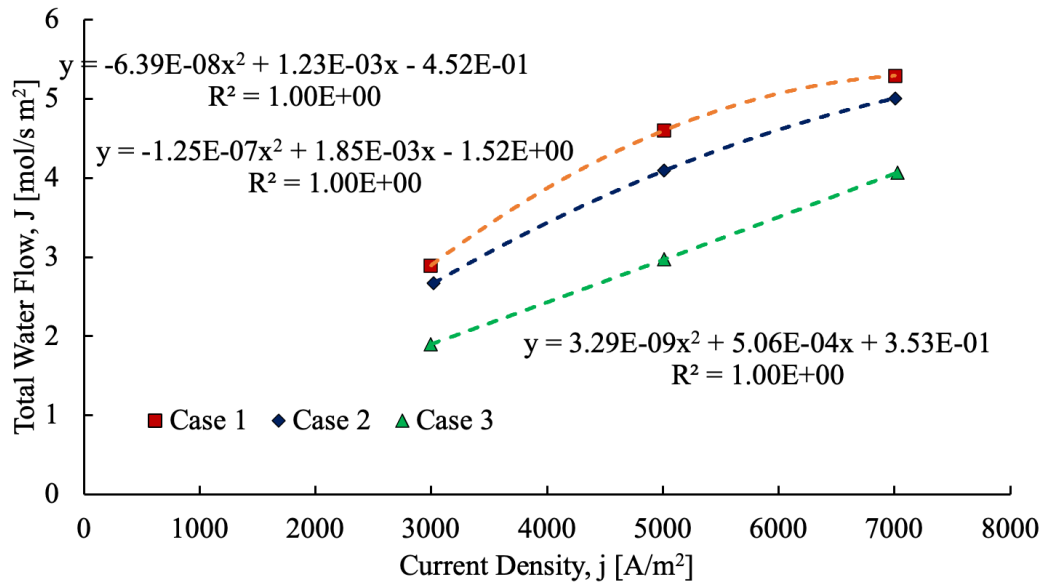


Figure 8.7.6 Total Water Flux the Membrane with MPL [71]

The testing was performed with the anode fully humidified and the cathode partial humidified. In the cases examined, the water flow was in the direction of anode to cathode for all current densities. The other case consisted of having the cathode fully humidified and the anode partially humidified shown in Figure 8.7.7:

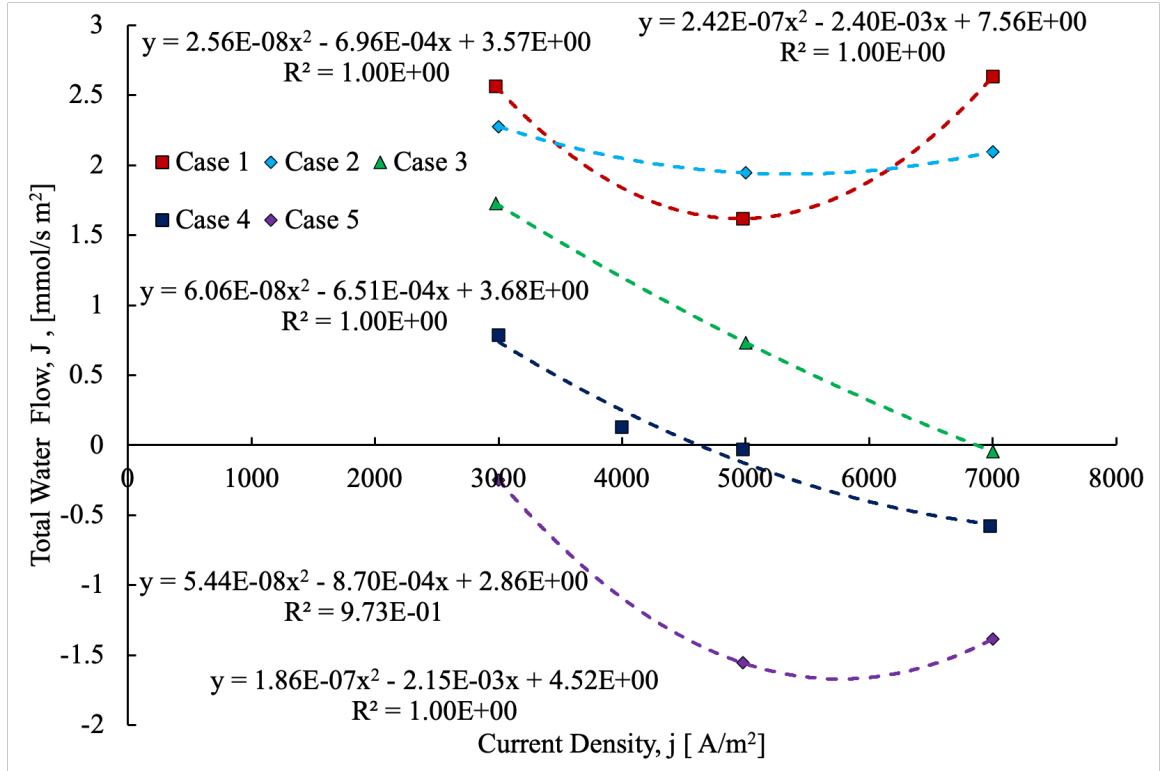


Figure 8.7.7 Total Water Flux the Membrane with MPL [71]

With the cathode humidification the direction of the water flow reversed and the direction of water flow from cathode to anode, the opposite of the previous experiment is 3.138.

Yau et al [72] examined water flow across the membrane and reported the total water flow, the total water flow was examined, and it was found that are two regions of water flow, the first region is the single-phase region, and the second region is the two-phase region as shown in Figure 8.7.8:

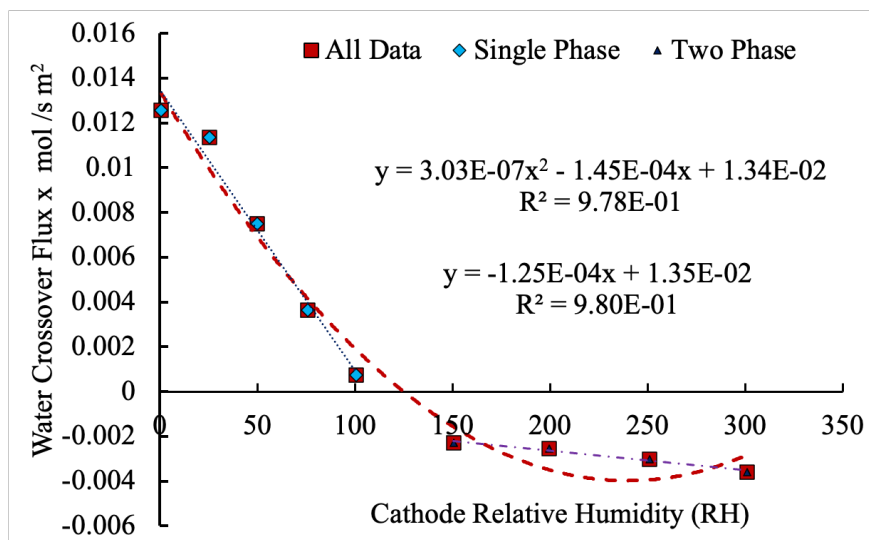


Figure 8.7.8 Total Water Flux the Membrane with MPL [72]

In the single-phase region, the flow followed the concentration gradient and, in the case, where there was liquid water the direction of water flow reversed the direction of water flow was in the direction of liquid to vapor.

Yau et al [72] examined a fuel cell with and without an MPL with the cathode fully humidified and the anode partially humidified, and the results are shown in Figure 8.7.9:

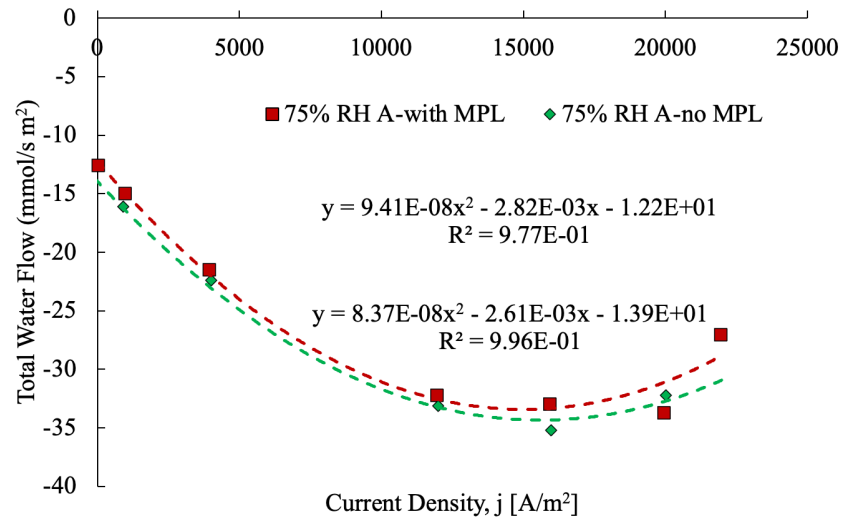


Figure 8.7.9 Total Water Flux the Membrane with MPL [72]

The total water flow data could not be fit to a linear trendline due to the total water flow pattern after 10,000 A/m². The water flow is in the direction of cathode to anode due to the liquid water present. Ingarra et al [128] has stated that the MPL only functions when liquid is present because the mode of water transport activated is either membrane distillation or osmotic distillation. The MPL is a hydrophobic material which is one of the criteria for membrane distillation and liquid water is present when the relative humidity exceeds 100%. In the case of experiments at isothermal conditions, the liquid water cannot move through the membrane, and it must evaporate and pass through the membrane as a vapor then condense. This is also the reason why when the cathode was dry the water flow was in the direction of anode to cathode, but once liquid water is formed membrane distillation will occur and the water flow will be liquid to vapor.

