ABSTRACT

Title of Dissertation: ANALYSIS OF MASS TRANSFER IN ELECTROCHEMICAL MEMBRANE PUMPING DEVICES Joseph Baker, Doctor of Philosophy, 2022 Minta Martin Professor Reinhard Radermacher Department of Mechanical Engineering Description

Considering the environmental challenges posed by traditional energy systems, we must strive to seek out innovative strategies to sustainably meet today's demands for energy and quality of life. Energy systems using electrochemical (EC) energy conversion methods may help us to transition to a more sustainable energy future by providing intermittent renewable energy storage and improving building energy efficiency. EC pumping devices are a novel technology that use chemical reactions to pump, compress, or separate a given working fluid. These devices operate without any moving parts. Unlike mechanical pumps and compressors, they operate silently, producing no vibrations and requiring no lubrication. In this dissertation, I investigate EC pumping devices for use in two applications: ammonia EC compression for intermittent renewable energy storage and EC dehumidification for separate sensible and latent cooling.

Hydrogen fuel cells are a promising technology for on-demand renewable power generation. While storage of pure hydrogen fuel remains a problem, ammonia is an excellent hydrogen carrier with far less demanding storage requirements. EC ammonia compression opens the door to several possibilities for separating, compressing, and storing ammonia for intermittent power generation. Using the same proton exchange membranes commonly used in fuel cells, I demonstrated successful ammonia compression under a variety of operating conditions. I examined the performance of a small-scale ammonia EC compressor, measuring the compression and separation performance. I also conducted experiments to investigate the steady-state performance of a multi-cell ammonia EC compressor stack, observing a maximum isothermal efficiency of 40% while compressing from 175 kPa to 1,000 kPa. However, back diffusion of ammonia reduced the amount of effluent ammonia by as much as 67%.

Dehumidification represents a significant portion of air conditioning energy requirements. Separate sensible and latent cooling using EC separation of water may provide an energy efficient thermal comfort solution for the hot and humid parts of the world. I conducted experiments of several EC dehumidifier, considering both proton exchange and anion exchange processes. Diffusion of the working fluid was significant in this application as well. I observed a maximum Faradaic efficiency for dehumidification of 40% for a 50 cm² cell using an anion exchange membrane under the most favorable case. I developed a novel open-air EC dehumidifier prototype. To alleviate the back diffusion issue, I investigated a method for mass transfer enhancement using high-voltage fields. I also developed a numerical model to simulate the performance of the EC dehumidifier devices, predicting the experimentally measured performance to within 25%.

ANALYSIS OF MASS TRANSFER IN ELECTROCHEMICAL MEMBRANE PUMPING DEVICES

by

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Dedication

To my family.

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Nomenclature

Α	Area, cm ²
С	Concentration, mol·cm ⁻³
CL	Catalyst layer
D	Diffusivity, cm ² ·s ⁻¹
Ε	Electric potential
EC	Electrochemical
F	Faraday's constant, 96,485 C·mol ⁻¹
GC	Gas chromatograph
GDL	Gas diffusion layer
h_m	Mass transfer coefficient
i	Current density, $A \cdot cm^{-2}$
Ι	Total current, A
j	Electrode current density, A.cm ⁻²
jo	Exchange current density, A·cm ⁻²
k	Heat transfer coefficient
М	Molar Mass g∙ mol ⁻¹
'n	Mass flow rate, $g \cdot hr^{-1}$
MEA	Membrane electrode assembly
MFC	Mass flow controller
MFM	Mass flow meter
Ν	Number of cells/molar flux, -/mol·(cm ² s) ⁻¹
'n	Molar flow rate, mol·hr ⁻¹
n_d	Electroosmotic drag coefficient, -
р	Partial pressure, kPa
Р	Total pressure, kPa
PEM	Proton exchange membrane
r	Area-specific resistance, $\Omega \cdot cm^2$
R	Universal gas constant, 8.314 J·(mol·K) ⁻¹
S	Source term
sccm	standard cubic centimeter per minute
Sh	Sherwood number
Т	Temperature, K
и	Velocity, cm/s
V	Voltage or overpotential, V
V	Specific volume, cm ³ ·mol ⁻¹
W	Compression work, W
X	Molar fraction/Through MEA distance, -/cm
Z.	Valency, -

Greek Characters

α	Charge transfer coefficient, -
δ	Experimental error, -
ε	Specific energy consumption for dehumidification, $\mu g \cdot J^{-1}$
3	Porosity, -
η	Efficiency/Overpotential, -/V
λ	Membrane water uptake, $mol_{H2O} \cdot (mol_{SO3-})^{-1}$
ρ	Density, g cm ⁻³
σ	Electrical/Ionic conductivity,
τ	Tortuosity, -
ω	Molar humidity ratio, $mol_{H2O} \cdot (mol_{O2})^{-1}$

Subscripts and Superscripts

Anode
Activation overpotential
Cathode, critical point
Concentration overpotential
Discharge
Electrochemical efficiency
Effective value
Inlet
Ohmic overpotential
Isentropic
Isothermal
Arbitrary index for chemical species
Knudsen diffusion
Limiting current density
Ionomer-phase
Reversible potential
Saturated
Total voltage
Water vapor
Water

1. Introduction

The electrochemical (EC) compressor is a solid-state compression device that uses an EC reaction to incite mass transport of a given working fluid across a solid membrane. For decades, scientists and engineers have conducted experiments and simulations focused on electrochemical hydrogen compression [1-3]. However, more recent experiments have demonstrated that electrochemical compression is possible with a variety of working fluids, including ammonia [4-6]. Moreover, these studies have demonstrated powered EC membranes are capable of more than just vapor compression.

EC membrane separation is a flexible technology suitable for both vapor compression and extraction. Using a series of chemical reactions, I can selectively transport vapor species from areas of low concentration to areas of high concentration. While there exist myriad potential applications for EC separations, I limited the scope of the present research to ammonia vapor compression and water vapor dehumidification. I explored the transport processes that occurred in the membrane and in the surrounding fluid streams. I evaluated the effectiveness and energy requirements of different EC process through laboratory experiments and numerical simulation.

An EC compressor, pump, or separator device consists of three main components: the gas distribution channels, the electrodes, and the membrane. The gas distribution channels, supply the working fluid to the electrodes, which are made of a porous, electrically conductive material. For any useful reactions to occur, at least two gas

species must be present: the working gas and a carrier gas. The working gas and the carrier gas react on the suction-side of the separator, forming a new ionic specie. Ions pass through the membrane, while neutral molecules do not. When the ions traverse the membrane from one electrode to the other, the reaction step causes the ion to decompose into its constituent molecules. A second gas distribution channel receives the fluid from the discharge electrode. Catalyst layers between the membrane and the electrode lower the reaction energy barriers, decreasing the energetic requirement of the process. Different reactions are unlocked through selection of appropriate membrane and catalyst materials.

I refer to the assembly of the membrane, catalyst layers, and the gas diffusion layers, which sandwich the catalyst-coated membrane and assist in the supply and removal of the products and reactants, as the membrane electrode assembly (MEA). Additionally, gaskets are required to prevent fluid leakage from the gas channels. A diagram of the cell assembly is depicted in Figure 1.



Figure 1. Diagram of an EC cell

The forward transfer of chemical species through the membrane is known as electrolysis. However, it is not the only form of mass transfer occurring in the membrane. While the membrane provides a high degree of separation between the anode and cathode flow channels, some species still readily diffuse across. Typically, diffusion occurs in the direction opposite to the electrolytic flow, hampering the cell's performance. Moreover, it is possible for ions to carry over some polar molecules through dipole interactions, a phenomenon known as electroosmotic drag. In the suction side of the EC cell, the working and carrier gases move into the gas diffusion layer (GDL). They must move through the porous GDL and catalyst layer (CL) through diffusion. Because of the mass transfer resistances between the membrane and flow channels, large concentration differentials may exist between the two sides of the membrane, which increases the amount of energy required to maintain the process and promotes parasitic back diffusion. Figure 2 diagrams the modes of mass transfer occurring in the MEA.

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Figure 2. Mass transfer phenomena in the MEA

1.1. <u>Ammonia Compression</u>

Ammonia is among the most useful and widely produced chemical products today. The naturally occurring compound is indispensable for agriculture and is one of the oldest known refrigerants. Additionally, ammonia may be a potentially significant carbon-free energy vector via ammonia fuel cells [7] or in internal combustion engines [8]. Vapor compression is essential to conventional heat pumps and power generation applications require high pressure storage of liquid ammonia; therefore, an efficient ammonia compressor becomes necessary for both refrigeration and energy storage applications. In recent years, researchers have become increasingly more interested in the use of ammonia for alternative power-generation and energy storage [9-13]. Traditional ammonia production generates a large amount of carbon dioxide, as the hydrogen needed for the process most often comes from fossil fuel sources. Researchers are investigating methods for low-carbon, membrane-based ammonia production via the Haber-Bosch process [11] and underscoring its importance as an energy vector in future carbon-free energy landscapes [12]. EC methods are a promising path forward toward the end of renewable ammonia production.

Tao et al. published the first demonstrations of EC ammonia compression available in open literature [14,15]. In their preliminary study, they performed small-scale, closedsystem compression experiments, demonstrating the ability of an EC cell to pressurize ammonia vapor, analyzing the composition of the effluent fluid via gas chromatography under atmospheric pumping conditions [14]. These studies are a useful proof of concept for electrochemical ammonia compression; however, they did not measure the flow rate or composition of the effluent fluid under pressurized conditions. Chouhan et al. provided the first published examination of the effect of ammonia back diffusion at elevated pressure [16]. They also investigated the back diffusion of a hydrogen EC compressor [17]. In their experiments, they observed the volumetric ratio of ammonia to hydrogen in the effluent gas stream decreased significantly when they applied pressure to the discharge side (cathode) of the compressor.

Prior to those publications, researchers had only investigated ammonia as a contaminant in fuel cells [18-22]. Uribe et al. first noticed that the presence of ammonia in their proton exchange membrane (PEM) fuel cell significantly degraded the performance [18]. They attributed the degradation to the replacement of H⁺ sites

in the anode catalyst layers with NH₄⁺; they noted that the membranes exposed to ammonia for long periods of time did not recover after flushing the system with pure hydrogen. Jung et al. studied the mobility of ammonia in these cells, finding that ammonia was able to traverse the membrane when they humidified the gas streams flowing into the cell, but not when the gas streams were dry [22].

1.2. <u>EC Dehumidification</u>

Like the ammonia EC compressor, EC dehumidification is a relatively new concept. While the process bears similarity to water electrolysis, EC water transport was not demonstrated until Iwahara et al.'s 2000 experiment, where they developed a proton conducting ceramic membrane to desiccate a stream of humid gas [23]. However, their ceramic membrane required temperatures on the order of several hundred degrees Celsius, making them rather impractical for the most common dehumidification applications. Nearly a decade later, Sakuma demonstrated electrolytic dehumidification at ambient temperatures using Nafion membranes and developed a numerical model for the process [5]. They published a follow-up study the following year as well [24]. Xiang et al. developed a method for modeling the electrochemical dehumidification as well in 2013 [25].

However, continuous, steady state dehumidification with a polymer membrane was not realized until Qi et al.'s 2017 experiment [6]. They continuously flowed humid air at varied relative humidities and flow rates and observed the rates of water removal and the energetic performance. They observed that the rates of forward transport of water vapor was lower than anticipated due to the role of back diffusion in the cell. In 2018, they also developed a comprehensive two-dimensional model to simulate the performance [26]. Their group has conducted several additional studies in the years since as they continue to optimize the dehumidification performance [27-29].

In all observed experiments, a proton-exchange process was responsible for the dehumidification. However, in the present work, I describe an electrochemical dehumidification process using an anion exchange membrane. The chemistry of this process is fundamentally different. The ionic species which carries water from one fluid stream to another bears a negative charge, while all previous EC dehumidifiers employed a protonic process. Thus, the contributions from this study are to demonstrate the potential for electrochemical dehumidification using an anion exchange process. I conducted experiments to understand the effects of varied humidity and dry gas flow rates on the water removal rate.

1.3. <u>Electrohydrodynamic (EHD) EC Dehumidification Enhancement</u>

As observed in the EC dehumidifier experiments, which were consistent Qi et al.'s reported results, there were significant mass transfer limitations in the MEA, which prevented high rates of water transfer [6]. Hence, there was a need to facilitate the removal of water vapor from the membrane. To that end, the mass transfer enhancement due to the electrohydrodynamic (EHD) effect was a promising candidate to improve the performance of the EC dehumidifier. The use of high-

voltage fields was demonstrated several times over to increase rates of heat and mass transfer, especially under two-phase conditions [30-35].

When a high voltage point source occurs in a dielectric material, such as air, ions generated near the source collide with neutrally charge air molecules. The resultant flow of gas is known as electric wind [36-38]. The effect is so significant that one can measure the pressure developed from the EHD force [39]. The reactive gas flow may cause secondary flows, for example if air is moving downstream in a duct, the EHD force may generate flow towards the wall of the duct, perpendicular to the primary flow direction. For decades, engineers have investigated this effect for heat transfer enhancement [40, 41]. However, my interest was in the EHD effects' ability to facilitate evaporative mass transfer.

I found several interesting studies demonstrating this very concept in a rather unexpected area. Food science researchers took a vested interest in EHD drying for the removal of water from organic matter, in other words, drying foodstuffs for longer shelf lives. In an early food-drying study, Isobe et al. demonstrated enhanced drying of agar gel using a single high voltage electrode [32]. Esehaghbeygi and Basiri showed that tomato sliced placed under a 10kV voltage field shed their water content at the same rate as those placed inside a drying oven [42]. Dinani et al. further demonstrated the value of the non-thermal EHD drying method by examining the quality of mushroom after exposing them to the high voltage field [43]. Martyneko and Zheng investigated the role of air velocity while drying sliced of apple in a duct, finding that drying was most effective under high voltage with low air velocity over the samples [35].

Outside of food science, Lai and Lai studied the effect of electrode shapes on the drying of moistened glass beads [44]. They also investigated enhanced drying with multiple configurations of needle electrodes [30, 31]. Ultimately, their findings are consistent with the food scientists' findings that, to an extent, higher voltages generally lead to faster evaporation; more electrodes are useful to span larger surfaces; and some air flow over the sample is useful, but if the flow rate is too high, the benefit of EHD enhancement is lost.

1.4. <u>Numerical Simulation of EC Dehumidification</u>

To investigate the processes occurring in the inner layers of the MEA during dehumidification, I developed a numerical model for simulating the EC cell performance. By applying the relevant physical models, I simulated my laboratory experiments and observed the agreement between the expected result and the actual one. Through this effort, I aimed to develop a robust and generalized model that would facilitate the development of more efficient energy systems.

While there is an abundance of published work simulating the coupled heat, mass, and charge transfer processes occurring in fuel cell MEAs, models specifically tailored to electrochemical compression and/or separation are far less common. Springer et al. developed an early and oft cited methodology for simulating the performance of PEM fuel cells [45]. The modeling work by Bernardi et al. was also quite prolific in fuel cell models [46]. However, more in-depth finite element models, such as those from Seigel et al.; Rowe and Li; and Mann et al., provided clearer understanding of the transfer phenomena in the different layers of the MEA [47-49]. Cheddie and Munroe provided a review of these early approaches to PEM fuel cell modeling [50]. Recent models took a more sophisticated approach to simulating the transport properties in PEM fuel cells, such Chiu et al.'s three-dimensional model of fuel cell transport phenomena [51]. Aghighi et al. predicted the water transport and liquid water formation through pore network modeling [52]. The review study by Tzelepis et al. provided a useful reference for the multitude of PEM published PEM fuel cell models. Most models considered the same types of membranes and catalyst layer that I used in the ammonia compression experiments, they were valuable resources towards the development of the generalized EC pump simulation.

Indeed, some researchers implemented these methods in their own EC compressor models [26,29,53,54]. Onda et al. observed the electrochemical performance of a hydrogen EC compressor operating under various pressurized conditions. They used their findings to predict the performance at low current densities and without significant mass transfer limitations [55]. Nordio conducted a similar experiment; however, they observed the limiting current conditions wherein the supply of hydrogen was insufficient to meet the demand. Their simulations were able to capture this behavior under several different conditions [56]. Regarding EC dehumidification, Sakuma et al. developed the first numerical models of the process based on their transient dehumidification experiments [5,24]. Qi et al.'s and, subsequently, Zhang et al.'s endeavors sought to develop a two-dimensional heat and mass transfer model for a PEM-based EC dehumidifier. In the former of the two studies, Qi et al. developed a preliminary simulation of a PEM dehumidifier [26]. In the latter, Zhang et al. optimized the simulation procedure for better results [29].

1.5. Motivation

As EC energy systems emerge as viable technologies amid the transition towards a sustainable energy future, I examine several different applications for membranebased EC pumping devices. The motivation for these studies is to reduce carbon emissions through the development of sustainable energy systems. EC pumps have a unique ability to selectively remove molecules from a gas mixture and may play a role in developing next generation energy system. I consider two practical applications that require efficient chemical separation: ammonia production and dehumidification.

Ammonia is a widely produced chemical that is most often used for agriculture. However, ammonia is also an effective energy carrier with a lower heating value (a measure of thermal energy produced by combustion) of 5.2 kWh kg⁻¹, roughly 40% of the energy content of gasoline. Ammonia may be useful for the transportation of renewable hydrogen, circumventing the energy intensive process of liquid hydrogen liquefaction [57]. Unlike hydrocarbon fuels, ammonia does not emit carbon dioxide when consumed. Ammonia could be synthesized from renewable hydrogen via the Haber-Bosch processes and then separated and compressed through an EC pumping device. Ammonia condenses at only 1 MPa and is easy to transport. EC compression, with renewable hydrogen generation, would facilitate the transportation of renewable energy from regions rich in renewable resources to regions where the demand for renewable energy is greater.

In hot and humid parts of the world, air conditioning is a necessity for an adequate standard of living. Cooling and heating represent one-third of building energy consumption; however, separate sensible and latent cooling could reduce air conditioning energy consumption by as much as 24% [58]. When cooling humid air, a substantial amount of the cooling energy is absorbed by water vapor condensation. The dehumidification cooling load is referred to as the latent cooling load and the dry bulb cooling load is referred to as the sensible cooling load. In most residential application, the total cooling load is processed by a vapor compression cycle.

Processing the latent load separately would not only reduce energy consumption. It would also reduce the required refrigeration capacity. Refrigerants often have adverse ecological impacts, contributing to the greenhouse effect and depletion of the ozone layer. Reduction of the cooling capacity in a system could reduce the amount of refrigerant charge required. Desiccants or physical membranes most commonly handle the latent load in separate sensible and latent cooling applications [58]. In this study, I propose the use of electrochemical membrane for humidity removal.