Membrane distillation is not covered by the Nernst-Planck equation. With this being true Darcy-Law would not apply to moving liquid water across the membrane. Note MPL must be hydrophobic material. The transport of water across the MPL is not fully understood. It is understood that the MPL has an impact on the fuel cell, but the mechanism of water transport is not understood. The common theme is that the MPL does remove water from the cathode, but there is not agreement on the mechanism.

8.8 The Microporous Layer Analysis of Total Water Flow

The MPL of the PEM of the fuel cell only functions when it is wet and does not provide function when the fuel cell is dry, this is due to membrane distillation. When liquid water is generated, it will start the membrane distillation process where vapor pressure difference will drive the water transport, since the water is formed in cathode the water transport will be in the direction of cathode to anode when the MPL is present on the cathode and with this new mode of water transport this will impact electro-osmotic drag and back diffusion.

Kim et al [68] ran experiments with a PEM fuel cell with different MPL configurations and with different inlet conditions. Everything was kept in the terms water transfer coefficient, and the total water flow was not broken down. Kim et al [68] first case examined was where the anode and cathode were fully humidified. The total water flow data was used to compute the electro-osmotic drag coefficient as shown in Figure 8.8.1:

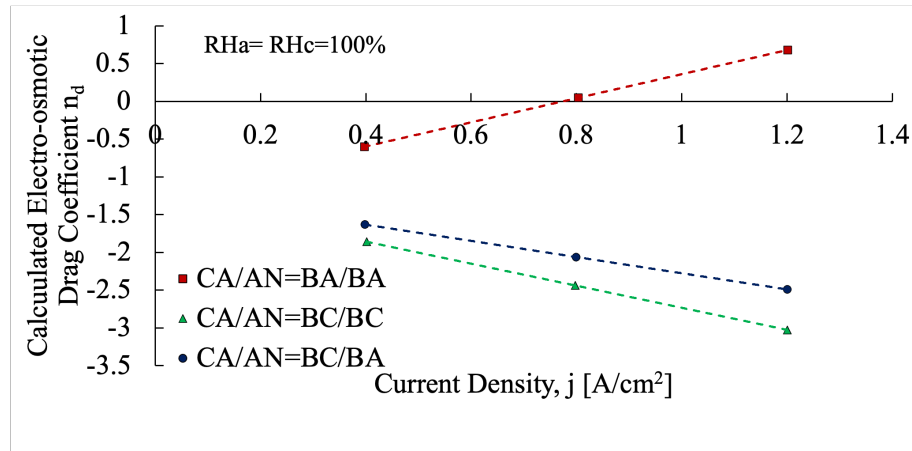
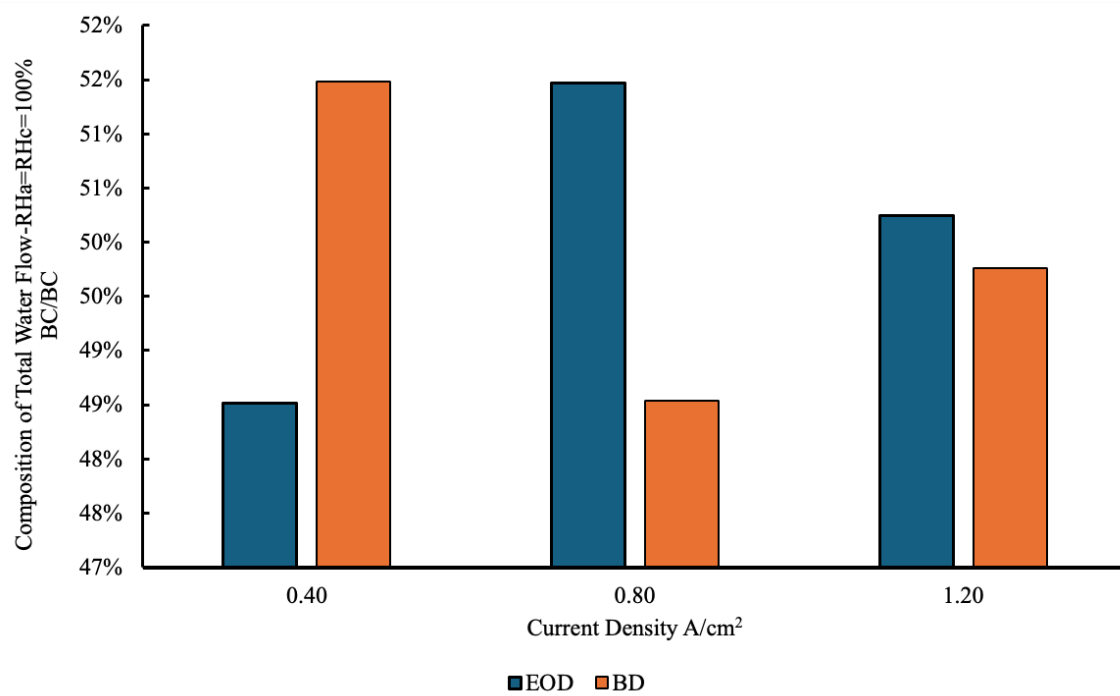
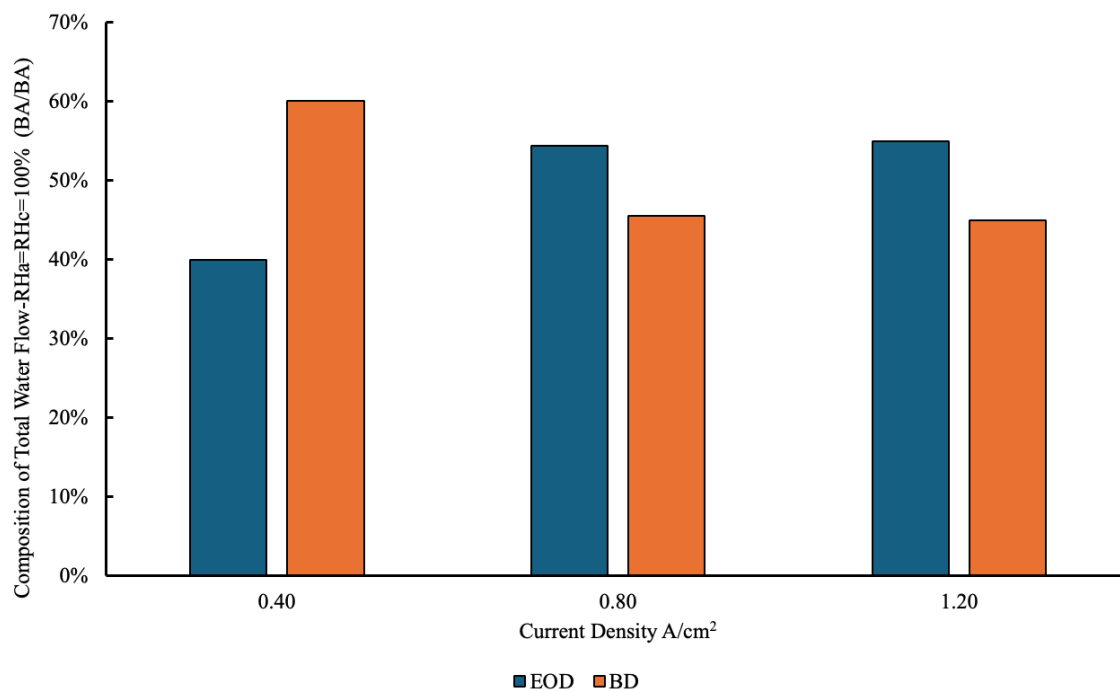


Figure 8.8.1 Electro-Osmotic Drag and Coefficient Calculations based on RH and MPL layer [68]

In the case without the MPL the electro-osmotic drag coefficient started off negative at lower current density and became positive. In the cases with the MPL, the electro-osmotic drag coefficient stayed negative for all current densities. In all cases the electro-osmotic drag is a function of the current density. The most severe cases are where the MPL are present. In the cases with the MPL present and liquid water is formed

The current Nernst-Planck equation only contains the electro-osmotic drag and back diffusion, thermal effects like thermal osmosis and membrane distillation. This the mechanism that is acting like back diffusion and masking electro-osmotic drag.

The total water flow was broken down into its electro-osmotic drag and back diffusion components as shown in Figure 8.8.2.



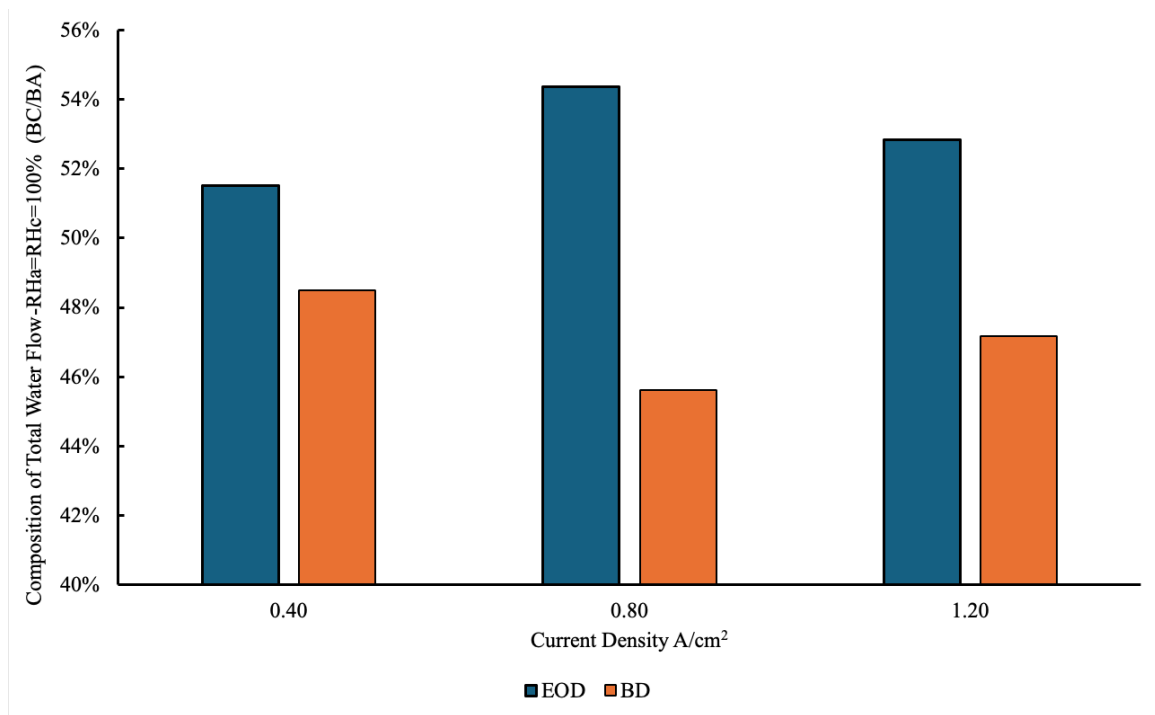


Figure 8.8.2 Composition of Total Water Flux [68]

In the scenario with both sides of the membrane were fully humidified and there is a high probability that liquid water will be produced at the cathode which would start membrane distillation. The cathode of the fuel cell will also be warmer than the anode and this difference will also drive fluid flow. The total water flow shows instance of electro-osmotic drag exceeding back diffusion and other instances where back diffusion exceeds electro-osmotic drag.

The second instance where Kim et al [68] examined was the 100% humidified anode and 70% humidified cathode. This scenario should promote electro-osmotic drag, and the total water flux was used to compute the electro-osmotic drag and back diffusion portion

of total water flow. The computed electro-osmotic drag coefficient is shown in Figure 8.8.3:

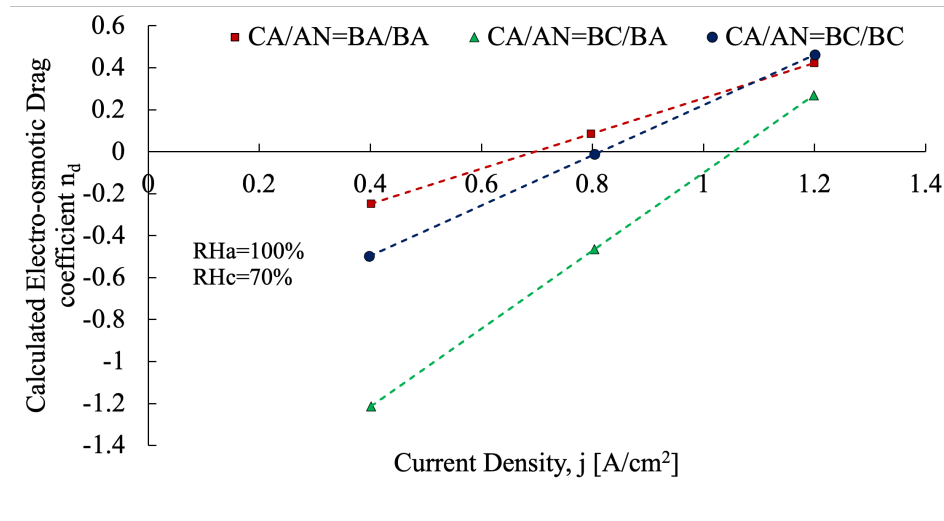
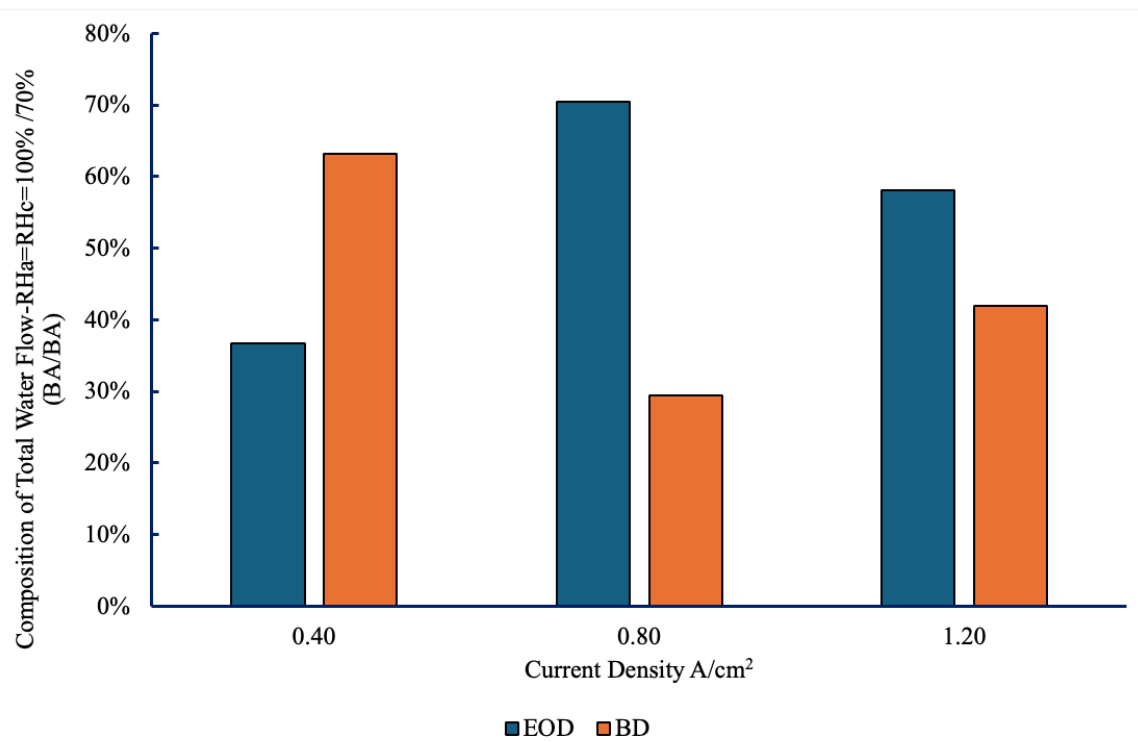
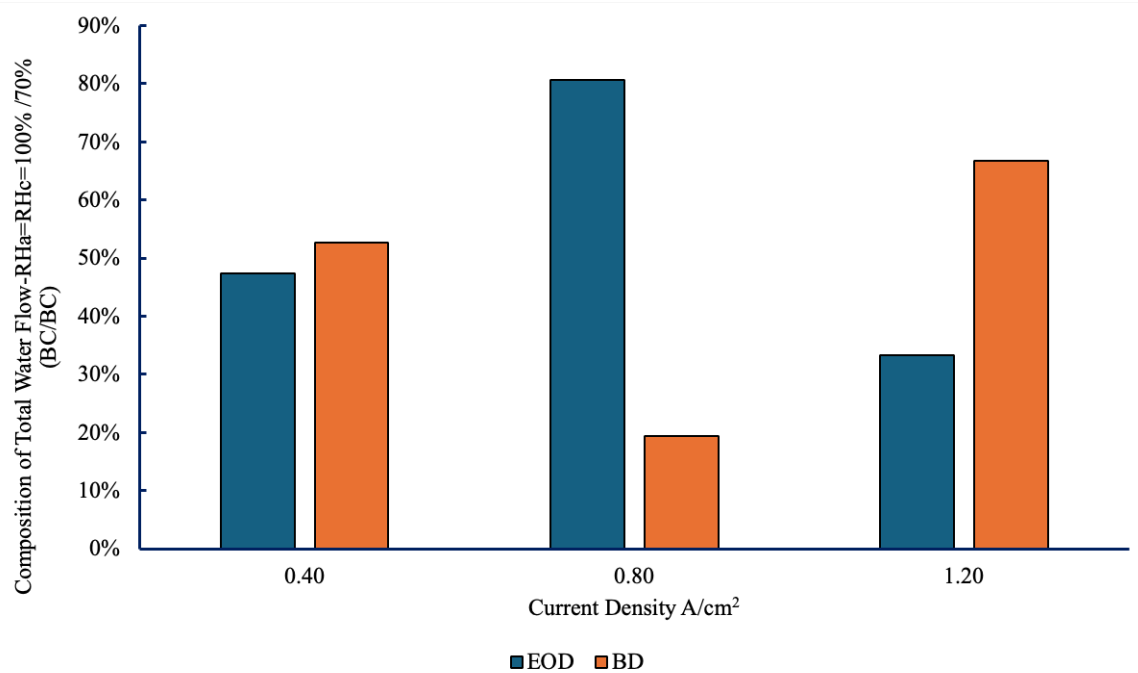


Figure 8.8.3 Electro-Osmotic Drag and Coefficient Calculations based on RH and MPL layer [68]

All the cases show the electro-osmotic drag coefficient is a function of current density.