1.6. Objectives

The main objective of the present work is to demonstrate the utility of EC pumping devices for ammonia storage and dehumidification. For ammonia EC compression, the specific objectives were to:

- Develop a test facility for analyzing the steady-state performance of an ammonia EC compressor
- To evaluate the ammonia EC pumping capabilities
- To demonstrate scaled-up ammonia EC compressor performance using a multi-cell stack

The objectives for the EC dehumidification work were to:

- Develop a test facility for evaluating EC dehumidifier cells
- Scale up EC dehumidifier performance
- Demonstrate efficient dehumidification performance using anion exchange process
- Improve the dehumidification efficiency using EHD mass transfer enhancement
- Develop a prototype separate sensible and latent cooling device using an EC dehumidifier
- Develop a numerical model for predicting the EC dehumidifier performance

Ammonia EC Compression

The ammonia EC compressor uses the same membrane electrolytes as most common proton exchange membrane (PEM) fuel cells. The material, often referred to as Nafion, is a PTFE polymer with a sulfonic acid sidechain. The acidity of the membrane enables the mobility of protons, enabling hydrogen power generation. However, the present application is slightly different. In the first half-reaction, the working fluid reacts to form an ammonium ion that is permeable through the membrane. Eq. 1 governs the oxidation reaction on the anode side, while Eq. 2 governs the reduction reaction on the cathode side. Figure 3 illustrates the process.

$$2NH_3 + H_2 \rightarrow 2NH_4^+ + 2e^- \qquad \text{Eq. 1}$$
$$2NH_4^+ + 2e^- \rightarrow 2NH_3 + H_2 \qquad \text{Eq. 2}$$



Figure 3. Ammonia EC compressor working principle.

From the reaction, mass transport is caused by the movement of electrons. Thus, to generate mass flow, current must be supplied to the cell, which requires an electrical potential. The forward transfer of chemical species is known as electrolysis. However, it is not the only form of mass transfer occurring in the membrane. While the membranes provide a high degree of separation between the anode and cathode flow channels, ammonia is still mobile in the humidified membrane and may diffuse through the ionomer in the direction of decreasing concentration. Typically, diffusion occurs in the direction opposite to the electrolytic flow, hampering the cell's performance. Because of the consumption/production of the working fluid in the catalyst layers and the mass transfer resistances between the membrane and flow

channels, large concentration differentials may exist in the inner layers of the MEA. The concentration differential increases the amount of energy required to maintain the process and promotes parasitic back diffusion. The energy required to maintain the compression or separation is given by the total call potential, which is the summation of the cell overpotentials. The total cell potential can be expressed by Eq. 3, where U_{tot} represents the total electrical potential in the cell, E_{rev} is the reversible cell potential, η_{ohm} is the Ohmic polarization loss, and η_{conc} is the concentration polarization loss.

$$U_{tot} = E_{rev} + \eta_{ir} + \eta_a + \eta_c$$
 Eq. 3

 E_{rev} is governed by the Nernst equation and is the cell potential required to maintain a given concentration difference across the membrane, for a reaction of the form of Eq. 4, is given by Eq. 5. According to the reactions occurring in the ammonia EC cell, I expressed the reversible cell potential as in Eq. 6, where R is the universal gas constant, *F* is Faraday's constant, *T* is the absolute temperature, and p_k represents the partial pressure of species *k*. The Ohmic loss term may be expressed as Eq. 7.

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D \qquad \qquad \text{Eq. 4}$$

$$E_{rev} = E_{cell}^0 - \frac{RT}{zF} \left(\frac{\{C\}^{\gamma} \{D\}^{\delta}}{\{A\}^{\alpha} \{B\}^{\beta}} \right)$$
 Eq. 5

$$E_{rev} = \frac{RT}{2F} \ln\left[\left(\frac{p_{NH_3,cat}}{p_{NH_3,an}} \right)^2 \frac{p_{H_2,cat}}{p_{H_2,an}} \right]$$
Eq. 6

$$\eta_{ir} = ir$$
 Eq. 7

The variable *i* is the current density and *r* is the area-specific resistance, a property of the membrane. The activation overpotential is determined from the flux of ions across the membrane and may be derived from the Butler-Volmer equation (Eq. 8), where j_0 represents a reference flux of ions, while α is a charge transfer coefficient, applicable to either the anode or the cathode.

$$j = j_0 \left[\exp\left(\frac{\alpha_a z F \eta_a}{RT}\right) - \exp\left(-\frac{\alpha_c z F \eta_a}{RT}\right) \right]$$
 Eq. 8

The concentration overpotential stems from restrictions to the supply of gas to the anode or, conversely, insufficient removal of gases from the anode. The corresponding voltage loss due to this effect may be expressed as Eq. 9 [59], where i_l represents a limiting current based on the maximum possible supply of reactants.

$$\eta_c = -\frac{RT}{2F} \ln\left(1 - \frac{i}{i_l}\right)$$
 Eq. 9

1.7. <u>Experimental Setup</u>

To investigate the ammonia EC process, I constructed a test facility based on the experiments conducted by Tao et al. [15]. Ammonia and hydrogen gases are supplied to the EC cell in known quantities two mass flow controllers (MFC). The hydrogen supply passed through a humidifier to introduce moisture into the fluid mixture. The inlet pressure was measured with an absolute pressure transducer. The EC was heated to a desired temperature inside a low-temperature oven. A constant stream of gas was

flowed through the suction side to ensure there were enough reactants for the electrochemical reaction. The suction side pressure was then regulated by a capillary expansion device. On discharge side, a second absolute pressure transducer measured the discharge pressure. Gases left the EC through a back-pressure regulator, which maintained constant pressure in the cell.



Figure 4. Schematic of small-scale ammonia EC facility.

The compressor consisted of two cells in parallel, as depicted in Figure 5. Gas was introduced to each membrane via graphite bipolar plates with embedded parallel flow channels. I used preassembled membrane electrode assemblies, consisting of Nafion 115 membranes and carbon cloth gas diffusion layers. Both sides of the membrane were coated with 0.5 mg/cm² of Pt supported carbon catalyst.

The experiments were carried out under galvanostatic conditions, with a constant current of 1.5 A for all experiments. I maintained inlet flow rates of 200 sccm of NH_3 and 100 sccm of H_2 for each experiment. In each test, I observed the increase in pressure of the discharge side and adjusted the back-pressure regulator to the desired outlet pressure. I ran the tests until steady states were achieved for both pressure and cell voltage.

Table 1 details both the set parameters for each test, including total current, stack temperature, and inlet humidity as well as the measured variables, suction pressure, discharge pressure, and total voltage. The Nernst voltage is a calculated variable based on temperature and pressure.



Figure 5. Photographs of the ammonia EC compressor assembled and disassembled.

Test	Current	Temp.	Cell	Suction	Discharge	Total	Nernst
	(A)	(°C)	RH (%RH)	Pressure (bar)	Pressure (bar)	Voltage (mV)	Voltage (mV)
1	1.5	27.7	28	1.77	9.88	354	133
2	1.5	51.7	41	1.73	9.92	295	147
3	1.5	25	33	3.70	12.28	219	92

Table 1. Steady-state, small scale ammonia EC compression experiments.

Figure 6 shows the cell pressurization process for Test 1. The pressure-time curve shows the gradual pressurization of the discharge side. At around 13 minutes, the pressure in the discharge side reached the setpoint of the back-pressure regulator, at which point gas began flowing out of the discharge line at a steady pressure. From the voltage-time curve, the stack voltage strongly correlated to the pressure. The real voltage increases until the pressure reaches its steady condition and the decreases. I noted that the voltage decreased significantly after the high-side pressure stabilized. However, the increase was likely due to changes in the low-side pressure. As the test ran on, the suction side pressure increased slightly even after the discharge pressure stabilized. The increase in suction pressure decreased the pressure ratio, which decreased the total voltage. I noticed a difference between the Nernst voltage and the real voltage is nearly constant, which implied there were not major electrochemical losses due to the differential pressure. The irreversible overpotentials in Test 1 were significantly larger than that of Test 3, despite the similar operating conditions.




Figure 6. Small-scaled ammonia EC pressurization from 2 bar to 10 bar.

(a) change in pressure over time (b) change in voltage over time.

1.8. <u>Compression Work Analysis</u>

In this work, electrochemical cells were heated to a constant, elevated temperature. Consequently, the suction and discharge sides were maintained at the same temperature. Because the Nernst equation (Eq. 5) is valid for constant-temperature electrochemical processes, researchers often expect isothermal compression behavior. Suermann et al. considered isothermal processes in their hydrogen compression experimentation, reporting very high efficiencies [60]. Onda et al. demonstrated steady-state compression of hydrogen at constant temperature, reporting reasonable power consumption [55]. Shen et al. report both values of isothermal and isentropic efficiency in their study to characterize a prototype electrochemical compressor stack [61]. While the cell temperature may not change perceptibly, any isothermal compression requires heat removal. It was expeditious to evaluate the minimum electrical power input required for both the isothermal and isentropic cases.

The total mass flow rate of the gas in the EC compressor, assuming a negligible amount of electroosmotic drag for the ammonia system, may be defined according to Eq. 10. In the expression, the subscript *k* refers to the different species present in the system, neglecting water, these include ammonia and hydrogen, both of which diffuse through the membrane at different rates, according to their respective diffusivities, D_k^{eff} . The variable C_k refers to the concentration of species *k*; z_k is the valency, or how many molecules of species *k* are electrolytically transported per electron; and M_k is the molar mass.

$$\dot{m}^{\prime\prime} = \sum_{k} M_k \left(\frac{i}{z_k F} - D_k^{eff} \frac{\partial C_k}{\partial x} \right)$$
 Eq. 10

For an isothermal system, the amount of mechanical work done for compression from initial presure P_{in} to final pressure P_{out} is given by Eq. 11.

$$\dot{W}_{iso} = \frac{\dot{m}RT}{M} \ln\left(\frac{P_{out}}{P_{in}}\right)$$
 Eq. 11

In much of the reported electrochemical compression experimentation, the compression cells were temperature controlled. However, for any isothermal compression process, the entropy of the working fluid after compression must be less than the fluid entropy prior to compression. The second law of thermodynamics requires that heat be removed from the system to decrease its entropy.

If the cell operates adiabatically, the Nernst voltage cannot represent the minimum voltage needed to maintain compression. The Nernst equation is only valid for constant temperature processes. The second law of thermodynamics tells us that an adiabatic and reversible process is the lowest energy compression without active thermal management. I theorized the minimum voltage required for the electrochemical reaction would be based on the power required for an isentropic process. The power requirement for an isentropic process for a given ideal gas with constant specific heat, is defined according to Eq. 12, where k is the ratio of the fluids specific heat for constant pressure to the specific heat for constant volume.

$$\dot{W}_{ise} = \frac{k}{k-1} \frac{\dot{m}RT_1}{M} \left[\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$$
 Eq. 12

I defined the specific heats of the fluid mixture according to the relative concentration of the two main fluids in the system so I could define the k value for the fluid mixture.

The discussion of isothermal versus isentropic is important because the different cases define the minimum amount of energy required to sustain the compression. If the EC compressor can operate close to an isothermal case, then the energy savings compared to conventional mechanical compression could be substantial. Figure 7 illustrates how the work requirements differ versus pressure ratios for the two cases. One observes that the difference between the two processes becomes more significant as the pressure ratio increases. Furthermore, unlike conventional mechanical compressors, which generally operate inside of a hermetically sealed housing, the EC compressor is easily outfitted with embedded heat exchangers to reject the heat generated during compression. Moreover, as the scale of the compressor increases, the amount of membrane area increases as well. Intuitively, we understand that more area for the reactions to occur also implies more area for heat transfer as well.



Figure 7. Paths of compression work.

1.9. <u>Ammonia Separation from a Dilute Stream</u>

Because most of the world's ammonia is produced via the Haber-Bosch process, it was interesting to understand the ammonia EC compressor's ability to separate ammonia from a gas mixture. The main three species present during the Haber-Bosch process are ammonia, hydrogen, and nitrogen. To that end, I modified the previous facility as detailed by the schematic diagram in Figure 8. The test facility was designed to evaluate the rate of ammonia separation at different concentrations as well as how varied inlet compositions affect the current developed under the same potentials. For these experiments, I used both columns in the gas chromatograph (GC) to analyze the suction and discharge streams individually.

The test matrix detailed in Table 2 was carried out in the experimental facility. I developed the test matrix to examine the EC performance under varying the inlet

fractions ammonia, hydrogen, and nitrogen. In experiments 1-4, no nitrogen was introduced into the EC compressor's suction sides. Experiments 5 and 6 test the EC compressor's ability to separate ammonia from mixtures with varying amounts of nitrogen. Additionally, for all tests, I flowed nitrogen gas through the discharge side to help sweep the discharge gases from the EC separator. The sweep gas prevented gases from pooling in the pipelines between the EC separator and the GC as well as preventing water droplet formation in the EC separator's discharge chamber, a phenomenon that I previously observed to interfere with experimentation. In these experiments, I used a wet membrane to ensure sufficient humidity. All experiments were done at ambient pressure under negligible pressure differentials in the EC separator. As I varied the inlet conditions, I ensured that the total molar flow rate supplied to the EC separator was kept constant as best I could. The total flow in experiments 1-4 was maintained around 150 sccm, while the total molar flow in experiments 5 and 6 was maintained at around 200 sccm. The flow rate was increased in the latter experiments due to limitations with the lower flow range of our mass flow controllers. The volume of an ideal gas at standard conditions is 22.4 L/mol, so the total molar flow was approximately held constant for each test with a given volumetric flow rate in sccm. Each test was conducted using a single 50 cm^2 cell.



Figure 8. Updated schematic of test facility for measuring NH₃ separation from a dilute stream.

Test	Temp.	Potential	MFC H ₂	MFC NH ₃	MFC N ₂	MFC N2 Sweep
	(°C)	(V)	(sccm)	(sccm)	(sccm)	(sccm)
1	25	0.1	51	100	0	11
2	25	0.1	50	99	0	10
3	25	0.1	50	49	0	10
4	25	0.1	106	31	0	11
5	25	0.1	105	30	34	10
6	25	0.1	128	15	41	10

Tal	ble	eί	2.	Am	moni	ia se	para	tion	test	matrix	ζ.
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The results of the experiments are presented graphically in Figure 9. Figure 9. Results from ammonia EC separation experiments. and in tabular form in Table 2. In these experiments, I noticed that the discharge transfer ratio, the ratio of ammonia to hydrogen appearing in the discharge gas stream, was significantly affected by varying the suction-side ammonia concentrations. From Figure 9(a), the transfer ratio

increases linearly with increasing suction-side ammonia mole fraction. The current was also affected in a less dramatic way. The transfer ratio deviated significantly from the stoichiometric value of 2, which I hypothesize was due to diffusive transport in the membrane.

For the low transfer ratio case, either diffusion carried ammonia backwards through the MEA or more protons to cross the membrane rather than ammonium ions, which is consistent with lower current at low ammonia fractions. However, proton conductivity decreases when ammonia the MEA is introduced to ammonia. For the cases where the transfer ratio was higher than the stoichiometric value, forward diffusion was responsible, as the sweep gas on the discharge side lowered the ammonia discharge concentration significantly. One notes that the EC was still able to achieve net positive ammonia transport even in low inlet concentration conditions.



Figure 9. Results from ammonia EC separation experiments.

Test	x _{H2} Suction	XNH3 Suction	x _{N2} Suction	Current	Discharge NH ₃ /H ₂
	(-)	(-)	(-)	(A)	(-)
1	0.33	0.65	0.00	0.73	4.21
2	0.33	0.65	0.00	0.99	3.61
3	0.49	0.49	0.00	0.97	2.34
4	0.76	0.22	0.00	0.85	1.30
5	0.61	0.17	0.22	0.60	1.43
6	0.67	0.08	0.25	0.56	0.96

Table 3. Dilute ammonia separation experimental results.

After measuring the significant deviation in the transfer ratio from the stoichiometric condition, I conducted several additional experiments to verify that diffusion was responsible for the increased transfer ratio in the high inlet concentration experiments. A two-to-one mixture of hydrogen and ammonia passed through the suction side of the EC while maintaining a constant flow of nitrogen sweep gas through the discharge side, as in the previous set of experiments. Measuring the flow rate of the gas leaving the EC the entire time, the GC measured the composition of both the suction and discharge gases before and after applying voltage to the cell.

Figure 10(a) shows chromatograms for the no-voltage case. The topmost chromatogram shows the suction side composition, and the bottom shows the discharge. A significant amount of ammonia exists in the discharge stream, even though no potential was applied to the cell. Furthermore, I see only trace amounts of hydrogen in the discharge side, which may have been due to residual hydrogen in the sample lines. Conversely, Figure 10(b) shows chromatograms for the voltage-applied case. Under these conditions, a mixture of hydrogen and ammonia appears in the chromatogram. The presence of a mixture implies that hydrogen transport occurs only under applied potential, while ammonia may freely traverse the membrane with or without electrochemical processes. In the second chromatogram, I again found the transfer ratio is much higher than the stoichiometric value.



Figure 10. (a) Chromatograms for non-voltage case. (b) Chromatograms under applied voltage.

Throughout these experiments, the Coriolis mass flow meter measured the flow rate of gas leaving the discharge side of the EC. Figure 12(a) presents the mass flow data, shown in red, as compared the cell current and the mass flow of the sweep gas. I observed that the measured mass flow under no-current conditions was nearly twice that of the of the mass flow introduced as sweep gas. Based on the GC data I concluded the additional mass flow was ammonia. Furthermore, the mass flow increased as I applied potential to the cell. Figure 12(b) shows the transfer ratio versus time for the current applied conditions. The transfer ratio for the no-potential experiment was undefined due to the absence of hydrogen in this case. The transfer ratio increases as the cell current decreases, which can be explained by decreased hydrogen flow through the cell while ammonia was still allowed to freely flow through the MEA.



Figure 11. Ammonia transfer ratio measured by GC.



Figure 12. Mass flow results from ammonia diffusion experiment.

To verify the measurement obtained over the course of these experiments, I employed titration flow measurement to verify the results. Introducing a known flow rate of ammonia via the mass flow controllers into 2 mL of 0.1 molar HCl solution, I recorded the time for the known flow rate to neutralize the acid in the solution. I established a relationship between the molar ammonia flow rate and the titration time, which is shown in Table 4. I used the established relationship to examine the flow rate of ammonia leaving the cell.

Measured	l NH3 Flow	Titration Time		
(sccm)	(mol/s)	(s)		
19.1	1.42E-05	18.0		
19.1	1.42E-05	19.0		
29.1	2.17E-05	14.0		
39.2	2.92E-05	10.0		

Table 4. Titration calibration.

I compared the molar flow rate of ammonia as measured by titration to the flow rate measured by the mass flow meter. I adjusted the mass flow meter value to account for the flow rate of sweep gas and hydrogen. Additionally, using Faraday's law coupled with the GC data to calculate the flow rate leaving the cell, I computed the molar flow of ammonia. Both flow rate data sets were plotted against the data from the mass flow meter. Figure 13(a) shows the data from the titration experiments. Figure 13b shows the data from the GC calculations. In both cases, the calculated value agreed with the measured value to within 10%, which implied good agreement between the hypothesized and the real flow rates.



(a) (b)
Figure 13. Ammonia mass balance two different ways (a) Titration results compared against GC results (b) GC results compared against calculated results.