The electro-osmotic drag started off negative briefly and became positive as current density increased. The most extreme change in electro-osmotic drag coefficient was when the fuel cell has a cathode MPL only. The total water flow was broken down into its electro-osmotic drag and back diffusion components as shown in Figure 8.8.4:



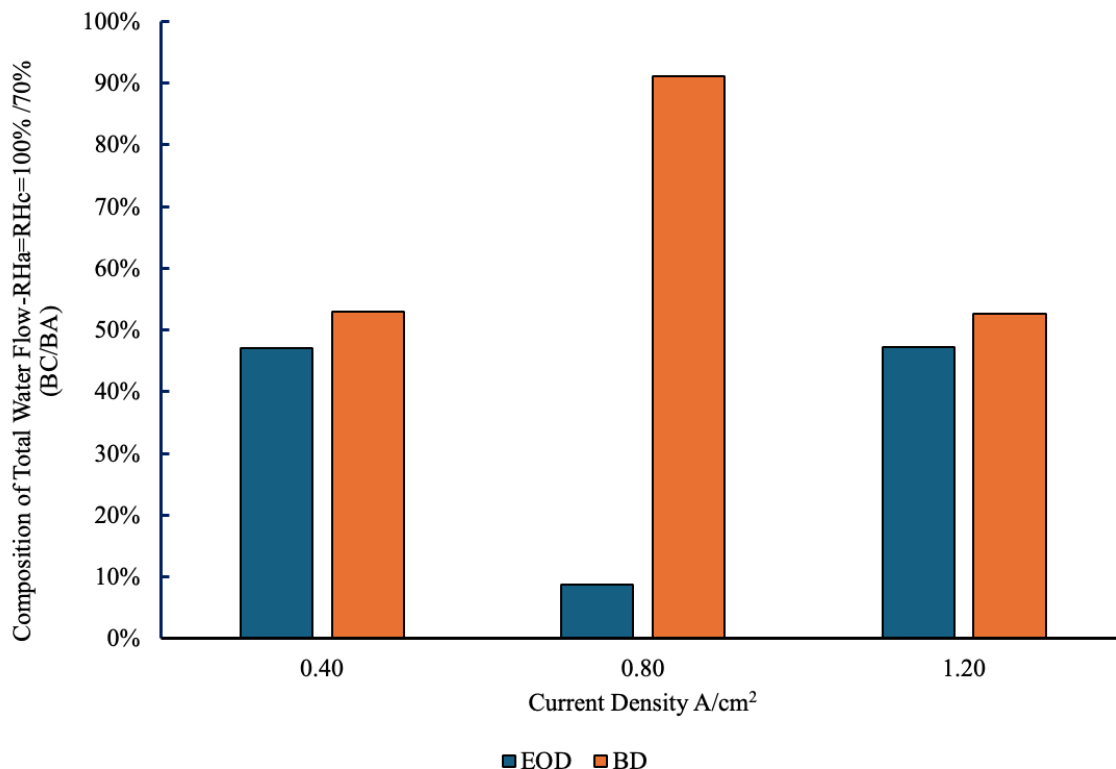


Figure 8.8.4 Composition of the Total Water Flow [68]

The water flow is broken down into two components electro-osmotic drag and back diffusion. With the anode fully humidified it should bias the water flow toward the cathode, but the cathode will typically be warmer than that anode. At lower current densities, the back diffusion does exceed electro-osmotic drag for all cases. At mid current density, the electro-osmotic drag exceeds back diffusion for two of the three cases, the exception is the cathode MPL, in this case the back diffusion does exceed electro-osmotic drag this could be due to the other fluid driver present, like membrane distillation. In the last case at high current density the electro-osmotic drag does exceed back diffusion for only one case when there is no MPL, but when the MPL is added the back diffusion does exceed electro-osmotic drag, this also due to the membrane distillation.

The last case examined the MPL configuration with the anode fully humidified with the cathode partially humidified. The total water flow data is being used to compute the electro-osmotic drag coefficient as well as the composition of the total water flow.

The computed electro-osmotic drag coefficient is shown in Figure 8.8.5:

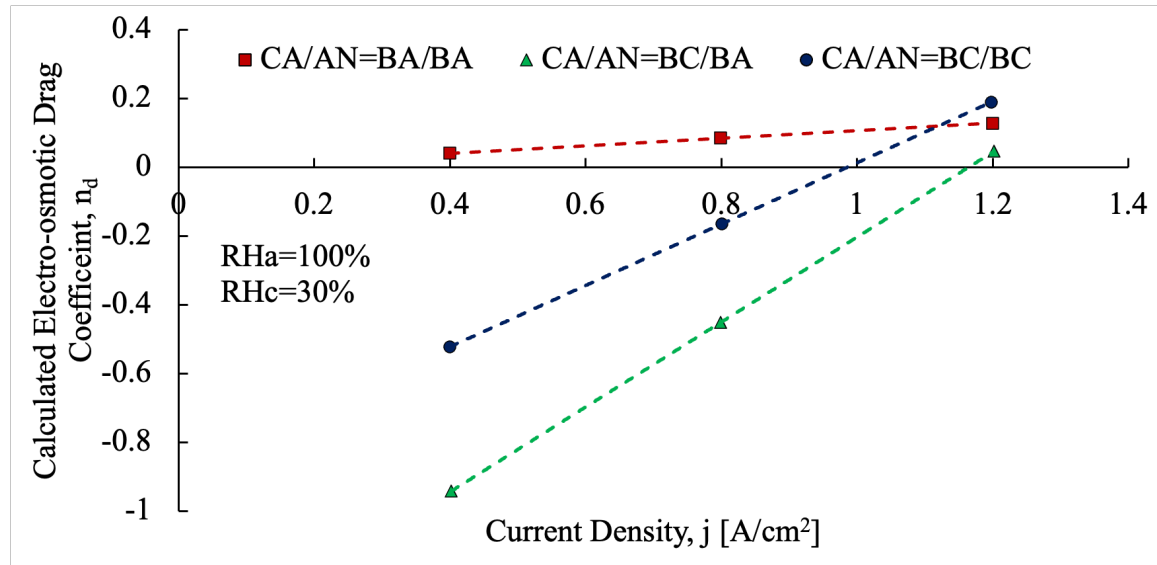
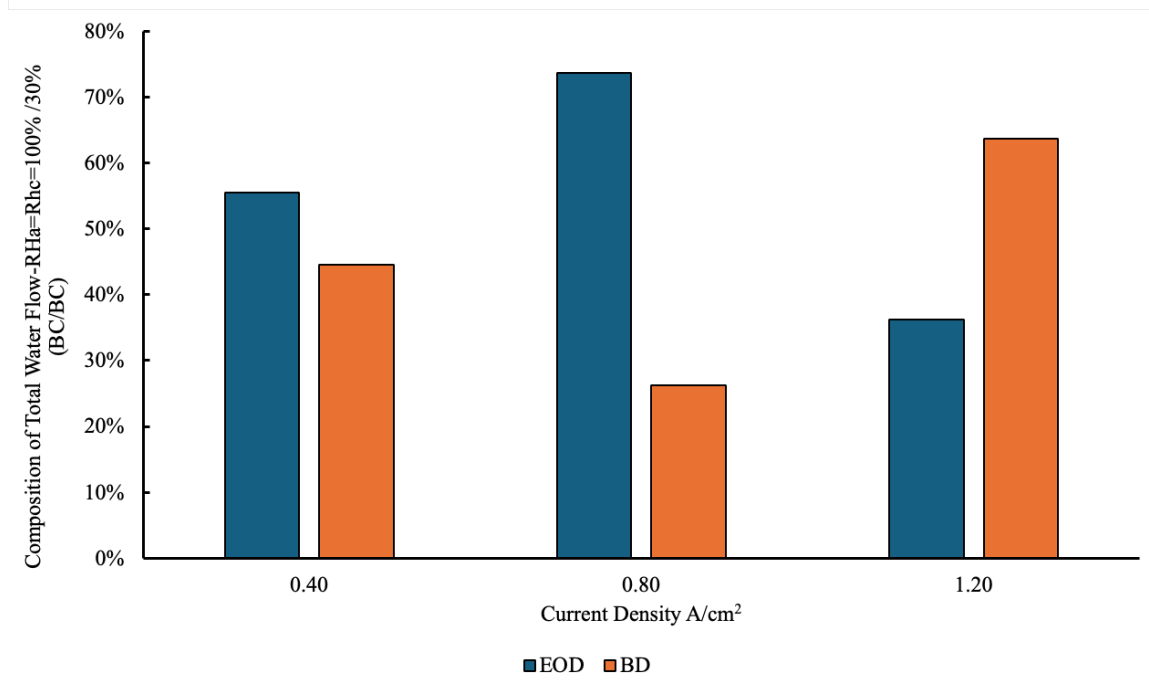
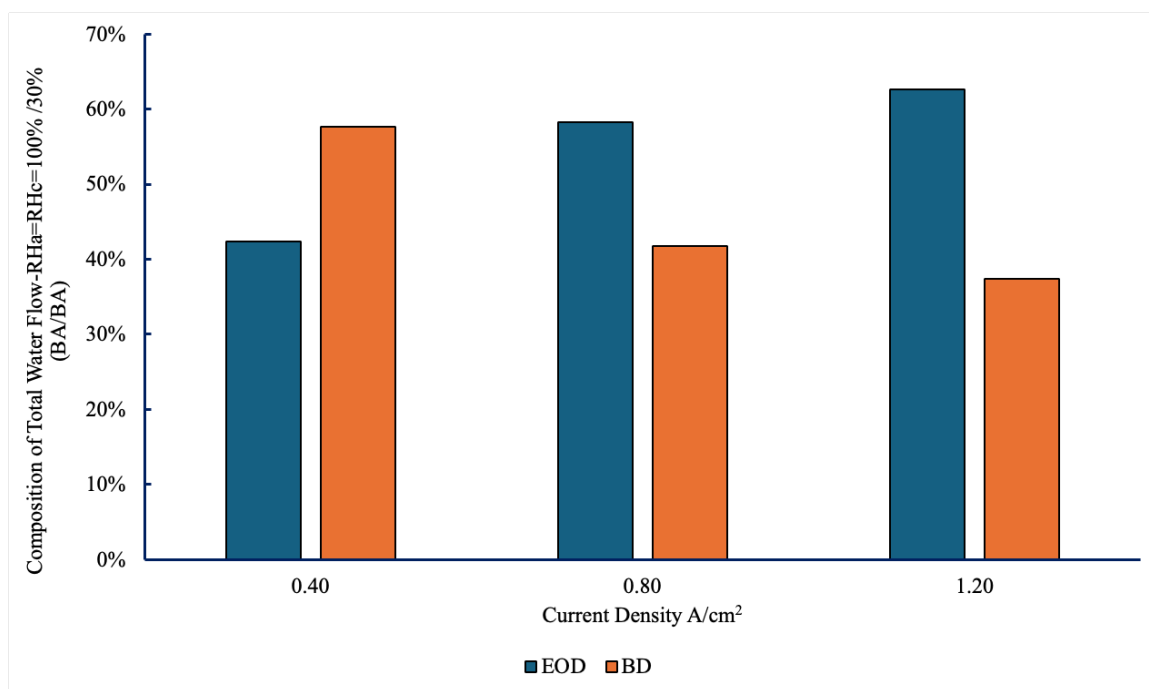


Figure 8.8.5 Computed Electro-Osmotic Drag Coefficient [68]

For the case with no MPL the electro-osmotic drag coefficient was positive for all current densities. When the MPL was added the electro-osmotic drag coefficient started off negative and became positive. In these scenarios with the anode is fully humidified and the cathode is partially humidified. The fully humidified anode will promote electro-osmotic drag. At higher current density the electro-osmotic drag coefficient becomes positive promoting flow from anode to cathode. The composition of the total water flow is shown in Figure 8.8.6:



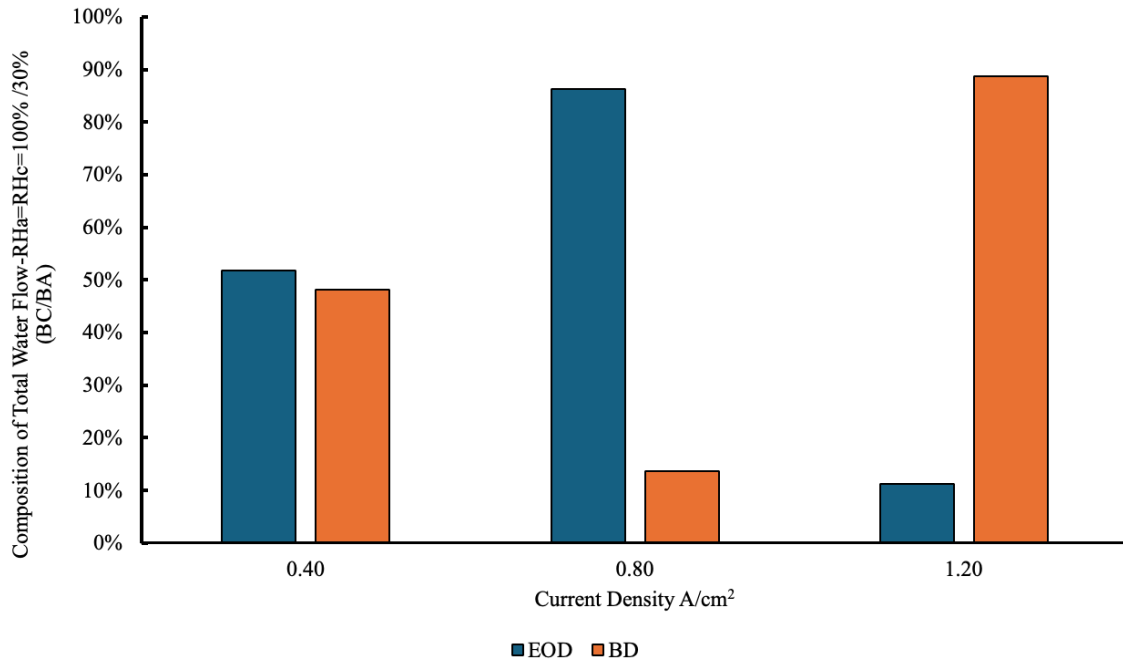


Figure 8.8.6 Composition of the Total Water Flow [68]

At low current density the back diffusion exceeded electro-osmotic drag for the case without an MPL. When the MPL was added electro-osmotic drag exceeded back diffusion for low current densities. At mid current densities electro-osmotic exceeded back diffusion in all cases. At high current densities the electro-osmotic drag exceeded back diffusion for only one case where no MPL was present. The other two cases with MPL the back diffusion does exceed electro-osmotic drag this is likely due to membrane distillation taking place. The MPL does play a role when the MPL is wet but not dry, this transport mechanism is not fully understood but Ingarra et al [128] indicates that the MPL will induce membrane distillation when liquid water is present on the cathode which will appear as back diffusion. The scenarios will out the MPL will only have electro-osmotic drag and back diffusion.

Weber et al [69] examined different configurations of the MPL for the PEM fuel cell only at full humidification of both the anode and cathode. The total water flow data was used to compute the electro-osmotic drag coefficient as well as the electro-osmotic drag and back diffusion components of total water flow. The calculated electro-osmotic drag coefficients are shown in Figure 8.8.7:

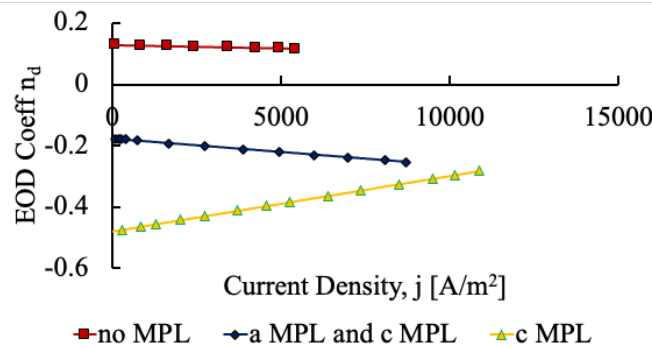
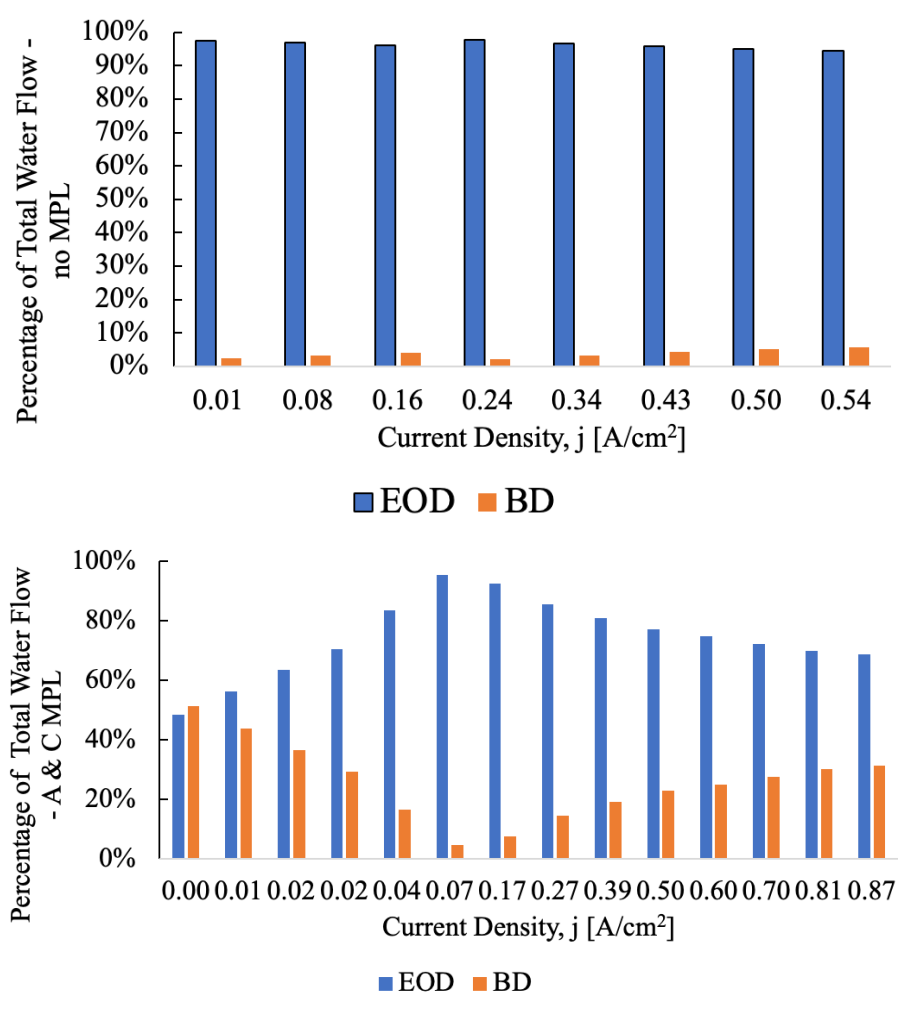


Figure 8.8.7 Calculated Electro-osmotic Drag Coefficient [69]

In the scenario without the MPL, the electro-osmotic drag coefficient is positive indicating the electro-osmotic drag is in the direction of anode to cathode. When the MPL is added to the fuel cell, the electro-osmotic drag coefficient becomes negative, and the direction of the electro-osmotic drag is cathode to anode. When only the cathode MPL is present the electro-osmotic drag coefficient is getting further negative, and when both the cathode and anode MPL present the electro-osmotic drag coefficient is starting negative and becomes less negative. In all three cases the electro-osmotic drag coefficient is a function of current density. The MPL is moving water flow in the direction of cathode to anode. Both the anode and cathode were fully humidified; at other inlet conditions it is not known how the MPL will function. When the MPL is not present the water flow in

the fuel cell is in the direction of anode to cathode, the MPL does switch the mode water of water transport and reverses it, and the electro-osmotic drag becomes a stronger function of current density. The composition of the total water flow is shown in Figure 8.8.8:



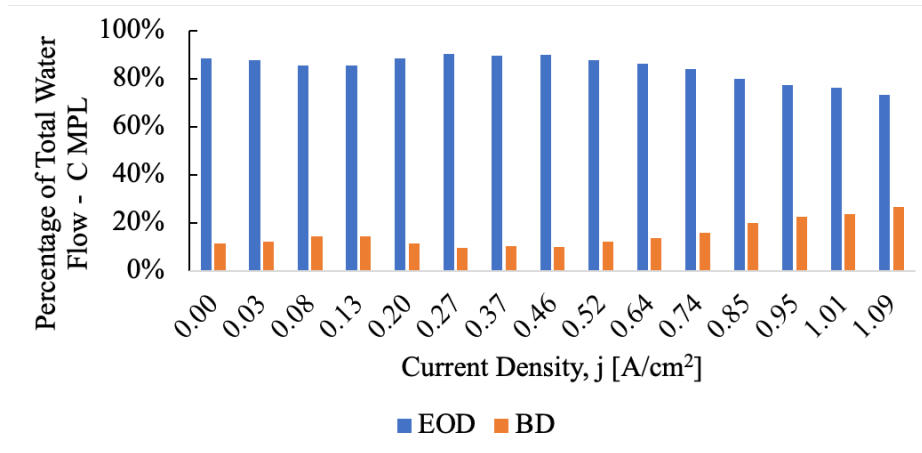


Figure 8.8.8 Composition of total water flow

Weber et al [69] did not break down the total water flow nor did they compute the electro-osmotic drag coefficient. The water generation of the fuel cell is proportional to the current density so as current density increases, the water produced on the cathode will increase also. All the cases have electro-osmotic drag dominate over back diffusion. The electro-osmotic drag portion could be dominate because with the 100% humidity water formed on the cathode would be condensed to liquid because of the oversaturation of air. The fluid driving forces changes when MPL is added, the MPL adds another mode of water transport.

Gandomi et al [70] theorized that the MPL could be used to engineer water flow across the membrane, their research consisted of running different configurations of MPL and different inlet conditions. The total water flow data is used to calculate the electro-osmotic drag coefficient as well as the electro-osmotic drag and back diffusion component of the total water flow. The first case examined was to examine the same

MPL on the anode and cathode. The three scenarios are where the anode is at 50% RH and the cathode is dry, the second is where the anode is at 50% and the cathode is 50% and the last where the anode and cathode are fully humidified. The calculated electro-osmotic drag coefficient is shown in Figure 8.8.9:

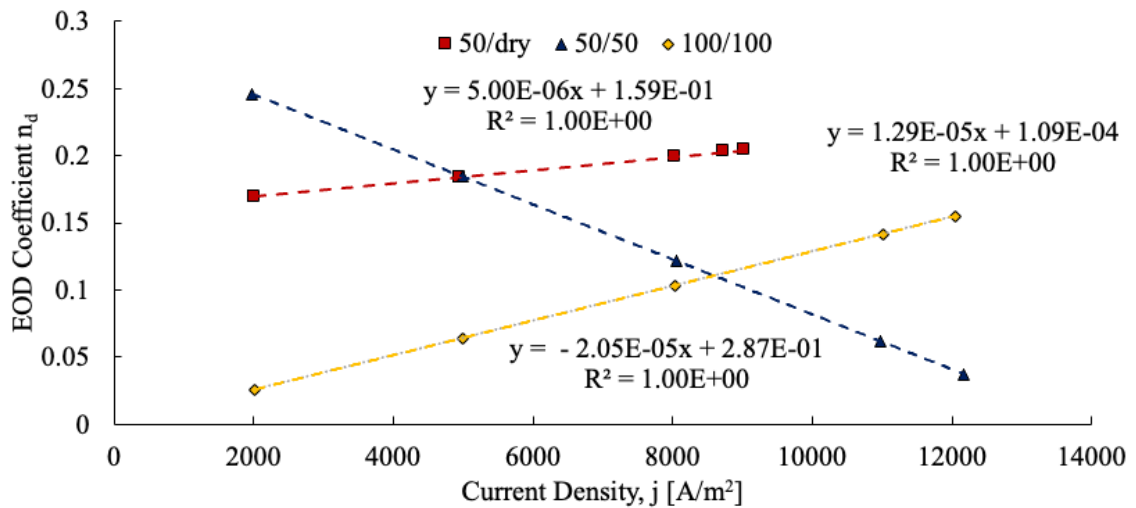
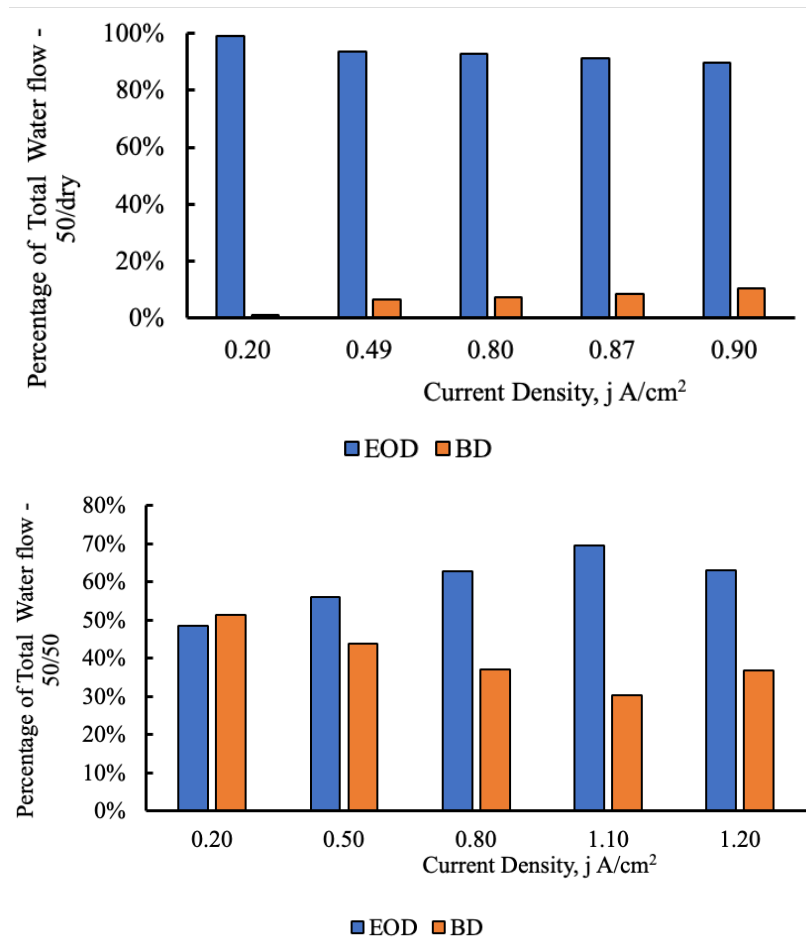


Figure 8.8.9 Calculated Electro-osmotic Drag Coefficient [70]

When the cathode is dry, the electro-osmotic drag coefficient is positive indicating the electro-osmotic drag is in the direction of anode to cathode. In this scenario there is no liquid water due to the cathode being dry and membrane distillation will not drive water from cathode to anode. When the cathode partially humidified, the electro-osmotic drag coefficient is still positive, but the electro-osmotic drag coefficient is lower than the scenario when the cathode is dry. In the 50%/50% RH scenario there will be a point where liquid water is formed and once membrane distillation occurs water flow start to reverse direction of water flow.

In the last case where the anode and cathode are fully humidified the electro-osmotic drag coefficient is decreasing with current density, the other two cases had the electro-osmotic drag coefficient increase with current density. The electro-osmotic drag coefficient is decreasing due to the liquid water formation on the cathode which will start membrane distillation. The total water flow broken down into its electro-osmotic drag and back diffusion components as shown in Figure 8.9.10:



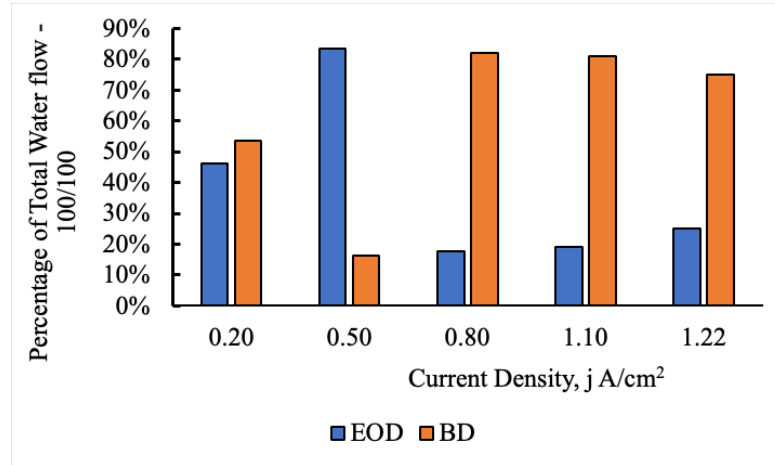


Figure 8.9.10 Composition of total water flow [70]

In the case where the cathode is dry, was the only case where electro-osmotic drag continuously exceeded back diffusion, in the 50/50 case the electro-osmotic drag exceeded back diffusion for all but once case and that was when the current density was low. When the anode and cathode were fully humidified the back diffusion was dominant in all but one case. When the cathode is dry electro-osmotic drag is dominant except for the higher current density, in the case where the cathode is partially humidified at higher current densities back diffusion exceeds electro-osmotic drag, this is due to the formation of liquid water and the start of membrane distillation. When both the anode and cathode are fully humidified the any water formed in the cathode will results in liquid water and this liquid water will produce membrane distillation which will look like back diffusion.

The addition of the MPL will impact the total water flow when added to the fuel cell, the MPL will act differently when liquid water is present, the hydrophobic nature of the membrane will introduce membrane distillation when liquid water is present.