1.10. Multi-Cell Ammonia EC Experiments

In previous research efforts, I demonstrated the working principle of EC ammonia compression on a small scale using 5 cm² PEM cell. I achieved sustained, steady-state compression of ammonia vapor under pressure differentials exceeding ten bar. To scale up these experiments, the UMD EC compressor team partnered with Skyre Inc., a US-based EC compressor manufacturer to evaluate the performance of an ammonia compressor with five PEM cells operating in parallel. I constructed the test facility diagramed in Figure 14. The two MFCs controlled and measured the respective flowrates of ammonia and hydrogen into the cell. The hydrogen passes through a humidifier to moisten the membranes. I measure the temperature and pressure on the suction side. The inlet gas mixture flows through the EC stack and I analyzed the exhaust gas composition using the GC. On the discharge side, a third MFC connected

to a digital control loop precisely regulated the discharge side pressure. I measured the flow rate of the gas using the Coriolis mass flow meter and the composition using a second column in the GC. A potentiostat supplied the electrical energy input to the cell and recorded the electrical power consumption.



Figure 14. Test facility schematic for multi-cell stack experiments.

The EC cells operated in parallel, each with 82 cm^2 of active membrane area. The catalysts were a carbon supported platinum material. A photograph of the stack is shown in Figure 15. A photograph of the test facility is shown in Figure 16.



Figure 15. Photograph of the multi-cell EC compressor stack.



Figure 16. Photograph of the multi-cell EC compressor stack test facility.

The most significant experimental parameters affecting the performance of the ammonia EC are the inlet-side ammonia content, the discharge-side pressure, and the

stack current. To investigate the effect of variations in each of these parameters, I developed the test matrix shown in Table 5. In each experiment, the values of hydrogen inlet flow rate and low-side pressure were maintained at a constant value. The goal of the experiments is to develop a map of the compressor performance under the various operating conditions.

Test Set	Ammonia	Hydrogen	Low-Side	Current	High-Side
No.	Flow	Flow	Pressure		Pressure
	(sccm)	(sccm)	(kPa)	(A)	(10 ² · kPa)
1	200	100	175	1	[2, 4,, 10]
2	200	100	175	2	[2, 4,, 10]
3	200	100	175	3	[2, 4,, 10]
4	200	100	175	4	[2, 4,, 10]
5	200	100	175	5	[2, 4,, 10]

Table 5. Multi-Cell Ammonia EC Test Matrix.

For each test, I specified the cell current and varied the pressure over the duration. For each current set point, the pressure regulator automatically adjusted to five different set points. I found that 45 minutes was sufficiently long enough to allow the system to achieve steady state. If left alone, the system was stable for at least several hours. I did not conduct experiments investigating the stability for continuous operation over longer durations. In Figure 17, I observed the changes in pressure over time for the duration of a single experiments. The test shown was conducted at 2 A of stack current. As the stack electronics were connected in series, such that each cell maintained the same current. The data set demonstrated at 2 A is representative of the other datasets at different current values. As the pressure increased in stages, I observed changes in the discharge mass flow as well. Figure 18 illustrates the decrease in the outlet mass flow rate at the pressure increases. One notices that the decrements in mass flow became smaller as the relative change in pressure step size increased. Furthermore, Figure 19 shows the concentration of ammonia at three state points: the suction-side inlet, the suction-side exhaust, and the discharge-side effluent. While the suction inlet was the same throughout, to maintain the stoichiometric inlet condition, the concentration of ammonia appearing in the discharge effluent gas stream decreased. Additionally, there was a greater concentration of ammonia appearing in the suction-side exhaust.



Figure 17. Pressure setpoints for multi-cell EC compressor stack.



Figure 18. Decrease in mass flow rate over time as stack pressure increased.



Figure 19. Ammonia molar fraction about the multi-cell EC stack.



Figure 20. Cell potentials within the multi-cell EC stack.

At the lowest pressure condition, the ammonia concentration at all state points hovers around the stoichiometric value of 66.7%. However, the concentration decreases at higher pressures. From the previous studies into ammonia contamination in PEM fuel cells, if there was a significant concentration of ammonia present in the system, the membrane would stop conducting protons [18]. Therefore, I concluded ammonium remained the primary species driving the electrolytic mass flow in the stack. Both the decrease in concentration at the discharge side and the increase in concentration at the suction exhaust were the result of back diffusion of ammonia. As the pressure increased, the ammonia, which Jung et al. showed is mobile in a humidified Nafion membrane [22], crossed over to the side of lower concentration. Hydrogen diffuses much more slowly, so it remained in the discharge-side. Consequently, I expected a higher relative concentration of ammonia in the suction-exhaust if virtually all the electrolyzed hydrogen remains on the cathode-side while a significant amount of ammonia returns to the anode.

The results of the experiments listed in Table 5 are summarized in the following figures. Figure 21 depicts the stack voltage required to maintain the galvanostatic current at the different pressure values. I observed the current set point had the more significant impact on the voltage. While the voltage requirement did increase slightly as the pressure increased, it was almost negligible compared to the increase corresponding to increasing current. This was partly because the reversible cell voltage was relatively small compared to the total voltage. However, backward transfer of ammonia also reduced the partial pressure difference across the membrane.



Figure 21. Multi-cell ammonia EC compressor stack voltage versus pressure.

Figure 22 shows the discharge ammonia molar fraction for the varied pressure and current set points. Here, I observed how the amount of ammonia appearing in the

effluent gas stream increases as the current increases. With increased current, I expected more forward transport of the reactants, while the rate of back diffusion was constant for a given partial pressure differential. Therefore, it was reasonable that higher current corresponded to higher net flow rate. These findings were supported by Figure 23, which depicts the flow rate of gas leaving the discharge-side for the given test conditions. On another note, one may notice that several of the current setpoints do not exactly meet the 200 kPa discharge condition. Greater pressure drop occurred with higher flow rate, which occurred in the equipment used the measure the flow rate and composition.



Figure 22. Multi-cell ammonia EC compressor discharge composition versus

pressure.



Figure 23. Multi-cell ammonia EC compressor flow rate versus pressure.

For practical applications of the EC compressor, it was imperative to note the efficiency for the various operating conditions. In each of the experiments, the compressor stack operated under virtually isothermal conditions, since I did not perceive any temperature increases from anode to cathode. Therefore, the work done by the compressor follows an isothermal compression path. This presents an advantage of the EC compressor over conventional mechanical compressors, which operate adiabatically. The work requirement for isothermal compression is always less than that of reversible adiabatic, or isentropic, compression. Such a distinction is noteworthy because, as I computed the efficiency of the EC compressor stack, I calculated the ratio of ideal stack voltage to the real voltage. The minimum work requirement for the present application is lower than the minimum work requirements considered for mechanical compressors since the ideal voltage represents an

isothermal compression path. Thus, the computed efficiency values may appear lower than expected for an ammonia compression device.

The single-cell efficiency is shown in Figure 24. I calculated the efficiency as the ratio of the Nernst voltage (the minimum voltage required to sustain the concentration difference across the membrane, Eq. 6) to the average voltage for each cell. Eq. 13 shows the relationship between the single-cell efficiency η_{EC} , reversible voltage, and the total voltage for the stack of five parallel cells. From Figure 24 I noted that the efficiency tended to increase with increasing pressure. It is an interesting quality of the EC compressor that the compression becomes more efficient when it maintains higher pressure ratios. However, the device was less efficient at higher currents, as the overpotentials needed to sustain the higher currents sharply increased the total voltage.

$$\eta_{EC} = \frac{E_{rev}}{(V_{tot}/5)}$$
 Eq. 13



Figure 24.Variation of single-cell EC efficiency with pressure and current.

Noting the significant decreases in ammonia concentration and flow rate seen in Figure 22 and Figure 23, I desired to estimate the rates of back-diffusive flux and Faradaic efficiency. Both calculations are comparisons of the measured data with the ammonia flow rates expected from Faraday's law of electrolysis, expressed in Eq. 14. In ideal conditions where back diffusion would not impede the flow of ammonia leaving the compressor, the molar flux of ammonia would be given by Faraday's law.

$$\dot{n}_{NH3,far}^{\prime\prime} = N_{cells} \frac{i}{2F}$$
 Eq. 14

The rate of diffusive flux of ammonia, according to Eq. 10, was the difference in the net molar flux of ammonia and the Faradaic flux of ammonia. These values are shown in Figure 25. The net molar flux was the molar flow rate of ammonia leaving the compressor divided by the total cell area. The Faradaic efficiency was the net

molar flow rate of ammonia divided by the flow rate calculate from Eq. 14, which is given by Eq. 15. The values of Faradaic efficiency are shown in Figure 26.

$$\eta_{far} = \dot{n}_{NH3} \left(\frac{N_{cells}I}{2F} \right)^{-1}$$
 Eq. 15

From the analysis in Figure 25, I observed the diffusive flux did not have a linear relationship with pressure, as one may expect from Fick's law of diffusion. Variations in concentration along the gas channels in the stack may explain the variation. Moreover, the effective diffusivity of ammonia may change under different setpoints. For example, as the pressure increases, the amount of water present in the ionomer material may have changed, affecting ammonia's ability to move through the membrane. As the diffusive flux increased in magnitude, the Faradaic efficiency decreased. Decrements in Faradaic also represented a loss of EC efficiency, since the partial pressure ratio of ammonia became smaller. As the ammonia partial pressure ratio decreased, the reversible voltage also decreased, which in turn decreased the apparent EC efficiency, according to Eq. 13.



Figure 25. Calculated diffusive flux of ammonia.



Figure 26. Faradaic efficiency of ammonia compression

While I did not measure the flow rate at the suction-side exhaust, I established a system-level mass balance by examining the suction-side exhaust composition to validate the results. Knowing the flow rate and composition of the effluent gas and

the inlet flow rates of hydrogen and ammonia, I calculated the expected values of the suction-side exhaust ammonia-to-hydrogen ratio. I compared it to the values measured by the GC. In Eq. 16, x_{NH3} is the molar fraction of ammonia, $\dot{n}_{NH3,in}$ is the inlet molar flow rate of ammonia, $\dot{n}_{NH3,dis}$ is the discharge molar flow rate of ammonia, I is the stack current, and N is the number of cells. The results of the analysis are shown in Figure 27, and demonstrates that all the gas in the system was accounted for.

$$x_{NH3} = \frac{(\dot{n}_{NH3,in} - \dot{n}_{NH3,dis})}{(\dot{n}_{NH3,in} - \dot{n}_{NH3,dis}) + (\dot{n}_{H2,in} - \frac{N_{cells}I}{2F})}$$
Eq. 16



Figure 27. Mass balance for ammonia EC compressor experiments via comparison of

measured and calculated suction-side exhaust molar fraction.

1.11. Conclusions

Considering the energy sector's growing need for green ammonia production, I present a performance analysis of an ammonia EC compressor. Where ammonia was once thought of as a detriment to fuel cells, I observed that the PEM cells could electrolytically transport ammonia using hydrogen as a carrier gas. Where no published experiments reported the steady-state compression of ammonia, I developed a map of the multi-cell ammonia EC compressor performance.

To address the lack of steady-state ammonia EC performance analysis, I studied the composition and flow rates of the gas leaving the EC compressor discharge. I noted that the concentration of ammonia decreased with increasing pressure. I also found higher current values consistently produced higher ammonia concentrations in the discharge side. I explained this phenomenon via diffusive mass transfer. Higher current resulted in higher electrolytic flow, while the rate of back diffusion was constant for a given concentration differential. By increasing the stack current, I increased the forward rate of ammonia flow. Thus, the net rate of ammonia flow increased. Additionally, hydrogen diffused at a negligible rate across the membrane at the pressure differentials considered in the current study. The back diffusion effect was significant, reducing the flow rate of the effluent fluid by as much as 67%. I also calculated the average single-cell efficiency, finding that the EC compressor operated more efficiently under high-pressure conditions, achieving a maximum of 40% against the ideal isothermal case. The cell efficiency was greatest at lowest current condition and consistently decreased with increasing current. The total stack

efficiency was lower than the single-cell efficiency due to the nature of maintaining the cells electrically in series. I performed a mass balance analysis using the compressor stack as a control volume to ensure that ammonia was not stored inside the cells. I concluded that ammonia dissolved in the humidified membrane and moved in the direction of decreasing concentration. This phenomenon presents a challenge for the EC ammonia compressor, as a humidified membrane is necessary for ion transfer.

The present studies showed that, while inefficiencies exist in the compression process, the technology obtained net-positive flows of ammonia against adverse concentration gradients. The power consumption was affected mainly by the stack current, as greater overpotentials were required to sustain higher currents. However, the voltage increased only slightly for a given current for increased discharge pressure. If the backward transfer of ammonia was smaller, the voltage required might increase. To reduce the parasitic back diffusion, it may be expedient to compress the working fluid over several stages.

Ammonia EC compression and separation are potential significant technologies that could drive a variety of alternative energy systems. Where ammonia was once thought of a detriment to fuel cells, I observe that the same membranes were capable of electrolytically transporting ammonia using hydrogen as a carrier gas. Whereas no published experiments report the steady-state compression of ammonia, a mapping of the compressor performance is presented. Furthermore, the EC compressor may be a valuable tool for separating product ammonia from the Haber-Bosch process.

2. EC Dehumidification

2.1. Working Principle

EC dehumidification can refer to any process where water vapor transfer occurs via an electrolytic process. Water is the working fluid and oxygen is the carrier gas in both the present applications. In a proton exchange EC dehumidifier, water vapor is reduced on the anode side, decomposing into protons and oxygen molecules. The proton transfer occurs in the direction of electric current, causing the protons to cross the membrane to the cathode. In the cathode the protons are oxidized, such that oxygen in the cathode side reacts with the proton and water molecules are formed. The reactions occur according to Eq. 17 and Eq. 18 for a proton exchange process. Figure 28 diagrams the proton exchange process.

Anode:
$$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$$
 Eq. 17

Cathode:
$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$$
 Eq. 18



Figure 28. Diagram of proton exchange dehumidification process.

The anion exchange dehumidification is different. In anion exchange dehumidification, water vapor in the cathode side is oxidized and forms a negatively charge hydroxide ion. The hydroxide passes through a cation exchange membrane, which is basic in nature. The ions flow in the opposite the direction of electric current. In the anode side, the hydroxide is reduced, forming water vapor and oxygen. Eq. 19 and Eq. 20 apply for an anion exchange process. Figure 29 shows a diagram of the process. $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$ Eq. 19

Cathode:

Anode:

$$4OH^{-} \rightarrow 2H_2O + O_2 + 4e^{-}$$
 Eq. 20



Figure 29. Diagram of anion exchange dehumidification process.

The flux of water \dot{m}'' in the EC dehumidifier is like that of ammonia in the EC compressor. However, additional consideration is necessary for the electroosmotic drag, as expressed by Eq. 21. The drag of water is governed by the drag coefficient n_d . Eq. 22 expresses the Faradaic efficiency of water transport: the ratio of net water removal to the value expected from Faraday's law of electrolysis. The energy requirement for dehumidification is expressed through Eq. 23, which gives a measure of the ratio of net mass flux to the electrical energy input per unit membrane area.

Higher values of the effectiveness ϵ_{EC} represent greater efficiency.

$$\frac{\dot{m}''}{M} = \frac{i}{2F} + n_d \frac{i}{F} - D^{eff} \frac{\partial C}{\partial x}$$
 Eq. 21

$$\eta_{far} = \dot{m}^{\prime\prime} \left(\frac{iM}{2F}\right)^{-1}$$
 Eq. 22

$$\epsilon_{EC} = \frac{\dot{m}''}{iV_{tot}}$$
 Eq. 23

2.2. <u>Experimental Setup</u>

I designed and constructed the MEA performance evaluation facility detailed in Figure 30 to measure the water transfer performance of the EC dehumidifier. The design is based on the work of Qi et al., who performed similar experiments [6]. In this facility, a set of MFCs introduced oxygen into the EC dehumidifier cell. On either the anode or cathode side, one flow controller regulated the dry gas flow rate, and another controller regulated the amount of gas saturated with water vapor. A humidifier tank saturated the wet gas stream with water vapor as the fluid bubbled up through a reservoir of liquid water. I controlled the humidity into both cell electrodes by adjusting the flow rates of moist and dry gas introduced in the system. I measured the temperature, pressure, and humidity at the inlet and outlet of both the anode and cathode gas streams. I used the MKS GE50 series MFCs, which had a maximum flow rate of 1000 sccm and could control the molar flow rate to an accuracy of 4 sccm. The humidifiers were stainless-steel bottles connected to the system via stainless steel fittings. A Gamry Reference 3000 potentiostat supplied the low voltage DC power to the EC and logged the electrical power consumption. A National Instruments cDAQ unit recorded the sensor data. All pipes and fittings in the test setup were stainless steel or PTFE to prevent corrosion from the humid air. The dehumidifier cells were always set up in a counterflow configurations. Figure 31 is a photograph of the completed test facility.



Figure 30. Schematic diagram of the EC dehumidifier experimental facility.



Figure 31. Photograph of the EC dehumidifier facility.

The experimentally observed rate of water transfer is given by Eq. 24, where ω is the molar humidity ratio. The humidity ratio is the measure of the number of moles of water vapor in a parcel of humid air to the mass of dry fluid, as expressed by Eq. 25. The partial pressure of water vapor at each of the four state points in the system may be found through Eq. 26, where θ is the relative humidity (RH).
$$\dot{n}_{w,exp} = \dot{n}_{O_2,in}(\omega_{out} - \omega_{in})$$
 Eq. 24

$$\omega = \frac{\dot{n}_w}{\dot{n}_{O_2}} = \frac{p_v}{P_{tot} - p_v}$$
 Eq. 25

$$p_v = \theta p_{v,sat}$$
 Eq. 26

2.3. EC Dehumidifier Uncertainty Analysis

Table 6 provides the systematic uncertainty for each sensor used in the test facility. The systematic error is inherent to a piece of measuring equipment. Random error is error due to environmental noise or random fluctuations in testing conditions. I considered the standard deviation of the steady state data points as the random error for each measurement. In Eq. 27, δx_i represents the total error of the measurement $x_{i,r}$, where $x_{i,syst}$ represents the systematic sensor error, and $x_{i,rand}$ represents the random error encountered during testing. Eq. 28 gives the experimental error for calculated variables where the total error depends on the error of the individual measurements.

$$\delta x_i = \sqrt{x_{i,syst}^2 - x_{i,rand}^2}$$
 Eq. 27

$$\delta Q = \sqrt{\sum \frac{\partial Q}{\partial_{x_i}} \delta x_i}$$
 Eq. 28

Sensors	Туре	Measure Range	Accuracy
RH sensor	Capacitive	0 - 100% RH	± (1.0+0.008 × reading) % RH
Mass Flow Controller	Thermal	0-1000 sccm	4 sccm
Absolute pressure transducer	N/D	0 – 345 kPa	± 1 kPa
Resistance Thermal Detector	Resistive	[-]50°C - 250°C	$\pm 0.03^{\circ}C$

Table 6. Specifications of sensors for EC dehumidification

I propagated the sensor errors to determine the uncertainty of the moisture removal rate as calculated from Eq. 24. The error is most significantly impacted by the humidity sensing equipment; however, pressure and temperature errors were important as well. Eq. 29 gives the uncertainty of the partial pressure of water vapor in terms of relative humidity and temperature. The water saturation pressure is a function of temperature only. Next, the error in molar humidity ratio is given by Eq. 30. The moisture removal rate depends on two measurements of molar humidity ratio: the inlet and the outlet. The humidity ratio, as defined by Eq. 25, depends on the water partial pressure and the absolute pressure. The moisture removal rate depends on the humidity ratios and the dry gas flow rate. The outlet flow rate differs from the inlet by the magnitude of the Faradaic transfer of oxygen. The cathode loses oxygen, while the anode gains oxygen. I represented this by the \pm in Eq. 31. I assumed the Faradaic flow rate contributed insignificantly to the total moisture removal error, as

the uncertainty of the current measurement was trivial in comparison to the other sensor errors.

$$\delta p_{\nu} = \sqrt{p_{\nu}^{sat^2} \delta \theta^2 + \left(\theta \frac{\partial p_{\nu}^{sat}}{\partial T}\right) \delta T^2}$$
 Eq. 29

$$\delta\omega = \sqrt{\left(\frac{-p_{\nu}}{(P-p_{\nu})^2}\delta P\right)^2 + \left(\frac{P}{(P-p_{\nu})^2}\delta P\right)^2}$$
 Eq. 30

$$\delta \dot{n}_w = \sqrt{\left((\omega_{out} - \omega_{in})\delta \dot{n}_0\right)^2 + \left(\left(\dot{n}_0 \pm \dot{n}_{far}\right)\delta \omega_{out}\right)^2 + \left(\dot{n}_0\delta \omega_{in}\right)^2} \qquad \text{Eq. 31}$$

2.4. Operating the EC Dehumidifier

To conduct EC dehumidifier experiments, I set the appropriate flow rates for each of the mass flow controllers to achieve the desired inlet conditions. I allowed the humid gas to flow through both channels of the dehumidifier cell until the outlet humidities reach a steady condition. Once the system became steady, I applied the voltage to the cell. I maintained the constant cell voltage long enough for the system to become steady again. I concluded the test upon reaching a stable condition with the applied cell voltage and recording the sensor data for at least five minutes after the system equilibrated. The example test result shown in Figure 33-Figure 35 demonstrates the dehumidifier operation for and AEM cell with 5 cm² cell operated with 2 V applied potential. The anode and cathode inlet humidities were both maintained at 50% RH to provide a measure of the electrolytic water transfer process without significant impacts of back diffusion prior to application of the cell potential. The inlet flow rates to the anode and cathode were both 400 sccm.