Aityeh et al [71] had tested fuel cell and reported the total water transfer coefficient, the total water flow was used to obtain the electro-osmotic drag coefficient and the electro-osmotic and back diffusion portion of the total water flow. The calculated electro-osmotic drag coefficient is shown in Figure 8.9.11:

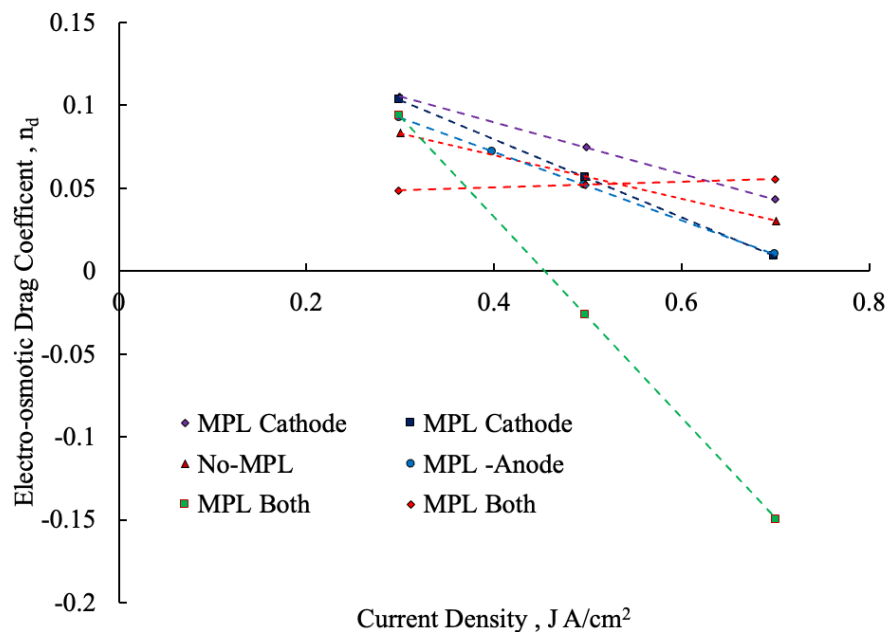
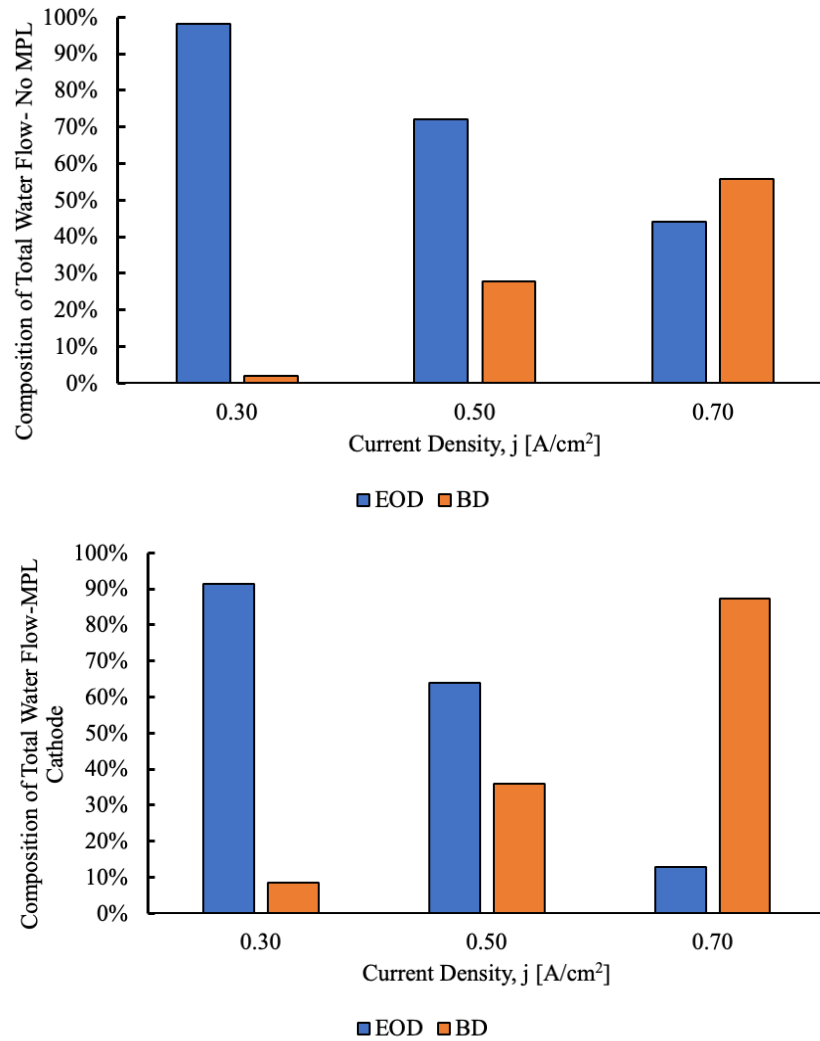
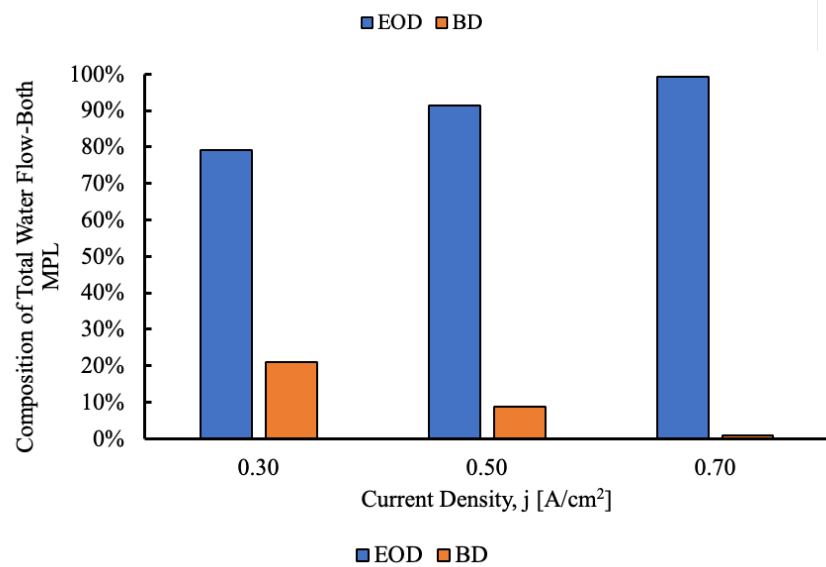
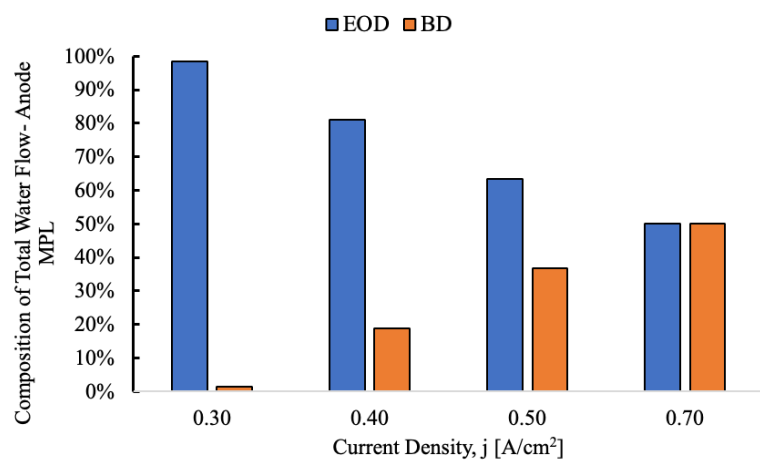
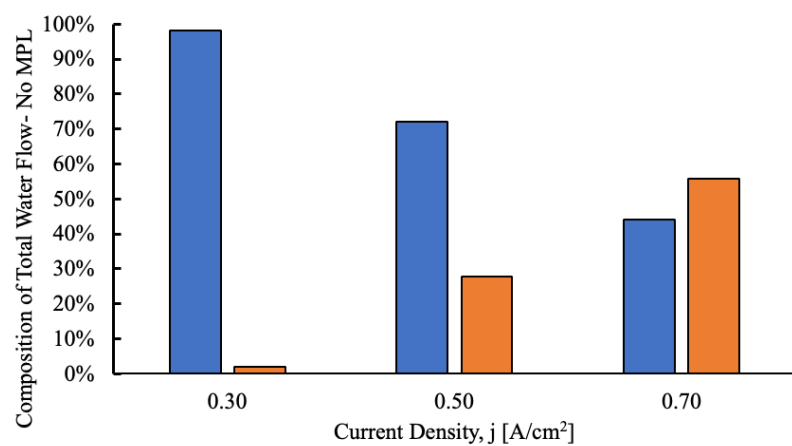


Figure 8.9.11 Calculated Electro-osmotic Drag Coefficient [71]

All the cases show that electro-osmotic drag is a function of current density. The electro-osmotic drag is decreasing with current density. The case with the most severe change was when the anode and cathode MPL are present. In this scenario the anode is fully humidified, and the cathode is partially humidified. At 100% humidity there is a high probability of liquid water present and with liquid water present membrane distillation

will occur. The fully humidified anode will maximize electro-osmotic drag. The cathode MPL will induce membrane distillation once liquid water is present. The composition of the total water flow is shown in Figure 4.96:





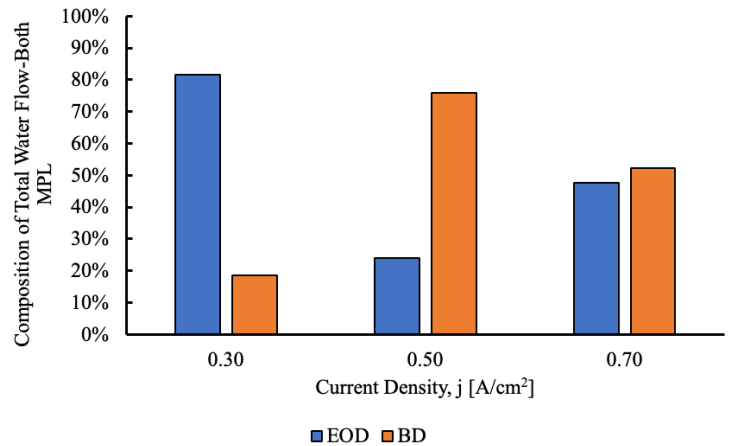


Figure 8.9.12 Composition of the total water flow [71]

In one of the Cathode MPL scenarios, the back diffusion at high current densities exceeds electro-osmotic drag. The anode was fully humidified, and the cathode was only at a 60% RH. The second scenario was where the cathode was fully humidified and the anode was partially humidified the total water flow is used to compute the electro-osmotic drag coefficient and compute the electro-osmotic drag and back diffusion portion of total water flow. The membrane distillation will occur once the liquid water is present by the MPL. The electro-osmotic drag and back diffusion portion of the water flow vary with current density and fuel cell configuration. With a fully humidified cathode, the cathode MPL makes back diffusion dominate because of the membrane distillation will occur when liquid water will be present. The cathode MPL has the most impact on the back diffusion.

Aityeh et al [71] did not break down the total water into its primary fluid drivers, everything was kept in terms of the total water transfer coefficient. The total water flow

can be decomposed into its primary drivers, when a MPL is added another fluid driver is added and it is membrane distillation.

Yau et al [72] experimented with understanding Schroeder Paradox and the Microporous Layer (MPL). In the first total water flow experiment, consisted of single-phase and two-phase water flow. The data was replotted where the total water flow was plotted against the concentration difference as shown in Figure 8.9.13:

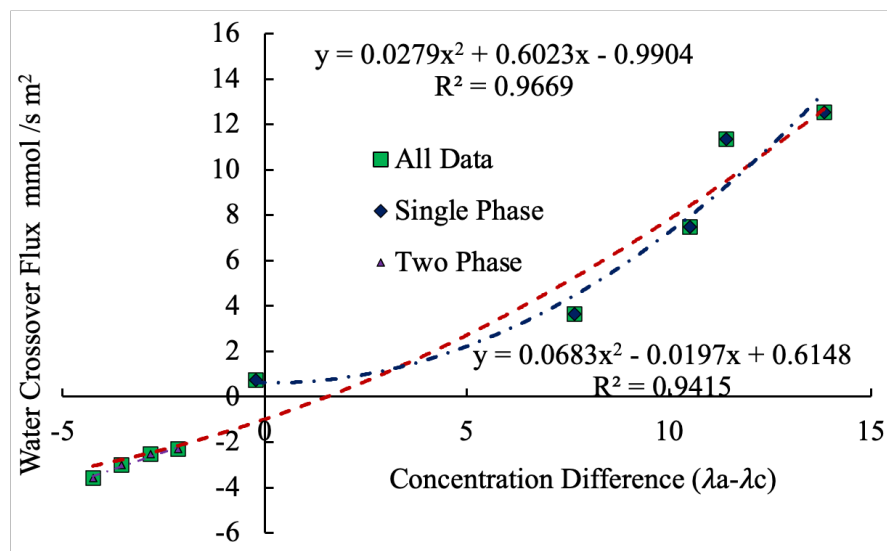


Figure 8.9.13 Total Water Flux vs Concentration Gradient [72]

When the data is replotted the concentration difference becomes negative, and this explains the difference in the total water flow. There is a difference in the single- and two-phase water flow. The one side was fully humidified, and the other side had a variable relative humidity. The concentration gradient is negative and that changes the direction of the water flow, this change could also be due to osmotic distillation. When

the cathode is about a 100% RH liquid water will be in the cathode and this will push water toward the anode.

Yau et al [72] also examined the total water flow with and without MPL in a fuel cell. The cathode was fully humidified, and the anode was partially humidified. The total water flow was used compute the electro-osmotic drag coefficient as shown in Figure 8.9.14:

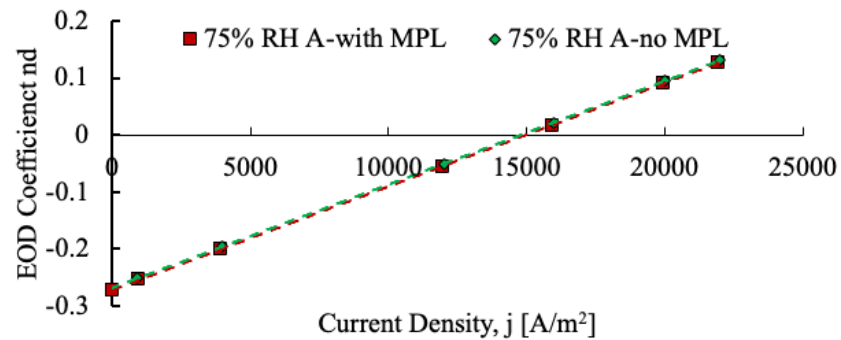


Figure 8.9.14 Calculated Electro-osmotic Drag coefficient [72]

The electro-osmotic drag coefficient is increasing with current density with and without the MPL. The cathode was fully humidified. With the electro-osmotic drag coefficient is known the electro-osmotic drag portion of the total water flow and back diffusion can be computed as shown in Figure 8.9.15:

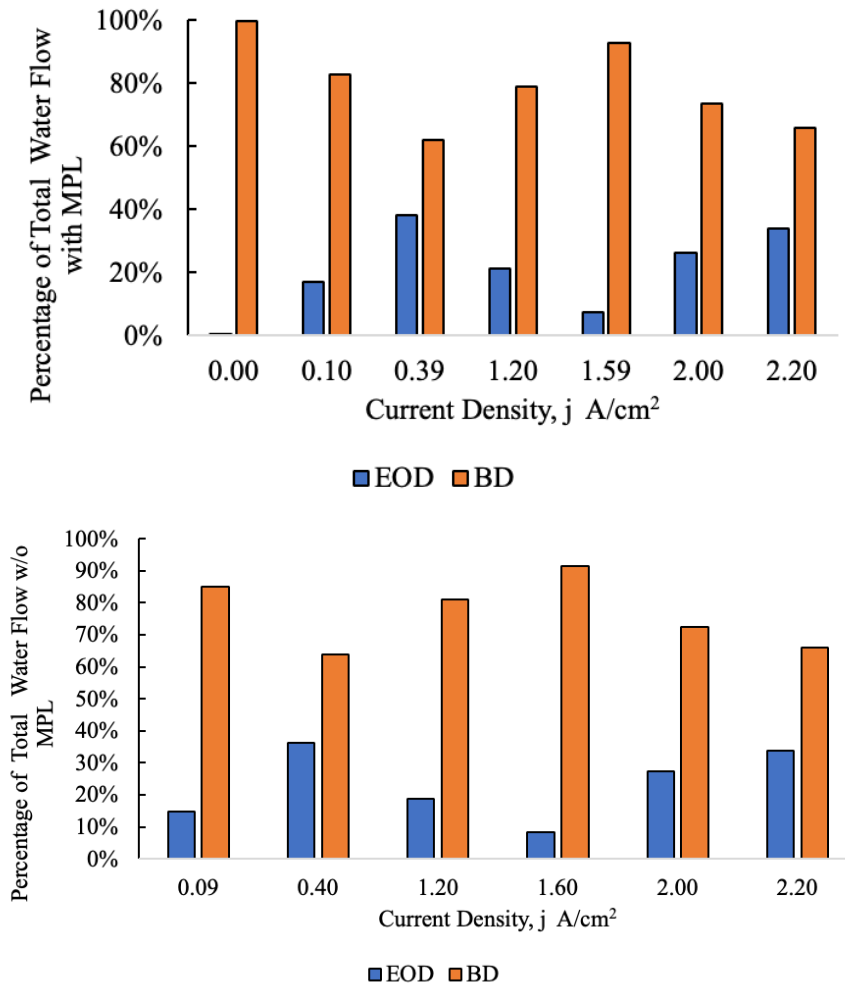


Figure 8.9.15 Total Water Flow Decomposed [72]

The back diffusion portion of the total water flow exceeds electro-osmotic drag. With the fully saturated cathode, back diffusion and membrane distillation will reduce the impact of electro-osmotic drag. The total water flow can be broken down into its primary fluid drivers without assuming any transport coefficients and the composition of the total water flow can be further examined. Membrane distillation also explains why the MPL only functions when wet. Membrane distillation was not broken out of the total water flow; it was still lumped in with electro-osmotic drag and back diffusion because additional

testing is required to obtain membrane distillation. Membrane distillation can be obtained by measuring the water transport liquid on one side and vapor on the other side with the vapor pressure known on one side along with temperature on both sides of the membrane known.

As in the other osmotic pressure case, the empirical model could be coupled with a theoretical model to determine the coefficient transport for osmotic pressure but based in other cases the proposed method shows that the total fluid flow is not the same as the osmotic pressure fluid flow. The reprocessed data shows that other fluid drivers are present besides osmotic flow. When gases are present, membrane distillation will not occur, but thermal osmosis will. The proposed method will calculate the thermal osmosis transport coefficient along with the thermal osmosis portion of the total flow fluid. The thermal osmosis fluid flow will confirm the magnitude and direction of the fluid flow.

8.9 Discussion

The MPL in the fuel cell only works there a temperature driven fluid drive, it is membrane distillation. Membrane distillation will occur when liquid water is present, and the membrane is hydrophobic. The liquid water cannot pass through the membrane so it must evaporate then it will pass through the membrane and then condense. This will only occur when liquid water is present. The direction will always be in the direction of liquid to vapor. The current analysis does not separate the membrane distillation from the back

diffusion, but it would appear as back diffusion because it will be in the same direction of back diffusion. More work needs to be done into membrane distillation and add it to fuel cell modelling.