Figure 33 shows the change in the RH over time for each of the four state points in the cell. The anode and cathode inlet humidities are constant throughout the duration of the experiment. The outlet RH of the gas streams pull apart from one another after the potential is applied just after the 1-hour mark. This behavior indicates that cell is removing water vapor from the cathode side and pumping the vapor into the anode side. When the potential is switched off just after the 2-hour mark, the humidity values at the outlet state points return to their initial equilibrium condition. The dehumidifier cell took roughly one hour to achieve steady state in most of the experiments I conducted. During the transient phase, the membrane water content was changing as dissolved water in the ionomer material moved because of the removal of water vapor from the anode side and a deposition of water vapor at the cathode side. Additionally, the RH sensors had a slow response time and could not detect the changes in RH very quickly, especially at the low flow rates considered in the present studies.



Figure 32. 5 cm² titanium hardware with embedded serpentine flow channel.

The cell current in Figure 34 shows the exact time of the application of the potential, as the current is zero when the potential is zero. The startup current is initially very high, but gradually decays. As membrane water uptake changes, so does the electrical conductivity of the membrane. The membranes also tend to swell with greater dissolved water content, causing the thickness to increase. An increase in the membrane thickness led to an increase in the overall electrical resistance and may account for the decrements in the cell current over time.

Figure 35 shows the rates of mass transfer for both streams as measured by the method given by Eq. 24-Eq. 26. The water transfer rate was approximately zero prior to the application of the electric potential. Once I applied the potential, these rates gradually increased, eventually achieving their steady state condition. I observed

negative rate of water removal in the cathode and a positive rate in the anode. However, while the absolute values of these two rates were close, they were not exactly the same. The difference may be attributed to in part to sensor error, as detection of the water vapor in the air can be difficult as the total water content in the oxygen stream is quite low. Calibration errors may have also been a factor for the RH sensors.



Figure 33. Change in RH for 5 cm² AEM dehumidifier at 50% RH anode and 50% RH cathode.



Figure 34. Measured electrical current for the 5 cm² AEM dehumidifier at 50% RH anode and 50% RH cathode.



Figure 35. Mass transfer in the 5 cm² AEM dehumidifier at 50% RH anode and 50%

RH cathode.

2.5. <u>Comparison of AEM and PEM</u>

In the present study, I examined the performance of an AEM-driven EC dehumidifier, which had not been demonstrated in prior literature. Using the test facility diagrammed in Figure 30, I conducted two sets of experiments: one to evaluate the small-scale performance of the AEM EC dehumidifier and another to establish the baseline PEM EC dehumidifier performance. The testing of the two types of compression processes provided a way to compare the two chemistries.

For each type of membrane, I tested the effects of two variables: the humidity gradient and the flow rate. The humidity gradient affects the physical water transport in the membrane. An adverse humidity gradient condition means that the concentration of water in the dehumidifier discharge side is greater than that in the suction side. In this case, water will diffuse in the direction opposite to the electrolytic water transfer, reducing the net dehumidification rate. Conversely, a favorable humidify gradient implies the concentration of water vapor is greater in the suction side than in the discharge side. Under a favorable humidity gradient, the net water vapor flow rate would increase. A neutral humidity gradient means the humidity is the same on both sides of the dehumidifier cell. I maintained consistent definitions of the humidity gradient cases, which were considered in all the present EC dehumidifier experiments:

- Adverse humidity gradient: 40% humidity in suction side, 80% humidity in discharge side
- Favorable humidity gradient: 80% humidity in suction side, 40% humidity in discharge side
- Neutral humidity gradient: 60% humidity in suction side, 60% humidity in discharge side

I conducted the six experiments each to evaluate the two different classes of membranes, as detailed in Table 7. I considered two flow rate conditions, which were equal for both the anode and the cathode sides. The whole of the test system was maintained at ambient temperature (25°C). Slight pressure was maintained in both the anode and cathode channels by needle valves placed on the fluid stream outlets. In previous trials and in the available literature, I noted that the inlet flow rate had a significant impact on the cell's performance, even though the current, which determined the electrolytic flow rate, was relatively constant. I applied a potential of two volts at room temperature and varied the air flow rate for three different humidity cases.

Test No.	Humidity Gradient	Anode/Cathode Flow Rate	Temp.	Anode/Cathode Pressure
	(-)	(sccm)	(°C)	(kPa)
1	Adverse	100	25	125
2	Neutral	100	25	125
3	Favorable	100	25	125
4	Adverse	200	25	125
5	Neutral	200	25	125
6	Favorable	200	25	125

Table 7. EC dehumidifier test matrix.

Both the AEM and the PEM cells had active areas of 5 cm^2 . The AEM assembly was made in-house. The cathode catalyst loading is 0.5 mg/cm^2 of platinum supported carbon. The cathode catalyst was 60% platinum and 40% carbon by weight. The anode catalyst loading was 1 mg/cm² ruthenium oxide. The membrane itself was an experimental AEM sent to us from the University of Delaware. It had a thickness of 150 μm. I built PEM cell with a commercially available catalyst coated membrane (CCM) from FuelCellStore. The anode side was coated with 3.0 mg/cm² of iridium ruthenium oxide, while the cathode side was loaded with 3.0 mg/cm² of platinum black. The membrane was Nafion 115. The net thickness of the CCM 127 μ m. When assembling both cells, I used a porous titanium frit with thickness of 300 µm on the anode side and ELAT LT 1400W carbon cloth on the cathode side. The uncompressed thickness of the carbon cloth was 454 µm. Titanium plates with embedded serpentine flow channels served as the current collectors for the cells. I used titanium hardware for the experiments to prevent corrosion at the high voltages needed to sustain the dehumidification reaction. Carbon based materials would be consumed and form CO_2 in the presence of oxygen, which could remove GDL material and reduce the operable lifetime of the cell.

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For each of the experiments, I analyzed the steady-state mass flux and power consumption. Through these two measured quantities, I calculated two metrics to compare the two processes: the Faradaic efficiency and the specific energy consumption. The Faradaic efficiency is the ratio of the net molar water flow to the value expected from Faraday's law of electrolysis and is defined in Eq. 22. The specific energy consumption is the amount of water removed per joule of energy consumed. This quantity is defined as the moisture flux divided by the current density divided by the voltage, expressed in Eq. 23. For each data point, I consider five minutes of steady data and determined the average water removal energy as well as the uncertainty of the measurement.

Figure 36 shows the results for moisture flux for both the AEM and the PEM experiments. In each case, the net moisture flux increased as the dry gas flow rate increased. This is likely because, for a given current density, the electrolytic flux in less significant compared to the flux of fluid travelling in the flow channel. Thus, the change in concentration of water vapor in the flow channel is less significant. I observed that the PEM outperformed the AEM in all observed cases, particularly for the lower inlet flow rate conditions. The AEM was unable to overcome the adverse concentration gradient when the dry gas flow rate was low. However, the moisture flux performance was comparable for the high flow rate condition under the neutral and favorable concentration gradient. I concluded that the rate of free water diffusion did not change significantly from the AEM to the PEM.



Figure 36. Moisture flux results for comparison of 5 cm^2 PEM and AEM dehumidification processes under different humidity gradient conditions.

In all observed cases, the current density achieved by the PEM was higher than that of the AEM, as shown in Figure 37. The effects of humidity gradient and dry gas flow rate on the current density were slight, but nontrivial. The current density developed by the PEM was more stable under the varied test conditions. Indeed, low moisture flux in the AEM moisture flux corresponded with lower current density. Such results may appear insignificant in small scale trials; however, changes in current density would become important when designing larger cells. Changes in localized current density would contribute to greater losses in efficiency in scaled up applications, as larger areas of the membrane would become inactive.



Figure 37. Current density for comparison of 5 cm² PEM and AEM dehumidification processes under different humidity gradient conditions.

The Faradaic efficiency provides a metric for the effectiveness of the dehumidification. It tells us about the relative rates of forward water transfer and backward diffusion. The fact that the Faradaic efficiency was less than 100% in all observed cases indicated that diffusive phenomena were important even when the inlet humidity gradient was favorable. Such an effect may be possible, as the humidity gradients in the inner layers of the MEA may be higher in magnitude than those measured at the inlets and outlets. It seems less likely that corrosion was responsible for the low Faradaic efficiency. This would imply that electrons flowing into the MEA were being consumed by the corrosion of carbon material. However,

such an effect would impair the MEA performance over time, which I did not observed in the considered experiments.

In Figure 38, I noted the Faradaic efficiency of the AEM was slightly higher than that of the PEM under the favorable humidity gradient. Under these conditions, the AEM had lower current density than the PEM; however, the mass fluxes were comparable. The Faradaic efficiency values measured at the high-flow conditions were comparable for the AEM and PEM under all humidity gradient conditions. The AEM's efficiency of dehumidification in the low-flow and adverse humidity gradient was less than zero because the forward flux of water vapor was not sufficient to overcome the rate of back diffusion. The PEM appeared more effective under the adverse humidity gradient. The AEM may exhibit higher moisture diffusivity overall as evidenced by its lower efficiency under the adverse conditions and its higher efficiency under the favorable conditions.



Figure 38. Faradaic efficiency for comparison of 5 cm² PEM and AEM dehumidification processes under different humidity gradient conditions.

The specific energy consumption tracked the mass of water removed per unit energy input. Again, Figure 39 show the AEM demonstrated poorer moisture removal under the adverse humidity condition. Per unit energy input, both dehumidifier cells provided greater water removal under the favorable conditions and poorer water removal under the adverse condition. The AEM outperformed the PEM under the neutral humidity condition at high flow rate but not at the low flow setting.



Figure 39. Specific energy consumption for comparison of 5 cm² PEM and AEM dehumidification processes under different humidity gradient conditions.

The polymeric PEM-driven EC dehumidifier is not yet an established technology, but several studies exist that explore the performance of this technology [6,24,27]. The AEM-driven device, however, is a novel concept. The AEM cell considered in the present studies exhibited comparable performance to the PEM cell. As evidenced by the Faradaic efficiency measurement, it is likely water diffused more easily through AEM than through the PEM. The PEM appeared to be better suited for removing water vapor under an adverse humidity gradient. Additionally, the PEM demonstrated greater current density in all observed cases, which signified fewer electrochemical losses. The AEM demonstrated more efficient water removal under the high flow rate 73

condition and neutral humidity gradient. To further demonstrate the efficacy of EC dehumidification, it is necessary to scale up the size of the dehumidifier cell.

2.6. Scaled-Up AEM EC Dehumidifier

An analysis of a larger dehumidifier cell would establish a precedent for system-level applications. The previous tests, while important to understand the performance of the EC dehumidifier, provided a trivial amount of dehumidification capacity. Thus, it was important to investigate the feasibility of constructing larger EC dehumidifier systems for use in practical application. To that end, I conducted experiments using a $50 \text{ cm}^2 \text{ AEM-based EC}$ dehumidifier, which was ten times larger than the 5 cm² considered in the previous tests.

I again used the test facility diagrammed in Figure 31 to carry out the experiments. The AEM was provided by Rensselaer Polytechnic University and had a thickness of 120 μ m. The electrocatalysts were applied to the carbon paper gas diffusion layers. The cathode catalyst loading was 1 mg/cm² of platinum on carbon black (60%Pt and 40%C by weight). The anode was treated with 1 mg/cm² of IrO₂. The bipolar plates in the 50 cm² hardware were of graphite with parallel flow channels.

I considered the test matrix shown in Table 8. I considered the same humidity gradient conditions as in the previous tests. The temperature was maintained at ambient, about 25°C and the pressure at 125 kPa. I considered a larger number of

flow settings, ranging from 200 to 800 sccm. I considered higher flow setpoints because the larger MEA was capable of greater dehumidification capacity.

Test	Cathode	Anode	Cathode	Anode	Temp.	Pressure
No.	Rel. Hum.	Rel. Hum.	Flow Rate	Flow Rate		
	(%RH)	(%RH)	(sccm)	(sccm)	(°C)	(kPa)
1	80	40	200	200	25	125
2	60	60	200	200	25	125
3	40	80	200	200	25	125
4	80	40	400	400	25	125
5	60	60	400	400	25	125
6	40	80	400	400	25	125
7	80	40	600	600	25	125
8	60	60	600	600	25	125
9	40	80	600	600	25	125
10	80	40	800	800	25	125
11	60	60	800	800	25	125
12	40	80	800	800	25	125

Table 8. Scaled-up dehumidifier test matrix.

The bipolar plate used for the 50 cm² dehumidifier tests is shown in Figure 40. For each of the experiments, I analyzed the steady-state mass flux and power consumption and calculated the water removal energy, the ratio of the mass flux to the electrical power consumption. The results are shown in Figure 41-Figure 44. Figure 41 shows the rate of water transfer for the different cases versus inlet oxygen flow rate. I noted the moisture flux is smaller in magnitude than in the small-scale case. However, the only direct comparisons are the data points taken at 200 sccm. While the total molar flow of water was significantly higher in the 50 cm², it was not the tenfold increase expected from the increased membrane area. The experimental uncertainty was also significantly larger in these experiments.



Figure 40. 50 cm^2 graphite plate with embedded parallel flow channels.

There appeared to be a logarithmic relationship between the flow rate and the moisture flux. The increasing dry gas flow rate in all cases except one led to increased moisture flux, which I attributed to improved mass transfer conditions in the flow channels. The most significant improvements in moisture flux occurred when the flow was increased from 200 to 400 sccm. Further increases led to smaller gains in moisture flux. Under the favorable humidity condition, the moisture flux decreased

when the flow rate increased from 600 to 800 sccm. This may imply that attempting to improve the dehumidifier performance by increasing the flow rate may not work in all cases. It may be that moisture flux improvements with increased flow rate diminish after a point.



Figure 41. Water removal rate versus dry gas flow rate for $50 \text{ cm}^2 \text{ AEM cell}$.

The current density decreased significantly after scaling up. Additionally, there was greater stratification of the current density values observed at the lowest flow condition, meaning there was greater variation in the current density as the humidity conditions changes. The variation in current was likely because the membrane became drier on the cathode side, especially as water moved from cathode to anode in the same direction as the diffusion. This effect is most significant in the favorable case, when the diffusion and electrolytic flow went in the same direction, and least significant for the adverse concentration gradient, when the diffusive flow opposed the electrolytic flow, maintaining a more even distribution of dissolved water in the ionomer. The more even distribution of water was beneficial to the ionic conductivity, which depends heavily on the water uptake. As the flow rates increased, the current density values converged and the effects of the internal humidity gradients on current density became less significant.

The reduction in current density could be due to the size and geometry of the flow channels. While there appears to be a limiting current condition as the flow settings decrease, the higher flow conditions still exhibit low current density. It may be the case that some areas of the membrane were inactive. Such an effect could be attributed to maldistribution of flow. The flow channels' hydraulic diameter was also significantly larger than in the small-scale hardware. The flow velocity in the channels was, therefore, lower for a given flow rate because the cross-sectional area was larger. The reduced flow velocity led to poorer mass transfer performance, causing higher internal concentration gradients, and requiring greater voltage to maintain. The flow channels were also arranged in a parallel configuration, which would have further compounded the reduced flow velocity in the channels.



Figure 42. Current density versus dry gas flow rate for $50 \text{ cm}^2 \text{ AEM cell}$.

Figure 43 shows the Faradaic efficiency. In the favorable and neutral cases, the Faradaic efficiency seemed to decrease from the small-scale tests. Both the mass flux and current density were reduced from the small-scale tests. With greater mass transfer area in the 50 cm² cell and larger areas of reduced local current density, there was a greater chance of back diffusion working against the forward electrolytic flow. However, it was notable that the mass flux in the larger cell was always greater than zero. While, in the small scale AEM trials, the forward dehumidification was overcome by back diffusion under the adverse, low flow condition, the larger cell proved more effective. In this case, the larger cell area was beneficial to the cell effectiveness. The larger cell may be less efficient under favorable conditions, but more robust under adverse conditions.



Figure 43. Faradaic efficiency in the EC dehumidifier for $50 \text{ cm}^2 \text{ AEM cell}$.

Figure 44 shows the dehumidifier energy consumption, measured by the mass of water transferred per unit energy input. As expected, when there was more forward diffusion, the efficiency increased because there was more transport of water in the direction of electrolysis. Conversely, as the humidity gradient became less favorable, the efficiency decreases.



Figure 44. Mass of water removal per unit energy input for 50 cm² AEM cell.

To validate the results obtained in these experiments, it was pertinent to conduct a mass balance of the water vapor at the four state points. The change in humidity content ought to be the same on either side of the membrane. Figure 45 shows the cathode transfer compared to the anode transfer. While there is a general agreement between the two metrics, I observed non-trivial discrepancies skewed towards greater transfer measured on the cathode-side. While leakage remains a possibility, given the methods used for measuring the transfer of water vapor, this may not explain the difference. The humidity ratio is the measure of the mass of water vapor per mass of dry air. If moist air was escaping from the system, the water vapor and dry air would likely leave the system at the same rate and the relative presence of vapor and dry gas would remain constant downstream from the point of leakage. Therefore, I concluded that the difference in transfer was the result either sensor calibration error or of water

storage in the membrane. Future experiments should increase the test time as the measurements may have been taken during a transient period of water distribution in the MEA.



Figure 45. EC dehumidifier mass balance for $50 \text{ cm}^2 \text{ AEM cell}$.

To better understand the methods of water transfer occurring in the membrane, I analyzed the diffusive transport without applied voltage. By varying the water content and flow rate of the oxygen streams, I could estimate the rate of diffusive transport under different conditions. Before applying a potential to the electrochemical cell, I flowed the humid gas over both electrodes until reaching a steady- state condition. By calculating the rates of diffusive transport, I isolated the rates of electrochemical transfer. From Figure 46. Pure diffusive flow in the scaled-up MEA for 50 cm² AEM cell., the rates of diffusion vary according to the concentration gradient. Under an adverse concentration gradient, the water transfer was negative. Under a favorable concentration gradient, the transfer rate was positive. When no gradient existed, the transfer rate was zero. I subtracted the diffusive transfer rate from the net rate of water transfer to isolate the electrically driven transfer. The electrically driven transfer rates are shown in Figure 47, where we see that, for given flow rates, the magnitude of the transfer was approximately the same for a given flow rate. Therefore, I concluded the low water transfer observed previously in the 50 cm² cell experiments is due to back diffusion.



Figure 46. Pure diffusive flow in the scaled-up MEA for $50 \text{ cm}^2 \text{ AEM cell}$.



Figure 47. Pure electrolytic flow in the scaled-up MEA for 50 cm² AEM cell.

2.7. Conclusions

Dehumidification contributes a significant portion of the energy consumption for both residential and commercial air conditioning applications. Management of room air humidity is essential for thermal comfort and wellbeing. I observed a novel means of removing water vapor from a humidifies stream of oxygen via EC processes. Water vapor in the air was oxidized, forming hydroxide ions, which were permeable through an anion exchange membrane. Through the anionic transport, water vapor and oxygen were removed from a process air stream. This EC dehumidification process may be advantageous for air conditioning applications, as it provides a means for removing the latent cooling load, corresponding to the condensation of water vapor, from the sensible cooling load, corresponding to a decrease in the dry bulb air temperature.

A facility to measure the performance of the EC dehumidifier was constructed. I observed that diffusive phenomena were important to the operation of the water vapor removal device, as high-rates of parasitic back-diffusion of water in the membrane impeded the electrolytics transport. While the experiments demonstrated the working principle of the anionic dehumidification device, the energy efficiency of the technology must increase to compete with the conventional methods of moisture removal.

High-Voltage Mass Transfer Enhancement and Open-Air EC Dehumidifier Prototype Development

Observing the limitations of the EC dehumidifier due to the back diffusion, it became important to investigate methods to improve the mass transfer performance. High-voltage fields have been demonstrated to increase rates of heat and mass transfer, especially under two-phase conditions. It is thought that the EHD force induces secondary flows in the air stream, which caused additional fluid mixing, leading to boundary layer destabilization, increasing rates of heat and mass transfer. The researchers generally argue that the cause of evaporation enhancement is due to the secondary flows resulting from the electric wind phenomenon, which disrupt the moisture boundary layers above the sample [30, 36]. Indeed, a point voltage source operating at several thousand volts can produce ions. If one increases the voltage high enough, they will observe the corona discharge, a glowing violet stream of ionized gas spanning from the tip of the electrode to the nearest grounded surface. If they increase the voltage past that point, arcing will occur. Figure 48 shows the different regions of the electric field for a needle electrode.



Figure 48. Diagram of EHD interactions at liquid-vapor interface.

A strategy to increase the mass transfer to the membrane is to employ a high voltage electrode, situated nearby the MEA, to generate electrohydrodynamic (EHD) force, which is well known to improve mass transfer rates in moist objects [30, 31, 35, 42]. The high voltage electrode ionizes particles in the air, which are then repelled by the like charge of the source electrode. The ionized particles then collide with neutral particles in the air, which creates the EHD force emanating from the source electrode [37]. Under the induced EHD field, a reactive flow of gas is developed, which is known as ionic or electric wind. These secondary air flows produced by the EHD force are believed to be largely responsible for the mass transfer enhancement, as they disrupt the convective boundary layer over the membrane surface [31]. Using the EHD enhancement, I ultimately hoped to improve the moisture removal rate by encouraging more water vapor to enter the cathode or exit the anode of the MEA, as illustrated in Figure 49.



Figure 49. EHD Enhanced EC Dehumidification.

3.1. <u>Experimental Setup</u>

To investigate the effect of the EHD on moisture removal or humidification, a test facility, based on Lai and Sharma's test system, will determine the EHD humidity transfer enhancement based on the change in weight of a moist sample over time [30]. In their experiments, Lai and Sharma flowed dry air over the moistened sample in the presence of the EHD field and recorded the weight of the sample throughout the experiment. From the change in weight, they were able to determine the drying rate. They compared this change in weight to that of a control sample. Figure 50 shows the system schematic.

I designed a flow straightening device the remove eddy currents from the air stream in the test section, promoting a more uniform velocity fields over the sample and reducing systematic error in EHD enhancement measurements. I selected a fan to provide the primary air flow through the duct. The fan was sized such that the velocity over the sample could be controlled from 0 to 3 m/s, which is a common range of air velocities presented in publication for EHD enhanced drying. The test setup was used to measure the temperature, T, pressure, P, and relative humidity, RH, of the air in the test section. A hot wire anemometer was inserted into the duct as well to measure the velocity of the air moving of the sample. I did not measure continuous anemometer data. Rather, I used the anemometer to establish a calibration for fan input signal. Having mapped the fan input signal to the downstream air velocity, I was able to set the experimental fan speed to the desired value. The change in the sample's moisture content was be measured by a digital balance located below the high voltage probes. Figure 51 shows a photograph of the test duct.

The high voltage electrode device was placed just above the sample. The high-voltage DC power was provided by a Glassman EW series voltage supply with a range of 0 to 30 kV. I constructed the facility such that the EHD electrodes could be moved up and down to the provide the desired gap length between the water surface and the electrode tips. The bottom of the sample dish was made of stainless steel and was connected to the ground of the power supply.

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Figure 50. Schematic diagram of EHD enhancement test facility.



Figure 51. Photograph of EHD evaluation facility.

The shape and size of the high-voltage electrodes impacted the EHD enhancement. However, there are no known methods of analytical methods of analyzing the effect of the electrode geometry on the drying enhancement. Thus, I constructed the EHD test section in such a way that I was be able to install several different electrodes. In this way, I could empirically observe the effect the electrode geometry has on the mass transfer enhancement.

I used the Sherwood number, the ratio of convective to diffusive mass transfer to compare different drying experiments. To calculate that metric, I determined the mass flux, as given by Eq. 32, where \dot{m}''_{emp} is the experimentally determined mass flux and *A* is the area of the sample.

$$\dot{m}''_{emp} = \frac{dm}{Adt}$$
 Eq. 32

I used the method from Poós and Varju to calculate the mass transfer coefficient, as in Eq. 33 [62].

$$h_m = \dot{m}''_{emp} \left(\frac{p_{v,sat}}{RT} - \frac{p_{v,amb}}{RT}\right)^{-1}$$
 Eq. 33

The Sherwood number was then given by Eq. 34. I use the relation from [63] to determine the binary diffusion coefficient for water vapor in air.

$$Sh = \frac{h_m}{D_{12}L}$$
 Eq. 34

$$D_{12} = \frac{0.43 \left(\frac{T}{100}\right)^{1.81} \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{0.5}}{P\left(\frac{T_{c,1}T_{c,2}}{10^4}\right)^{0.1406} \left[\left(\frac{\nu_{c,2}}{100}\right)^{0.4} + \left(\frac{\nu_{c,2}}{100}\right)^{0.4}\right]^2}$$
Eq. 35

I evaluated the magnitude of the mass transfer enhancement effect for different air velocities and applied voltages. To this end, I conducted enhanced drying experiments by evaluating the rate of dehumidification via the change in weight over time of a dish filled with water. For each experiment, I set to electrode voltage at a constant value and varied the air velocity in stages. I allotted at least three hours for each datapoint to accurately determine the rate of dehumidification over time. I also employed several different electrode shapes, noting that the type of electrode significantly affected the dehumidification performance. Ultimately, I found that a multiple needle configuration, as described by Lai and Sharma. in their experiments, was sufficiently effective [30]. The electrode configuration, which consists of three stainless steel sewing needles arranged in an equilateral triangle above the sample, is shown in Figure 52.



Figure 52. Photograph of EHD electrode setup.

Figure 53 shows the raw data results from one set of experiments conducted without any applied EHD condition and air velocities ranging from 0.5 m/s to 3 m/s. The results are stable over the duration of the trial, while the random error increases as the air velocity increases and the fluid flow becomes more turbulent. I calculated the rate of dehumidification through a finite difference differentiation method and then applied a one-hour moving average to the rate to smooth out the results.



Figure 53. Mass of moisture removed from sample over time.

To evaluate the Sherwood number for each of the tests, I computed the rate of change in weight of the sample over the duration of the test. The random error of the sample weight led to a significant amount of noise in the time derivative of the mass removal. Therefore, I applied a moving average filter with a width of one hour to smooth out the data sets. The results, shown in Figure 54, were mostly consistent. However,
especially at high fan speed, the drying rate decreased over time. This was likely because the water level in the dish decreased as the water evaporated, decreasing the rate of evaporation.



Figure 54. Time-averaged drying rate over time.

Using these measurement techniques, I conducted similar experiments at varied EHD voltages. I increased the EHD from no applied voltage to 5 kV to 10kV. The electrode spacing was maintained 0.5 in, meaning the needle points were positioned 0.5 in above the water surface. After 10 kV, arcing was likely to occur, thus that was the highest possible voltage condition. The test matrix is shown in Table 9.

Test Set	EHD	Air Velocity	Upstream Rel.	Temp.
	Voltage	(m/s)	Hum.	
	(kV)		(%RH)	(°C)
1	0	[0.5, 1.0, 1.5	40	25
		2.0, 2.5, 3.0]		
2	5	[0.5, 1.0, 1.5	40	25
		2.0, 2.5, 3.0]		
3	10	[0.5, 1.0, 1.5	40	25
		2.0, 2.5, 3.0]		

Table 9. EHD evaporation enhancement test matrix.

The graph in Figure 55 shows a summary of the results of these experiments. From the graph, I saw the largest increases in the Sherwood number occur at lower air velocities. As the air velocity increases, the enhancement due to the electric field diminishes. In general, as the EHD voltage increased, the evaporative mass transfer increased. The effects were most evident at low air velocities. At 10 kV electrode potential and 0.5 m/s air velocity, I noted a four-fold improvement in the Sherwood number. The results indicate that there may be an optimal solution to the EHD-enhanced EC dehumidification problem, as the moisture transfer enhancement is most significant at low air velocity; however, as noted in the EC dehumidifier experiments, the dehumidification performance improves with increasing gas flow rate in the flow channels.



Figure 55. Effect of air velocity and electric field strength with multiple needle electrode.

3.2. Open-Air EC Dehumidifier Experimental Setup

I identified a need to develop new hardware for the EC dehumidifier to integrate the EHD mass transfer enhancement. The EHD required a clear line of sight to the liquid vapor interface. Thus, the cell hardware needed to be open to the air. Moreover, an open-air configuration would be practical for real world dehumidification applications. For example, the EC dehumidifier could be installed in an air handling unit. The use of embedded graphite flow channels would be prohibitively expensive and cause significant pressure drop at the air flow rates needed for building cooling systems.

Open air fuel cell have been a topic of research discussion for decades. Early studies into air-breathing fuel cells examined direct methanol fuel cells for portable power solutions [64-66] and PEM fuel cells [67,68]. Despite these cells attractive characteristics, such as portable power and free convection oxidant supply, the lack of control in balancing the water in these cells and other factors often led to reduced power density [69]. The open-air cell performance is often influenced by the geometry [70,73]. Kumar and Parthasarathy investigated methods for passive water management in the open-air fuel cell by allowing the cell to achieve higher temperatures and increasing the saturation of water in the air [74]. Lee et al. and Bullecks et al. both developed open-air cylindrical PEM fuel cell designs showing improved volumetric power density [75,76]. However, a challenge of the open-air cells remains that their performance may degrade over time [77].

I borrowed from Kim et al.'s design to develop the air breathing ECD, who made a built a stack of several planar air-breathing PEM fuel cells [78]. Jeong et al.'s investigations into the effects of the percentage of open cell area revealed that an open area ratio of roughly 50% would give the best chance of success in the open-air dehumidification experiments, meaning 50% of the cell active area is open to the air and 50% is covered by the current collector material [70]. For this test, I considered a 5 cm² PEM fuel cell. The 2 V of EC potential were applied to the anode. The cathode side served as the counter electrode for the EC reactions and was grounded to the EHD power supply. The cathode was made of a 1/8th in thick copper sheet, which was CNC machined to the desired opening configurations. A polycarbonate top plate

pressed down onto a copper grounding plate, which contacted the MEA. A representative drawing of the copper grounding plate is shown in Figure 56. The thin copper plate ensures a sufficiently small EHD electrode gap while still providing sufficient sealing capability for the membrane. A photograph of the prototype is shown in Figure 57. Photograph of open-air EC dehumidifier.

To ensure proper sealing, I conducted a finite element analysis (FEA) of the cell assembly and examined the simulated deformation in the copper grounding plate. I represented the tightening force from the bolts as an axial force applied around the through-holes around the perimeter of the cell. I simulated an applied torque of 4 N-m on each of the bolts. From the FEA, which I performed with the Solidworks simulation toolbox, I determined the maximum resultant deformation in the ground plate was on the order of several micrometers and, therefore, represented an acceptably low risk for leakage.



Figure 56. Drawing of copper grounding plate.



Figure 57. Photograph of open-air EC dehumidifier.

I combined the MEA evaluation test facility with the EHD enhancement test section, which enables us to measure the performance of an ECD prototype simply and accurately with one side exposed to the air. Figure 58 details the combined test facility. Humidified oxygen flowed through the anode flow channels via the two MFCs, which maintained the humidity on the cathode side. I evaluated the moisture removal rate via the dry gas mass flow and the difference in RH as I did in the closed-cell EC dehumidifier experiments. The experiments required two power supplies: one for the low-voltage EC potential and one for the high voltage EHD potential. I adjusted the upstream air velocity from 0.5 to 2. 5 m/s for the present experimental trials. I moved the test system into an environmental chamber to precisely control the ambient conditions. The chamber provided control of temperature and humidity. For each test, I kept the ambient temperature and humidity at a constant 24°C and 50% RH, respectively.



Figure 58. Schematic of the EHD enhanced ECD test facility.



Figure 59. Photograph of combined test station for EHD-enhanced EC dehumidification experiments.

The experimental test matrix is shown in Table 10. I controlled four independent variables: the anode-side inlet RH, the low voltage EC potential, and the high voltage EHD potential, and the cathode-side air velocity. The upstream anode RH changes the direction of the humidity gradient. Again, I consider three cases: adverse, neutral, and favorable. The EC potential and EHD potentials are either on or off and I did not consider other values of these electrical potentials. The cases where both EC and EHD potentials are zero serve as a control for the experiments. They allowed me to evaluate the effects of the electrolytic flow independent of the diffusive flow. I only consider the EHD potential where the EC potential is on, as the purpose of the study was to evaluate the EHD as a means of enhancing the EC dehumidification.

Test Set	Anode In. RH	VEC	VEHD	Upstream Air Velocity	Air- Side RH	Temp.	O ₂ Flow
	(%RH)	(V)	(kV)	(m/s)	(%/RH)	(°C)	(sccm)
А	95	2	0	[0.5,1.5,2.5]	50	24	200
В	50	2	0	[0.5,1.5,2.5]	50	24	200
С	25	2	0	[0.5,1.5,2.5]	50	24	200
D	95	0	0	[0.5,1.5,2.5]	50	24	200
Е	50	0	0	[0.5,1.5,2.5]	50	24	200
F	25	0	0	[0.5,1.5,2.5]	50	24	200
G	95	2	5	[0.5,1.5,2.5]	50	24	200
Н	50	2	5	[0.5,1.5,2.5]	50	24	200
Ι	25	2	5	[0.5,1.5,2.5]	50	24	200

Table 10. Open-Air, EHD-Enhanced EC Dehumidifier Test Matrix.

I built a custom high-voltage electrode for these experiments. The electrode array was design to provide even coverage of the high-voltage source across the entire open cell area. The array consisted of nine evenly spaced nickel-plated steel needles, shown in Figure 60. The needles were spaced 7.5 mm apart. I epoxied them into place, supported on a Delrin block. The Delrin prevented electrical insulation to the other components in the system. The electrodes were mounted above the open area of the EC dehumidifier cell.



Figure 60. Photographs of the needle electrode array.

3.3. <u>Results</u>

For each test point, I ran the experiment for three hours, which was long enough to achieve a steady-state condition. I recorded several minutes of data at the steady-state conditions. To evaluate the efficacy of the open-air dehumidifier, I looked to the moisture removal rate achieved for each point. Figure 61 shows the experimental results for the adverse condition (when the anode inlet humidity was set to 25%). The control case with no applied potential, the EC-only case, and the EHD enhanced EC case are all plotted next to one another.

Under the adverse condition, the forward EC transfer was able to narrowly overcome the back diffusion. I observed the diffusive mass transfer rate increased as the fan speed increased, which was likely due to better mass transfer performance at increase air velocity. The moisture transfer rate observed in the EC-only case appeared to decrease with increasing air velocity, as the rate of back diffusion increased. However, contrary to the hypothesis that EHD enhancement would speed up the rate of evaporation, I observed an opposite trend. In all cases, the combined EHD and EC moisture removal was lower than the EC-only condition.



Figure 61. Open-air EC dehumidifier moisture transfer under adverse humidity gradient.

The neutral case, shown in Figure 62, gives a clear measurement of the pure EC transfer rate, which varied insignificantly with increasing fan speed. The control case shows that the diffusive transfer between the anode and cathode flow channels was virtually zero. I concluded the air-side flow velocity did not have as significant effect on the dehumidification for the open-air experiments as in the closed-cell experiments in Figure 41. In the neutral humidity case as well the EHD voltage did not present any

benefits over the EC-condition. Indeed, at higher air velocity, the EHD seemed to have a detrimental effect on the moisture removal rate.



Figure 62. Open-air EC dehumidifier moisture transfer under neutral humidity gradient.

Under the favorable gradient, the electrolytic mass transfer was higher than the purediffusive case by a constant amount. However, the diffusion increased with increasing air velocity, meaning the upstream air was more effective at removing water vapor from the anode channel. The poor performance of the EHD enhancement may be attributed to the cell geometry. In the baseline EHD evaporation enhancement tests, the high voltage electrodes were positioned directly above a water reservoir. However, in this case, the interface of the dissolved water in the membrane phase and the water vapor was buried beneath several layers of material. The titanium frit gas diffusion layer was essential for maintaining contact between the cathode-side of the membrane and the current collector. However, it also obstructed the line of sight between the high voltage electrodes and the dissolved water interface. Furthermore, the EHD electrodes were shown to be effective at increasing the speed of liquid water evaporation, but not the speed of water dissolution from the ionomer material. While the EHD effect seems likely to facilitate the evaporative transfer from the membrane phase, such an effect has not been demonstrated empirically. Furthermore, the secondary flow resulting from the EHD could have caused air to stagnate in the cathode current collector because the open-air EC dehumidifier design was optimized for maintain constant pressure on the MEA and not for facilitating airflow over the cathode.



Figure 63. Open-air EC dehumidifier moisture transfer under favorable humidity

gradient.

3.4. System Integration

Another challenge of the EHD integration is the stack development. While fuel cells can have stacks of multiple cells back-to-back, this is not feasible in an air conditioning application, as the pressure drop created by the narrow flow channels will be too great. There must also be larger spacing between the cells to accommodate the high-voltage electrodes. Therefore, I developed a concept for an enhanced ECD stack design shown in Figure 64. In this design, both sides of the MEA were open to external flow and EHD electrodes will be interspersed between cells. Manifolds would supply air to the designated locations to avoid mixing of water vapor and dry air. The high-voltage electrodes would help to pull moisture out of the membranes, humidifying an exhaust air stream.



Figure 64. Multi-cell enhanced ECD concept.

An air handling unit is the device that cools, dehumidifies, and circulates air through a building. A certain portion of the air passing through the air handler is fresh air from outside, while a larger portion is recirculated from the building return vents. The air handler traditionally consists of a blower, heating/cooling elements, dampers, and filters. In air conditioning, air is cooled via a vapor compression cycle. The evaporator coils provide the cooling work to the air in the air handler. Generally, the evaporator coils handle both the sensible and the latent load, meaning they reduce the dry bulb temperature of the air (sensible cooling) and remove the humidity through condensation (latent cooling). However, in the present application, the EC dehumidifier would serve as the latent cooling device, or latent evaporator. This would leave the vapor compression cycle with only the sensible cooling load, saving a significant amount of energy. I envisioned three possible configurations for integrating the EC dehumidifier into the air handling unit, diagrammed in Figure 65.

The different configurations would have their own distinct advantages. For example, if the dehumidifier only processes the outdoor air, the total volume of air to dehumidifier would be reduced. If the sensible evaporator comes before the EC dehumidifier, the RH would be higher, but the temperature would be reduced, having potential impacts on the membrane conductivity. Conversely, if the EC dehumidifier comes before the sensible evaporator, the RH would be lower, potentially requiring more energy to remove.



(a) ECD used as a ventilator, processing only outdoor air.



(b) ECD used as latent evaporator after the sensible evaporator processing the full flow rate of indoor air with or without ventilation



(c) ECD used as latent evaporator before the sensible evaporator, processing the full flow rate of outdoor air with or without ventilation

Figure 65. Three configurations for EC dehumidifier system integration.

3.5. <u>Conclusions</u>

As EC dehumidifier experiments revealed significant mass transfer limitations hampering the moisture removal performance inside the MEA, I investigated EHD evaporative mass transfer enhancement as a method of increasing the net rate of water transfer. When a high DC voltage is applied to a sharp electrode, such as a needle, air nearby the electrode ionizes and gains momentum due to electrical repulsion. The ions collide with neutral air molecules, exchanging momentum. The reactive flow of gas is referred to as electric wind. The electric wind phenomenon may crease secondary flows in a fluid stream and destabilize moisture boundary layers at the liquid-vapor interface. The effect of which is improved evaporative mass transfer.

EHD mass transfer enhancement is a well-documented phenomenon. In this study, I investigated its potential as a means of improving the efficiency of an EC dehumidifier. I constructed a test duct to evaluate the EHD mass transfer enhancement for controlled water evaporation. Operating at different electrode voltages and air velocities over the sample, I measured the rate of change in weight of a small pool of water to evaluate the Sherwood number. The study demonstrated that greater mass transfer enhancements were possible at lower air velocities. At higher velocities, inertial forces of the upstream fluid dominated the EHD force developed by the high-voltage electrode.

I constructed a prototype of an EHD-enhanced EC dehumidifier. The moisture removal device was configured such that the high-voltage field helped to remove water vapor from the discharge (anode) side of the dehumidifier. One side for the dehumidifier MEA was situated atop of the fuel cell end plate with embedded flow channels. On this side, I was able to measure the change in relative humidity before and after the MEA. On the opposite side, the MEA was open to the air. Preliminary experiments demonstrated that dehumidification increased when a voltage was applied to the cell. However, applying the voltage to the EHD electrode had a more significant effect. When I applied both EC voltage and EHD voltages, the dehumidification was greatest.

4. Mathematical Modeling

4.1. <u>Generalized Model Approach</u>

Three generalized transport equations, summarized in Table 11, apply to any arbitrary control volume in the EC pumping device. The coupled equations are solved to determine the rates of transfer of mass and charge. Because the EC pumping devices considered in this work operated isothermally, I did not consider heat transport in the generalized model. These equations are of the same form as those employed by Seigel et al [47]. In these equations, the index *i* refers to the species in consideration. Such species may refer to: hydrogen gas, ammonia vapor, oxygen gas, water vapor, liquid water, and ionic species. The source terms in these governing equations vary from fluid to fluid and from MEA layer to layer. The source terms is compiled in

Table 12.

Table 11. Governing Equations.

Governing Equation	Vector Form	
Mass	$\nabla \cdot (-D_i \nabla C_i) - \bar{u} \nabla C_i + S_{m,i} = 0$	Eq. 36
Charge	$\nabla \cdot (-\sigma \nabla \phi) - S_{\phi} = 0$	Eq. 37

Table 12. Source Terms.

Source Term	Equation		Applicability
EC species	$S = \pm \left(\frac{1}{2}\right) \frac{dj}{dj}$	Eq. 38	Catalyst
generation/consumption	$S_{m,i} = \pm \left(\frac{1}{zF}\right) \frac{1}{dy}$		layers
Dissolved water vapor	$S_{m,diss} = h_{m,diss} (C_{mem}^{v})$ H	Eq. 39	Catalyst
transfer	$-C_{\nu H_2 O})$		layers
Ion generation	$s - \frac{dj}{d}$	Eq. 40	Catalyst
	$S_{\phi} = -\frac{1}{dy}$		layers
Activation loss	$S_a = \eta_a$ H	Eq. 41	Catalyst
			layers

4.1.1. Flow Channels

For simplicity, I assumed transfer in the MEA is purely one-dimensional and occurs in the y-direction, perpendicular to the membrane surface. Thus, I advance the model by considering the loss or gain of mass and heat in the flow channels. I consider the mass transfer boundary condition at the interface between the flow channel and the gas diffusion layer as in Eq. 42.

$$\left(\frac{\partial \left[\bar{u}C_{ch,i}\right]}{\partial y}\right)dx - h_{m,i}(C_{ch,i} - C_{gdl,i}) = 0$$
 Eq. 42

4.1.2. Gas Diffusion Layers and Catalyst Layers

Tartakovski and Dentz derives a model to estimate the effective diffusion coefficient through a layer of porous material, such as the catalyst layer on the MEA [79]. They describe the effective diffusivity via the Bosanquet relation (Eq. 43), which takes the harmonic mean coefficient of molecular diffusion defined by kinetic theory (Eq. 44)

and the Knudsen diffusivity (Eq. 45). Knudsen diffusion describes the movement of fluid through narrow pores. If the Knudsen number, $\text{Kn} = \lambda/w$, where λ is the mean free path of a particle diffusing in a narrow channel with the characteristic length *w*, is small, then the Knudsen diffusivity is negligible. However, if $Kn \gg 1$, then the Knudsen diffusion dominates [79].

$$D = \left(\frac{1}{D_0} + \frac{1}{D_{Kn}}\right)^{-1}$$
 Eq. 43

$$D_0 = \frac{\lambda v}{3}$$
 Eq. 44

$$D_{Kn} = \frac{1}{3} d_p \sqrt{\frac{8RT}{\pi M}}$$
 Eq. 45

Furthermore, the effective diffusivity for a porous media must consider the porosity, ε , and the tortuosity, τ , of the material, as in Eq. 46.

$$D_{eff} = \frac{\varepsilon D}{\tau}$$
 Eq. 46

Kucernak and Zaliris developed generalized models of hydrogen oxidation and hydrogen evolution reactions and agglomerate catalyst geometry [80]. Their findings were helpful for solving for the activation overpotentials in the present modeling effort. The flux of ions and the activation overpotentials in the cell is governed by the Butler-Volmer equation, expressed for both anode and cathode in Eq. 47 and Eq. 48

$$j_a = j_{0,a}^{ref} \left(\frac{C}{C_{ref}}\right)^{\gamma} \exp\left(\frac{\alpha_a zF}{RT}\eta_{a,a}\right)$$
 Eq. 47

$$j_c = j_{0,c}^{ref} \left(\frac{C}{C_{ref}}\right)^{\gamma} \exp\left(\frac{\alpha_c zF}{RT} \eta_{a,c}\right)$$
 Eq. 48

The study conducted by Dickinson and Hinds provided a critical discussion into the appropriate expressions of the Butler-Volmer equation for modeling electrode kinetics [81]. They posited that superfluous parameterization of the electrode kinetics could lead to incorrect data or misleading conclusions; they cite the intentionally simple kinetic expressions used by Um et al. as reliable for accurate results and numerical stability [82].

4.2. <u>Membrane</u>

In the membrane, I must include an additional source term, Eq. 49, to account for the electroosmotic drag phenomenon. Fuel cell researchers often find that the ionic species traversing the electrolyte layer carry water molecules with then via dipole interactions [83]. The flow of water molecules which is neither due to diffusion no electrolysis is known as electroosmotic drag. Springer et al. developed a method for modeling electrochemical processes and water transport in fuel cells using Nafion membranes [45]. Their model provides a widely used relation to estimate the number, n_d , of water molecules that are dragged across per ion for Nafion membranes. Additionally, I also rely on their model to estimate several other membrane

parameters, including the diffusivities of water, hydrogen, and oxygen in the membrane; the protonic conductivity; and the thermal conductivity.

$$S_{m,H_{2O}} = \pm \left(n_d \frac{i}{zF} \right) \frac{dj}{dy}$$
 Eq. 49

I assume electroneutrality, which states a proton occupies every fixed SO3- charge site in the electrolyte. A flux of proton results from a potential gradient and not a concentration gradient. The polymer electrolyte contains water and protons. The principle driving forces for liquid water motion are diffusion, electrostatic force. Electrolysis transport water via hydrogen ions; however, the process does not actually involve liquid water crossing the membrane. Two important fluxes, or material balances, are the flux of protons and the flux of water molecules. The flux of water molecules may be expressed as Eq. 50. The drag coefficient n_{drag} is given by Springer et al in Eq. 51.

$$-D_w \nabla C_{H20}^m = n_{drag} \frac{i_x}{F}$$
 Eq. 50

$$n_d = \frac{2.5}{22} \lambda$$
 Eq. 51

$$\lambda = \frac{C_{H2O}^m}{\frac{\rho_{dry}^m}{M^m} - bC_{H2O}^m}$$
Eq. 52

The membrane diffusivity is an integral part of the model. The model's success was largely determined by the expressions used for water diffusivity in the dissolved phase. Springer et al. considered a diffusivity expression that considered membrane swelling, which eliminated the need to track the expansion of the membrane in their model [45]. Their numerical expressions for diffusivity were based on the work of Zawodzinski et al., whose measurements showed a non-linear relationship between the dissolved-phase diffusion coefficient and the membrane water uptake [84]. Further fuel cell modeling efforts by Dutta et al. considered piecewise expressions for water diffusivity based on the membrane hydration [85]. The diffusion coefficients from Dutta et al. were implemented by Misran et al., who used the expressions for evaluate PEM fuel cell water transport behavior at various pressures and temperatures [86]. To construct a reliable model for predicting the EC dehumidifier performance, I considered Raso et al.'s work, which investigated new expressions for determining the water diffusion coefficient in PEM fuel cells [87]. Their estimations of water diffusivity differed from previous studies in that it showed a sharp increase in diffusivity as the membrane became saturated with dissolved water.

I combined elements from Dutta's expressions and tabular data from Raso et al.'s model to develop a piecewise regression for water diffusivity. I chose to use a piecewise expression, rather than linear interpolation of the tabular data because of the higher computational cost of interpolation. All considered expressions of water diffusivity had a term to adjust the diffusion coefficient D_w based on the operating temperature, as shown in Eq. 53. The water diffusion reference temperature is 30°C [45]. The diffusivity coefficient D_λ is dependent on the membrane water uptake.

$$D_w = D_\lambda \exp\left[2416\left(\frac{1}{303} - \frac{1}{T}\right)\right]$$
 Eq. 53

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I used the diffusivity expression given by Eq. 54. Figure 66 shows the relationship between the D_{λ} and water uptake. The expressions from Dutta et al. and Raso et al. are shown. Dutta et al.'s model has a discontinuity when λ is equal to 4.5, which provided nonphysical results during model implementation [85]. Raso et al.'s model provided a continuously differentiable relationship between D_{λ} and λ [87]. The expression in Eq. 54 approximates Raso et al.'s model in a relatively simple and computationally inexpensive way. Eq. 54 is continuous and therefore provided more consistent results than the expressions from Dutta et al.

$$D_{\lambda} = 10^{6} \begin{cases} 0.37\lambda^{2} - 0.51\lambda + 0.37, & \lambda \leq 3.75 \\ -0.03\lambda^{3} + 0.78\lambda^{2} - 6.7\lambda + 19.29, & 3.75 < \lambda \leq 5.4 \\ 1.25, & 5.4 < \lambda \leq 13.2 \\ 10^{-6} \exp(1.07\lambda), & 13.2 < \lambda \end{cases}$$
Eq. 54



Figure 66. Comparison of membrane water diffusivity expressions.

Ion Transport

The total ion transport, driven by the potential gradient, is given in terms of current and the convective flow of ions. The ionic flux is expressed by Eq. 55.

$$\frac{\partial \Phi_m}{\partial x} = -\frac{i}{\sigma_m}$$
 Eq. 55

The ionic conductivity affects the rate electrolytic transport and the ohmic voltage losses. Ions are generated in the catalyst layers according to the Butler-Volmer equations. In these reactions, the ions dissolve into the ionomer material and flow according to the direction of decreasing ionic potential. The ionic conductivity depends on the temperature as well as the water uptake. Eq. 56 and Eq. 57 express the relationship between the ionic conductivity, temperature, and water uptake. The equations are derived empirically from experiments conducted by Springer et al. [45], where $\sigma_{m,303}$ is the conductivity of the membrane at a reference temperature of 303 K. The expressions are valid for $\lambda > 1$.

$$\sigma_m = \sigma_{m,303} \exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right]$$
 Eq. 56

$$\sigma_{m,303} = 100(0.00513\lambda - 0.000326)$$
 Eq. 57

4.3. <u>Simplified Modeling Methodology</u>

I developed a simplified approach, implementing the governing EC transport equations in a pseudo-two-dimensional modeling methodology. The coupled transport phenomena consist of processes that occur in each of the layers in the MEA: the GDLs, the CLs, and the membrane. I restricted efforts to predicting the smallscale PEM cell performance. In the present study, I limited focus to the closed cell counterflow dehumidifier and the open cell dehumidifier. The model considered an isothermal case. The heart of the simulation was a mass balance of water vapor in the MEA. Borrowing the solving procedure from Springer et al., I developed a numerical solver that found the steady-state behavior of the ECD element where electrolytic flow, electroosmotic drag, and liquid water diffusion were all present [45].

The solution domain consists of seven elements in the y-direction, perpendicular to the membrane surface and any number of elements in the x-direction, parallel to the direction of flow in the gas channels, as shown in Figure 67. I solved the concentration of water vapor and oxygen in each of the flow channel elements via a control volume analysis. The flux of water and oxygen for each element was determined by the coupled mass and charge transfer solution. I solved each element to determine the flux of water vapor, the flux of oxygen, and the current density. I represented the coupled heat and mass transfer processes through a series of boundary-value ordinary differential equations (ODEs). I solved the coupled ODEs numerically through finite difference methods using appropriate boundary conditions [88].



Figure 67. Diagram of pseudo-two-dimensional EC dehumidifier model.

4.3.1. Transport of Oxygen

I discretized the transport equations to run the simplified modeling methodology in MATLAB. Applying conservation of mass of oxygen in an arbitrary control volume the GDL gives Eq. 58. I applied a first order central finite difference method to arrive the discretized conservation equation in Eq. 58.

$$-\nabla \cdot (D_{02}\nabla C_0) = 0$$
 Eq. 58

$$-D_{02}\left(\frac{C_{i-1}^{0} - 2C_{i}^{0} + C_{i+1}^{0}}{\delta x^{2}}\right) = 0$$
 Eq. 59

Similarly, the conservation of oxygen in the CL gives the expression in Eq. 60. In this case, oxygen is produced in the anode in the anode and consumed in the cathode. Thus, the second term on the left-hand side of Eq. 60 is appears. The expression is discretized in Eq. 61. Eq's Eq. 58 through Eq. 61 apply for both anode and cathode sides, so long as appropriate signs of the source terms are chosen.

$$-\nabla \cdot (D_{ov} \nabla C_o) \pm \frac{1}{4F}i = 0$$
 Eq. 60

$$-D_{0v}\left(\frac{C_{i-1}^{0} - 2C_{i}^{0} + C_{i+1}^{0}}{\delta x^{2}}\right) = \mp \frac{1}{4F}i$$
 Eq. 61

4.3.2. Transport of Water Vapor

I considered only water vapor and dissolved water in the simplified modeling methodology, abstaining from the rigorous two-phase flow modeling that would be necessary to account for the presence of liquid water. Some models account for liquid water via a saturation term, assuming liquid water droplets form in the pores of the CL and GDL. The liquid water is assumed to be stationary and decreases EC activity by occupying volume in the CL [89]. However, I considered the approach from Springer et al., wherein water vapor may become supersaturated and is carried away by the flow channels [45]. Such an approach is reasonable, as less water is present in the EC dehumidifier than in fuel cells. Fuel cells produce water via the EC reactions in addition to the water that is used to humidity the membranes. The EC dehumidifier transport water, drying out one side of the membrane more than the other. Thus, there is a smaller chance for flooding in the PEM dehumidifier cathode than in a PEM fuel cell cathode. Indeed, the relative humidity leaving the EC dehumidifier in the prior experiments was less than 100% in most cases, which strengthened the assumption that liquid water was less likely to be a significant factor in EC dehumidifier

modeling methodology. The vector form continuity equations for water vapor in the GDLs are shown in Eq. 62 and discretized in Eq. 63.

$$-\nabla \cdot (D_{0\nu} \nabla C_{\nu}) = 0$$
 Eq. 62

$$-D_{0v}\left(\frac{C_{i-1}^{v} - 2C_{i}^{v} + C_{i+1}^{v}}{\delta x^{2}}\right) = 0$$
 Eq. 63

Water vapor is consumed in the anode catalyst layer and produced in the cathode catalyst layer. Thus, the source terms for water vapor in the catalyst layers have opposite signs of the source terms for oxygen. Additionally, values of the water vapor source terms are twice as great of those for oxygen, as one mole of water vapor is exchanged per every two moles of electrons, while one mole of oxygen is exchanged for every four moles of electrons.

$$-\nabla \cdot (D_{0\nu} \nabla C_{\nu}) + \frac{1}{2F}i = 0$$
 Eq. 64

$$-D_{0\nu}\left(\frac{C_{i-1}^{\nu} - 2C_{i}^{\nu} + C_{i+1}^{\nu}}{\delta x^{2}}\right) = \pm \frac{1}{2F}i$$
 Eq. 65

Boundary Conditions

I solved two sets of boundary-value ODEs for water vapor and oxygen: one set for the anode side and one set for the cathode side. The membrane provided a barrier to the vapor on either side, separating the two fluid reservoirs. The concentrations of vapor species (water vapor and oxygen) at the first and last cells were determined by the concentration of the flow channels, according to Eq. 42. This provided a Dirichlet boundary condition for both sets of ODEs. The concentration in the flow channels changed according to the flux through the MEA and the active area of the MEA.

The flux of vapor species at the interface of the CL and the MEA was assumed to be zero. Thus, at the last cell in the CLs, the boundary condition expressed by Eq. 66 and Eq. 67 applied.

$$D_{Ov} \nabla C_v = 0$$
Eq. 66
$$D_{Ov} \nabla C_O = 0$$
Eq. 67

Solution Procedure

The flowchart in Figure 4 shows the solution procedure for solving the mass fluxes and current density in each element. The input variables were the concentrations of water vapor and oxygen for both the anode and cathode flow channels and the voltage. I initiated guess values for both the current density, *I*, and the water vapor transfer ratio, α , which is defined as the ratio of net water transfer to the Faradaic water removal rate. The Faradaic water removal rate is directly proportional to the current density via Faraday's law of electrolysis. After guess values are initiated, the net water flow rate, N_w , is calculated. From the guess value for N_w , I calculated the internal concentrations of water vapor and oxygen in the inner layers of the MEA. I used data from Springer et al.'s study to predict the equilibrium water uptake, λ , based on the water vapor concentration in the MEA. If the solver finds that the λ value at the interface between the cathode catalyst layer and the membrane is the same for both the forward and backward directions. The solver calculates two values of λ at this instance. One value is achieved via the mass transfer equations assuming N_w as the water flux from the anode-direction and the other is achieved using N_w from the cathode direction. If these values of λ differ outside of the specified tolerance, a new guess value for α is chosen.

Finding an appropriate value of α , the solver then calculated the electrochemical overpotentials using the guess value of current density. The overpotential equations depend on the water and oxygen concentrations and the current density. The different overpotentials consist of the ohmic resistance, the reversible overpotentials (Nernst equation), and the activation overpotentials. The solution converges if the sum of the overpotentials is equal to the input current value. The parameters used for the simplified model are given in Table 13.



Figure 68. Flow diagram of EC dehumidifier element solution procedure.

Quantity	Value	Source
Electrode porosity, ε_{gdl}	0.4	[46]
CL void fraction, ε_{cl}	0.09	[47]
ionomer volume fraction in CL, <i>ɛion</i>	0.4	[82]
Cell active area, A_{cell}	5 cm^2	Meas.
Width of GDL, <i>w</i> _{gdl}	0.0254 cm	[82]
Width of membrane, <i>w_{mem}</i>	0.0127 cm	Est.
Width of CL, <i>w</i> _{cl}	0.00287 cm	[82]
Channel thickness, <i>w</i> _{ch}	0.1 cm	Meas.
Total channel length, <i>l</i> _{ch,tot}	30 cm	Meas.
Dry membrane density, ρ_{dry}	2 g cm ⁻³	[45]
Membrane equivalent weight, M_m	1100 g mol ⁻¹	[45]
Anode charge transfer coeff., α_a	0.5	[82]
Cathode charge transfer coeff., α_c	0.5	[82]
Anode reference current density, <i>j</i> _{0,ref,an}	1.50e-06 A cm ⁻²	Est.
Cathode reference current density, $j_{0,ref,cat}$	1.50e-06 A cm ⁻²	Est.

Table 13. Model Parameters.

4.4. <u>Results</u>

An example calculation is shown in Figure 69-Figure 71. The anode and cathode inlet humidities were set at 62% RH and the inlet flow rates was equal to 400 sccm. Figure 69 shows the evolution of the relative humidity down the total length of the flow channel. The real flow channel that the simulation aimed to reproduce had a single serpentine channel with several passes. I approximated the flow channel as a straight line with an equivalent channel length. I did not consider pressure drop in the flow channel. The anode channel flows from its inlet at the 0 cm position to its outlet at the 30 cm position, while the cathode channel flow in the opposite direction.



Figure 69. Evolution of relative humidity along the length of the flow channels under a neutral humidity gradient.

The current density along the length of the flow channels is shown in Figure 70. I observed that the model predicts the current density decreases as the membrane dries out nearer to the anode outlet. The local current density is not uniform along the length of the channels. It is higher in the regions where both the anode and cathode humidity were higher. In the areas where less water was present, the current density decreased. The relationship between the current density and the humidity is explained by the relationship ionic conductivity. More water uptake equates to less resistive losses.

As shown by Figure 71, the evolution of the various fluxes through the MEA are highly nonlinear. The Faradaic flux is directly proportional to the current density,
while the diffusive flux depends on the water uptake and the strength of the humidity gradient. The water diffusivity varies nonlinearly with the water uptake, and the relationship is exemplified by the evolution of the diffusive flux through the flow channel. At points, the Faradaic flux and the diffusive flux were nearly equal in magnitude, yet the net flux was greater than zero everywhere along the channel length. The difference may be explained by the electroosmotic drag, which helped provide useful dehumidification.



Figure 70. Evolution of current density along the length of the flow channels under a neutral humidity gradient.



Figure 71. Comparison of water fluxes in the EC dehumidifier model.

Figure 72 shows a contour plot of the humidity in the MEA cross section. It depicts the evolution of the humidity through the GDLs and the CLs. The fluid is driest at the anode outlet and wettest at the cathode outlet. The plot shows the relative size of the CL to the GDL, and the mesh used for the simulation. The CL had a finer mesh, as it was significantly thinner than the other layers. I assumed water vapor did not exist in the membrane, located between the anode and cathode CLs, thus this area of the graph is blank. In the cathode, the darker color indicates a greater concentration of water vapor. The concentration was greatest inside the cathode CL. The EC reactions occurred in the CL; however, the mass transfer resistance was more significant in the area compared to the GDL due to the fine pore size. Thus, the concentrations of water vapor adjacent to the membrane were highest on the cathode side and lowest on the

anode side. These effects contributed to larger concentration losses in the cell, as a greater fraction of the applied potential was needed to maintain the concentration differences in these locations.



Figure 72. Contour plot of relative humidity in the MEA cross-section.

Figure 73 shows a summary of the simulation results compared to the measured values. I used the inlet conditions from each of the nine experimental data points to solve for the total water removal rate, which I defined as the change in water vapor mass flow from the anode inlet to the anode outlet. The experiments considered three cases for flow rates of dry oxygen into either flow channel: 100 sccm, 200 sccm, and 400 sccm. The humidity was also varied among three cases: an adverse case, in which

the anode humidity was 40% RH and the cathode humidity was 80% RH, a neutral case where the anode and cathode humidities were maintained at 60% RH, and a favorable case, where the anode humidity was 80% and the cathode humidity was 40%. Was observed that the model faithfully reproduced the experimental data for both the adverse and neutral humidity cases along the range of flow rates. However, the simulated results for the water removal rates were higher than the measured data for the favorable humidity cases, especially at the higher flow rates. I suspected this may be the result of membrane swelling, which may have not been fully accounted for in the model. The average error for the water removal prediction was 24% and the average error for the current density prediction was 9%.



Figure 73. Comparison of modeled and experimentally obtained moisture removal rates for the 5 cm^2 closed-cell PEM dehumidifier.

As observed in previous EC dehumidifier results, the current density did not vary as significantly with dry gas flow rate and cell humidity. Still, the model successfully captured the general trends of the current behavior. Under the adverse humidity gradient, the current density decreased with increasing flow rate. The model additionally predicted that, at low flow rates, the current would be highest for the adverse condition and lowest for the favorable condition. The simulation results were least accurate for the favorable condition at high flow rate. However, counterintuitively, the model also over-predicted the moisture removal rate at the same condition.



Figure 74. Comparison of modeled and experimentally obtained current for the 5 cm² closed-cell PEM dehumidifier.

Figure 75 compares the experimental and simulated results for the Faradaic efficiency. While the prediction was accurate for the neutral humidity condition, errors in both the moisture removal rate and the cell current compounded, leading to greater inaccuracy in the simulated results for this metric.



Figure 75. Comparison of modeled and experimentally obtained Faradaic efficiency for the 5 cm^2 closed-cell PEM dehumidifier.

The model tended to over-predict the cell moisture removal rate. As observed in Figure 76, which compares the modeled and experimental results for moisture removal rate, the simulated moisture removal rate is skewed to towards overpredictions. The equivalent comparison for cell current in Figure 77 shows a less consistent trend. The modeled current results are also significantly more accurate than those of moisture removal rate. The findings may indicate the limitations of such the simple modeling methodology, as more sophisticated methods may be required to increases the current prediction accuracy.



Figure 76. 5 cm² Closed-cell PEM model moisture removal rate accuracy.



Figure 77. 5 cm² Closed-cell PEM model current rate accuracy.

4.5. Open Air Cell Model

Predicting the open-air EC dehumidifier performance was relatively simple compared to predicting the performance of the closed-cell device. While the closed cell, counterflow configuration required several iterations to converge to the solution for humidity distribution in the flow channels, the open-air cell did not require such an elaborate solution method. For the open-air case, I assumed the cathode-side humidity to be constant. Such was the case for the open-air dehumidifier cell because ambient air removed water from the cathode side rather than the flow channels. Because the water vapor flow rate from the dehumidifier cell was trivially small compared to the flow rate of air over the cathode-side, I could safely assume the air-side humidity was constant. Similarly, the change in concentration of oxygen on the cathode-side was virtually zero as well.

Figure 78 compares the modeled and experimental results. In these experiments, the prediction accuracy was significantly higher than that of the closed-cell tests, particularly for the adverse and neutral humidity conditions. While the model overpredicted the favorable humidity condition by a significant amount, the predictions neutral and adverse conditions fell within the experimental uncertainty. Overall, the average error for the moisture removal rate was 18% and the average current error was 11%. The current error increased over the closed cell tests. Like in the close cell tests, the simulated moisture removal rates were skewed towards overprediction, as shown in Figure 79.



Figure 78. Comparison of modeled and experimentally obtained moisture removal

rates for the 5 cm² open-air PEM dehumidifier.



Figure 79. 5 cm² Open-air PEM model moisture removal rate accuracy

4.6. <u>Conclusions</u>

Modeling the EC compression/separator cells in an important tool to understand the underlying physics of mass transport in the MEA. A plethora of EC membrane models exist, thanks to the vast body of literature into hydrogen fuel cells. A much smaller number of studies look specifically at electrochemical compression. Indeed, there are no published numerical simulations delving into ammonia electrochemical compression. Qi et al. have performed extensive modeling work on their PEM dehumidifier [26]. In this section, I laid out a modeling methodology and presented some initial results. The pseudo-two-dimensional method solved a series of coupled heat and mass transfer equations for an array of points spanning the length of a single flow channel. It considers the convective mass transfer from the gas channels into the gas diffusion layer. From there, it accounts for the diffusive transport through the porous matrices that make up the diffusion layers and the catalyst layers. It solved the governing electrochemical equations that determine the rates of ionic flux through the catalyst layers into the membrane and accounts for diffusive transport through the membrane as well.

I developed a numerical model to predict the performance of an EC dehumidifier and verified it against our experimental data. The model considered a counter flow configuration and a proton exchange EC process. I discretized the MEA into a quasitwo-dimensional grid. I considered each of the layers of the MEA and the total length of the serpentine flow channel. For each element along the length of the flow channel, I solved for the net water transfer rate and the current density. Using the moisture flux at each point, I calculated the change in concentration of water vapor along each point of the flow channel.

I used this methodology determine the evolution of relative humidity and current density along the length of the flow channels. I verified the model against the experimental data. I found good agreement between the simulated and measured results at the adverse and neutral humidity gradient cases. The modeled results were less accurate for the favorable humidity case. Localized swelling in the membrane may be partly responsible for the disagreement. The average error in the closed cell model was 24% for moisture removal and 9% for the current. In the open-air model, the average moisture removal error was 18% and the average current error was 11%.

5. Summary and Conclusions

The present studies investigate EC pumping devices driven by applied electric fields and chemical reactions. Such pumps, compressors, and separators are fundamentally different from conventional technologies and may have a variety of interesting applications in energy systems. A polymer electrolyte membrane partitions the highside from the slow-side of the pump, while ion exchange processes enable forward transfer of the working fluid. Due to the nature of the process, the EC cells do not require any mechanical parts, enabling fully vibration-free operation. To facilitate the design of practical EC membrane-driven energy systems, it is imperative to first understand the transport processes occurring in the cells. I studied the performance of an EC ammonia compressor, evaluated the capabilities of an EC dehumidifier, investigated methods for improving dehumidification performance through mass transfer enhancement, and conducted numerical simulation to predict the performance of a PEM-based EC dehumidifier.

5.1. Outcomes for Ammonia EC Compression

Ammonia is a potentially important fluid in energy-systems designed for minimal environmental impact. It is one of the oldest refrigerants and, unlike modern synthetic refrigerants, it does not deplete atmospheric ozone and does not contribute the greenhouse effect. Additionally, it may be used as a means of renewable energy storage, either as a hydrogen-carrier for in fuel cells or as fuel for carbon-free internal combustion processes.

5.1.1. Test Facility for Ammonia EC Compressor Performance

I constructed a test facility to supply known flow rates of ammonia and humidified hydrogen gases into the EC cell. Using a back pressure regulating device, an external electric field operating in galvanostatic conditions supplied power to the cell, enabling continuous fluid flow across the cell. Small-scale experiments verified the constant-pressure operation of the ammonia EC compressor using hydrogen as a carrier gas.

5.1.2. Ammonia EC Separation

I evaluated the cell's ability to remove ammonia and hydrogen from a stream diluted with nitrogen. The molar ratio of ammonia to hydrogen appearing in the effluent gas stream, deviated significantly from the stoichiometric value of two. While forward transfer of ammonia existed in all cases, backward diffusion played a significant role in the amount of ammonia present in the discharge-side (cathode) of the cell. This effect could pose a serious challenge to the development of EC compressor-based ammonia storage systems. The back diffusion of ammonia was likely due to dissolution of ammonia in the water contained in the ionomer.

5.1.3. Scaled-Up Ammonia EC Compression EC Separation

The existence of diffusive phenomena in the ammonia EC compressor was further supported by scaled-up experiments using a stack of five parallel cells. In the experiments, I mapped the performance of the compressor stack for varied current and discharge pressure. The flow rate decreases with increasing pressure due to the backward flow of ammonia. The stack operated more efficiently under high-pressure low current conditions. Increased current lead to significantly increased power consumption, due to the irreversible losses in the EC compressor. Despite the increased capacity, the amount of compressed ammonia obtained in the multi-cell experiments was not large enough to power any practical energy system. The high rate of back diffusion also poses a challenge to efficient and reliable ammonia energy storage.

5.2. Outcomes for EC Dehumidification

Dehumidification is a necessary, yet energetically expensive in building air conditioning. Management of room air humidity is essential for thermal comfort and wellbeing.

5.2.1. Test facility for EC dehumidifier evaluation

I designed and constructed a test facility to measure the moisture removal rate and electrical power consumption for EC dehumidifier prototypes.

5.2.2. AEM EC dehumidification

I demonstrated EC dehumidification on a small scale. Through the anionic transport, water vapor and oxygen were removed from a process air stream. I observed that diffusive phenomena were also detrimental to the operation of the water vapor removal device. While the experiments demonstrated the working principle of the anionic dehumidification device, the energy efficiency of the technology must increase to compete with the conventional methods of moisture removal. There was no clear benefit for using an anion exchange water transport process over a proton exchange process.

5.2.3. Scaled-up EC dehumidifier

I investigated the performance of a 50 cm² AEM EC dehumidifier. I found that the performance observed in trials of the 5 cm² cells did not scale linearly with the increased MEA size. The 50 cm² demonstrated increased moisture removal capacity; however, the increase was less than anticipated from the tenfold increase in active membrane area. I achieved only a two-to-threefold increase in moisture removal rate. The larger 50 cm² was more effective under adverse concentration gradients.

5.2.4. Prototype separate sensible and latent cooling device

I designed a prototype of an open-air PEM EC dehumidifier and constructed a test facility for controlling the flow of ambient air over the anode-side of the EC cell while also measuring the moisture removal rate on the cathode-side. The open-air EC dehumidifier was able to provide useful dehumidification even under adverse humidity gradients. While the prototype was successful in small-scale trials, I did not integrate a sensible evaporator to perform a system-level experimental trial. The dehumidification capacity for the open-air dehumidifier was prohibitively small. System-level experimentation with the prototype EC dehumidification device was impractical.

5.2.5. Dehumidification improvement using EHD mass transfer enhancement To overcome the mass transfer limitations of the EC dehumidifier, I examined EHD evaporative mass transfer enhancement as a method of increasing the net rate of water transfer. High voltage points sources sharply increased the rate of evaporative mass transfer through the production of secondary air flows. The secondary flows, caused by the exchange in momentum between ions generated at the high-voltage source and neutral molecules, may disrupt the moisture boundary layer at the liquid-vapor interface, increasing the rate of evaporation. I investigated the possibility of improving the efficiency of an EC dehumidifier through the EHD mass transfer enhancement. I tested the EHD mass transfer enhancement for controlled water evaporation, finding significant mass transfer enhancements were possible at lower air velocities. At low air velocities, I observed up to a fourfold increase in the rate of evaporation. At higher velocities, inertial forces of the upstream fluid dominated the EHD force developed by the high-voltage electrode.

During EHD-enhanced EC dehumidifier trials, the anode-side of the cell was open to the air, allowing a direct line of sight between the MEA and the EHD electrodes. The cathode side was placed against a plate with embedded flow channels, enabling measurements of the change in relative humidity before and after the MEA. The EHD enhancement had little effect on the dehumidification energy. The poor performance of the EHD enhancement may be due to obstruction of the liquid-vapor interface by the gas diffusion layer material. EHD enhancement may still prove effective in other dehumidification applications, such as regenerating desiccant material.

5.2.6. Develop a numerical model for predicting the EC dehumidifier performance To further analyze the experimental results, I developed a numerical model to simulate the EC dehumidifier performance. I based the model off early simulation studies for PEM fuel cells [45]. I employed the model to simulate the 5 cm² closedcell PEM dehumidifier performance as well as the open-air dehumidifier performance. The model used empirically observed measurement for water diffusivity in PEM cells. Through modeling the electrochemical transport, physical diffusion, and electroosmotic drag over the total length of the cell's flow channels, I achieved good agreement with the experimental results, giving 24% error in moisture removal rate for the close cell application and 18% error in moisture removal rate for the open-air application.

6. Contributions and Future Work

6.1. Ammonia EC Compression

I completed experimentation into the role of diffusive transport in the ammonia compression process. I conducted novel experiments the effects of varied discharge pressure on the EC compressor stack. I determined that back diffusion of ammonia was significant and impeded the performance in both small-scale experiments and multi-cell stack experiments. I observed reduced flow rate of ammonia with increased pressure. However, the compressor also operated more efficiently at higher pressure ratios. Previous investigations into ammonia EC compression did not measure the composition of the effluent gas and did not consider multi-cell stack compressors. Chouhan et al. conducted the most relevant experiments to this work. They also examined the effect of back diffusion for ammonia compression during pressurized and unpressurized conditions for a single cell [16]. However, the present studies offer a more in-depth analysis of the ammonia EC compressor due to the continuous flow rate and composition measurement at controlled pressure.

Compressed ammonia is a promising vector for intermittent renewable energy generation because of its high storage density as compared to hydrogen. In this method, hydrogen would be generated via electrolysis, converted into ammonia through the Haber-Bosch process, and compressed and stored though EC methods. I demonstrated the performance of an ammonia EC compressor stack. While I was able to achieve useful compression work, back-diffusion was an impediment to the performance. The back diffusion phenomenon was the result of water dissolved in the membrane ionomer material. Some fuel cell membranes, which operate at high temperature, do not require hydration. The results of the ammonia EC compressor stack experiments highlighted the need to identify methods for reducing the rate of ammonia back diffusion.

Additional experiments are currently underway to address the back diffusion issue. Because the ammonia diffusion was likely due to dissolution of ammonia in the membrane water content, eliminating the need for membrane hydration could prevent unwanted ammonia transport. The UMD EC compressor team partnered with Giner Inc. to test a high-temperature, water-free membrane for ammonia compression. The experimental MEAs are based on polybenzimidazole membranes activated in phosphoric acid. Preliminary experiments show the dry, high-temperature membranes have promise for increasing the Faradaic efficiency of the ammonia EC compression.

6.2. Enhanced EC Dehumidification

Dehumidification is a necessary step in air conditioning under humid conditions. The amount of energy required for dehumidification may be substantial because of water's high latent heat of condensation. I considered EC separation as a means of removing the water vapor without the need for condensation. My contributions for EC dehumidification are threefold. First, I demonstrated conducted novel experimentation on an EC dehumidifier using an anion exchange chemistry, considering a small-scale 5 cm² cell and a larger 50 cm² cell. Prior studies were limited to a proton exchange process [6]. Second, I developed a prototype for and

open-air EC dehumidifier. While air-breathing fuel cells have been previously developed for portable power generation applications [78], no such work has been conducted for EC pumping applications. Lastly, I attempted experiments to improve the EC dehumidifier efficiency with active EHD mass transfer enhancement and evaluate the water removal performance at different upstream air flow rates. No prior experiment had considered using the EHD effect to enhance and EC dehumidifier.

Additionally, I developed a numerical model for modeling the PEM EC dehumidifier. While prior studies have already conducted numerical heat and mass transfer modeling of the PEM dehumidifier, no such studies attempted to predict the performance of an open-air device. My modeling methodology solved the coupled mass and charge transfer processes occurring in the MEA. I validated the model against my empirical data, observing an average moisture removal error of less than 25%.

My experimental and simulation results revealed that back diffusion of water decreased the dehumidification efficiency for both the PEM process and the AEM process. The results are significant as the back diffusion problem must first be understood before it can be resolved. The numerical model I developed may be used to design EC dehumidifiers that work with the EHD enhancement. The data gathered from the experiments may also be useful for proof-of-concept analyses for systemlevel EC dehumidifier applications, which can be modeled using the numerical formulation I developed. I have proposed several designs for integrating the EC dehumidifier in air handling units.

Water transport is a common issue in fuel cell research [14,54,57,58]. Like with the ammonia EC compressor, reduction of the required membrane hydration may be beneficial to increase the EC dehumidifier performance. If the EC dehumidifier can be improved, it may be useful for separate sensible and latent cooling applications. Efficient separate sensible and latent cooling would lower the energy required for air conditioning, reducing building energy consumption and decreasing the amount of refrigerant required for air conditioning in humid parts of the world.

Future work may seek to improve the design of the open-air EC dehumidifier to benefit from the EHD enhancement. Additionally, EHD enhancement may prove useful in other dehumidification applications, such as desiccant regeneration. Vacuum membrane dehumidification is another promising technology for separate sensible and latent cooling. Vacuum membrane dehumidification could potentially be enhanced by EC dehumidification and/or EHD evaporation enhancement.

6.3. List of Publications

6.3.1. Conference publication

Baker, J., Hwang, Y, and Wang, C.S. "Design of Gas Channels for an Electrochemical Compressor" (2018). International Compressor Engineering Conference. Paper 2616.

6.3.2. Proposed manuscript

Baker, J., Cao L.S., Hwang, Y., Wang, C.S. "Performance investigation of an electrochemical ammonia compressor stack" (2022). [Unpublished manuscript].Department of Mechanical Engineering, University of Maryland.

Baker, J., Cao L.S., Hwang, Y., Wang, C.S. "Development of an Open-Air Electrochemical Dehumidifier" (2022). [Unpublished manuscript]. Department of Mechanical Engineering, University of Maryland.

Baker, J., Cao L.S., Hwang, Y., Wang, C.S. "Electrochemical Dehumidification with an Anion Exchange Membrane" (2022). [Unpublished manuscript]. Department of Mechanical Engineering, University of Maryland.

Appendix

Tabular forms of experimental data.

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	Inlet Flow Rates		Press	sure	Discharge		Stool	Applied	Ammoni	a Molar F	raction
Trial	H2	NH3	Discharge	Suction	Mass Flow	Temp.	Current	Voltage	Discharge	Suction Exhaust	Suction Inlet
	(sccm)	(sccm)	(kPa)	(kPa)	$(g hr^{-1})$	(°C)	(A)	(V)	(-)	(-)	(-)
1	218	399	200.0	142.5	1.89	22.02	1.00	0.41	0.56	0.67	0.65
2	218	399	417.4	145.3	0.64	22.56	1.00	0.44	0.30	0.68	0.65
3	218	400	600.0	146.0	0.60	22.79	1.00	0.45	0.19	0.68	0.65
4	218	399	800.0	146.3	0.51	22.12	1.00	0.47	0.14	0.69	0.65
5	218	399	1000.0	146.5	0.46	21.87	1.00	0.48	0.10	0.68	0.65
6	218	399	200.0	135.5	4.74	23.28	2.00	0.71	0.62	0.67	0.65
7	218	399	400.0	141.2	2.04	24.08	2.00	0.74	0.38	0.71	0.65
8	218	399	600.0	142.8	1.35	23.38	2.00	0.76	0.26	0.72	0.65
9	218	399	800.0	143.4	1.04	23.35	2.00	0.77	0.18	0.72	0.65
10	218	399	1000.0	144.0	0.89	23.46	2.00	0.78	0.14	0.72	0.65
11	218	400	239.1	128.0	7.19	23.15	3.00	1.06	0.61	0.69	0.65
12	218	400	400.0	133.7	3.94	22.57	3.00	1.06	0.46	0.74	0.65
13	218	400	600.0	136.8	2.51	22.48	3.00	0.00	0.33	0.75	0.65
14	218	400	800.0	138.6	1.88	23.44	3.00	0.00	0.25	0.76	0.65
15	218	400	1000.0	139.0	1.51	22.76	3.00	0.00	0.19	0.77	0.65
16	218	400	279.4	121.3	9.56	23.44	4.00	1.20	0.61	0.70	0.65
17	218	400	400.0	126.3	6.74	23.51	4.00	1.25	0.53	0.76	0.65
18	218	400	600.0	131.2	4.33	23.33	4.00	1.25	0.40	0.79	0.65
19	218	400	800.0	133.8	3.15	23.52	4.00	1.53	0.31	0.81	0.65
20	218	400	1000.0	135.3	2.49	23.26	4.00	1.54	0.25	0.81	0.65

Table A.1. Data for ammonia EC compressor stack testing.

	Inlet Flo	ow Rates	Press	Pressure			Stack	Applied	Ammonia Molar Fraction			
Trial	H2	NH3	Discharge	Suction	Mass Flow	Temp.	Current	Voltage	Discharge	Suction Exhaust	Suction Inlet	
	(sccm)	(sccm)	(kPa)	(kPa)	$(g hr^{-1})$	(°C)	А	V	-	-	-	
21	218	400	324.7	115.4	12.61	24.00	5.00	1.66	0.63	0.73	0.65	
22	218	400	400.0	118.6	10.42	24.47	5.00	1.65	0.58	0.78	0.65	
23	218	400	600.0	124.8	7.00	24.14	5.00	2.00	0.48	0.84	0.65	
24	218	400	800.0	128.3	5.13	23.76	5.00	2.03	0.39	0.86	0.65	
25	218	400	1000.0	130.7	4.01	24.24	5.00	2.02	0.32	0.87	0.65	

Table A.1. Data for ammonia EC compressor stack testing (Continued).

	O2 Mas	ss Flow		Relativ	e Humidity				Mc	Moisture Removal Rate				
Trial	Anode	Cathode	Anode In.	Anode Out.	Cathode I	n. Cathode Out.	Voltage	Curren	t Anode	±	Cathode	±		
	(sccm)	(sccm)	(%RH)	(%RH)	(%RH)	(%RH)	(V)	(A)	(sccn	n)	(sccn	n)		
1	99	99	43.5	99.7	82.7	16.8	2.00	0.71	1.43	0.17	-1.92	0.14		
2	99	99	67.5	100.6	62.6	16.4	2.00	0.73	0.83	0.20	-1.42	0.11		
3	99	99	88.3	100.8	42.8	15.2	2.00	0.74	0.21	0.21	-0.81	0.08		
4	199	199	42.3	94.5	82.8	34.6	2.00	0.78	2.56	0.16	-2.67	0.15		
5	199	199	64.6	96.9	62.7	27.9	2.00	0.79	1.57	0.18	-1.95	0.12		
6	199	199	85.8	99.4	42.3	22.0	2.00	0.75	0.60	0.21	-1.18	0.09		
7	399	399	41.0	74.2	82.2	49.2	2.00	0.82	2.93	0.13	-3.16	0.16		
8	399	399	62.9	81.3	62.4	38.3	2.00	0.80	1.77	0.16	-2.39	0.13		
9	399	399	83.4	88.6	41.5	26.9	2.00	0.74	0.61	0.19	-1.44	0.10		
		Tei	mperature			Pressure								
Trial	Anode In.	Anode Out	. Cathode	In. Cathod	e Out. And	ode In. Anode O	out. Catho	ode In.	Cathode Ou	t.				
	(°C)	(°C)	(°C)	(°C	C) (1	kPa) (kPa)	(k	Pa)	(kPa)					
1	24.3	23.5	24.4	23.	4 1	10.8 109.1	10)8.3	107.4					
2	25.0	24.3	25.2	24.	0 1	10.0 108.3	10)7.5	106.6					
3	24.3	23.6	24.5	23.	5 1	10.7 108.9	10	08.0	107.1					
4	24.1	23.3	24.2	23.	2 1	19.5 115.7	11	4.4	112.2					
5	24.5	23.7	24.6	23.	7 1	19.7 115.9	11	4.5	112.3					
6	25.0	24.2	25.1	24.	0 1	20.3 116.4	11	5.1	113.1					
7	23.8	23.1	24.0	22.	9 1	42.9 133.4	13	31.9	126.6					
8	24.7	23.9	24.8	23.	7 1	42.8 133.4	13	31.8	126.6					
9	24.4	23.7	24.6	23.	4 1	42.9 133.5	13	31.8	126.5					

Table A.2. Data for 5 cm^2 PEM EC dehumidifier experiments.

	O2 Ma	uss Flow		Relativ	e Humidity	Voltaga	Curront	Moisture Removal Rate				
Trial	Anode	Cathode	Anode In.	Anode Out.	Cathode In.	Cathode Out.	voltage	Current	Anode	±	Cathode	±
	(sccm)	(sccm)	(%RH)	(%RH)	(%RH)	(%RH)	(V)	(A)	(scci	n)	(sccm	n)
1	202	202	40.9	100.4	83.0	2.4	2	2.06	3.01	0.56	-3.80	0.42
2	202	202	62.5	101.1	63.1	4.3	2	2.39	2.01	0.60	-2.74	0.36
3	201	202	82.8	100.8	42.3	6.0	2	2.80	1.08	0.67	-1.76	0.31
4	802	802	58.9	91.3	64.7	19.0	2	2.99	4.81	1.59	-6.62	1.17
5	802	802	77.7	92.5	40.3	14.3	2	3.01	2.32	1.65	-3.69	0.92
6	802	802	39.9	86.6	82.1	24.4	2	2.86	6.41	1.36	-7.88	1.24
7	401	401	61.8	100.8	61.9	8.6	2	2.83	3.66	1.05	-4.82	0.69
8	401	401	81.9	100.3	41.5	8.4	2	3.01	1.89	1.15	-3.08	0.59
9	401	401	39.9	100.9	81.7	9.3	2	2.70	6.17	1.08	-7.26	0.88
10	601	602	40.2	95.9	82.7	19.4	2	2.98	7.43	1.41	-8.85	1.26
11	601	601	61.7	94.9	62.5	16.2	2	2.85	4.07	1.36	-5.76	0.98
12	601	602	80.1	96.5	40.6	12.8	2	2.94	2.07	1.41	-3.38	0.79

Table A.3. Data for $50 \text{ cm}^2 \text{AEM EC}$ dehumidifier experiments.

		Tem	perature		Pressure						
Trial	Anode In.	Anode Out.	Cathode In.	Cathode Out.	Anode In.	Anode Out.	Cathode In.	Cathode Out.			
	(°C)	(°C)	(°C)	(°C)	(kPa)	(kPa)	(kPa)	(kPa)			
1	22.3	21.9	22.4	21.4	112.8	112.7	119.0	119.0			
2	21.9	21.5	22.0	21.1	111.1	111.0	117.7	117.8			
3	22.6	22.2	22.7	21.7	111.2	111.1	118.5	118.6			
4	21.9	22.0	21.9	21.0	153.4	153.3	152.4	152.4			
5	21.5	21.6	21.5	20.6	153.2	153.1	151.8	151.9			
6	21.0	21.1	20.9	20.1	154.0	153.9	152.2	152.2			
7	22.1	22.0	22.1	21.1	123.6	123.5	121.8	121.9			
8	22.4	22.3	22.5	21.5	123.4	123.3	121.8	121.9			
9	23.7	23.5	23.7	22.8	123.5	123.4	121.7	121.7			
10	23.6	23.4	23.7	22.7	137.1	137.0	132.6	132.6			
11	21.9	21.8	21.9	21.0	137.3	137.2	132.7	132.7			
12	21.5	21.4	21.5	20.6	137.2	137.1	132.7	132.7			

Table A.3. Data for 50 cm^2 AEM EC dehumidifier experiments (Continued).

	Air	EC	EC	EHD		Re	lative Hun	nidity		Temperatu	ıre	Pressure		
Trial	Vel.	Volt.	Curr.	Volt.	O_2 Flow	Amb.	An. In.	An. Out.	Amb.	An. In.	An. Out.	An. In.	An. Out.	
_	(m s ⁻¹)	(V)	(A)	(kV)	(sccm)	(%)	(%)	(%)	(°C)	(°C)	(°C)	(kPa)	(kPa)	
1	0.5	2	0.853	0	204	43.4	94.1	58.3	26.6	26.6	26.6	104.8	103.6	
2	1.5	2	0.765	0	204	43.5	94.1	52.8	26.6	26.6	26.7	104.9	103.7	
3	2.5	2	0.737	0	204	43.5	94.1	51.3	26.6	26.6	26.7	104.9	103.7	
4	0.5	2	0.602	0	203	53.1	54.7	35.8	26.1	26.1	26.0	104.6	103.7	
5	1.5	2	0.542	0	203	53.0	54.5	34.2	26.1	26.1	26.0	104.5	103.6	
6	2.5	2	0.514	0	203	53.1	54.5	34.5	26.2	26.2	26.0	104.4	103.6	
7	0.5	2	0.340	0	203	53.1	25.3	17.0	26.1	26.1	26.0	104.9	104.0	
8	1.5	2	0.342	0	203	52.4	25.2	17.5	26.1	26.1	26.0	104.9	104.0	
9	2.5	2	0.334	0	203	51.8	25.1	18.2	26.1	26.1	26.0	104.8	103.9	
10	0.5	0	0	0	204	43.6	94.1	79.0	26.6	26.6	26.6	104.9	103.6	
11	1.5	0	0	0	204	43.6	94.1	75.0	26.6	26.6	26.7	105.0	103.7	
12	2.5	0	0	0	204	43.6	94.1	73.5	26.6	26.6	26.7	105.1	103.8	
13	0.5	0	0	0	203	52.6	54.4	55.6	26.1	26.1	26.0	104.5	103.7	
14	1.5	0	0	0	203	51.9	54.3	55.6	26.1	26.1	26.0	104.5	103.7	
15	2.5	0	0	0	203	51.6	54.3	55.5	26.2	26.2	26.0	104.5	103.7	
16	0.5	0	0	0	201	52.3	25.1	33.4	26.1	26.1	26.0	104.0	103.1	
17	1.5	0	0	0	201	52.1	24.9	36.3	26.1	26.1	26.0	104.1	103.2	
18	2.5	0	0	0	201	53.3	24.9	38.6	26.2	26.1	26.0	104.3	103.4	
19	0.5	2	0.623	0	203	49.2	94.5	56.4	26.1	26.0	25.9	104.7	103.8	
20	1.5	2	0.693	5.01	203	52.3	94.6	54.3	26.1	26.1	25.9	104.9	103.8	
21	2.5	2	0.705	5.01	203	53.1	94.7	54.3	26.2	26.1	26.0	104.9	103.8	
22	0.5	2	0.445	5.01	203	50.3	54.6	37.1	26.4	26.3	26.2	105.2	104.4	
23	1.5	2	0.459	5.01	203	51.2	54.5	38.8	26.4	26.4	26.3	105.4	104.5	

Table A.4. Data for open-air EHD enhanced EC dehumidifier experiments.

	Air	EC	EC	EHD	O Elam	Relative Humidity				Temperatu	Pressure		
Trial	Vel.	Volt.	Curr.	Volt.	U ₂ F10W	Amb.	An. In.	An. Out.	Amb.	An. In.	An. Out.	An. In.	An. Out.
	(m s ⁻¹)	(V)	(A)	(kV)	(sccm)	(%)	(%)	(%)	(°C)	(°C)	(°C)	(kPa)	(kPa)
24	2.5	2	0.458	5.01	203	51.1	54.4	39.1	26.2	26.2	26.1	105.4	104.6
25	0.5	2	0.309	5.01	203	51.1	25.2	21.4	26.4	26.1	26.0	103.8	103.0
26	1.5	2	0.304	5.01	203	50.9	25.1	19.3	26.3	26.1	26.0	103.8	102.9
27	2.5	2	0.312	5.01	203	52.9	25.1	20.3	26.4	26.1	26.0	103.7	102.9

Table A.4. Data for open-air EHD enhanced EC dehumidifier experiments (Continued).

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