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DEPARTMENT OF ENGINEERING SCIENCE AND MECHANICS

CONDUCTIVITY AND PERMEABILITY OF ION CONDUCTIVE
MEMBRANES FOR COPPER CHLORIDE ELECTROLYSIS

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ABSTRACT

This project was carried out to develop methods to test the in-plane conductivity and copper permeability of a number of ion-exchange membranes. The conductivity of the membranes was measured using Electrochemical Impedance Spectroscopy (EIS). A Gamry EIS system was used in conjunction with a BekkTech conductivity cell. This system was previously used to measure membrane conductivity in gaseous mediums, but was converted for use in liquids during this project. The permeability of the membranes was measured using a basic diffusion cell. The change in copper concentration was measured using a complexometric titration method. The solution was titrated with EDTA (Ethylenediaminetetraacetic acid), with a murexide indicator.   The membranes considered in this study are intended for use in CuCl electrolysis. The CuCl thermochemical cycle is promising for its relatively low temperature and high efficiency. This cycle could be an economically feasible and environmentally safe way to produce hydrogen. Hydrogen used as an energy carrier could store excess energy produced by renewable technologies and allow that energy to be transferred to where it is needed.

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Chapter 1

Introduction

Harnessing energy for transportation has been a crucial element of humanity's technical achievements over the past century. Starting with steam powered riverboats, leading up to today's gasoline engines, motive force has long been dependant on the use of fossil fuels. The continued use of such fuels is unsustainable even in the near-term future. The use petroleum in vehicles releases pollutants such as NO_x, SO_x, CO, and CO_2. All of these pollutants are hazardous to the environment in different ways. NO_x is known to produce smog, SO_x causes acid rain, and CO is poisonous. Although the effects of CO_2 in the atmosphere are debated, most would agree that reducing carbon emissions is desirable.

In addition to these environmental concerns, fossil fuels, as a limited resource, force countries into political and economic dependence on fossil fuel rich nations. The U.S. uses around 37 quadrillion BTU or 3.9×10^7 GJ of petroleum a year, and about 50% of this is imported from other countries. This dependence on foreign oil is a weakness that can be exploited, and gives undue power to oil rich countries. Added to this, oil is a limited resource, which will not be available indefinitely. Many experts estimate that the world's oil production will reach a peak in the next decade, if it hasn't already.[1] Even the coal reserves, currently in abundance in the United States, are a limited resource and will eventually run out. Hydrogen, which can be cleanly oxidized to produce power, is being considered as an alternative to these conventional fuels.

Hydrogen as an Energy Carrier

Instead of using fossil fuels directly processed from natural materials as primary fuels, a chemical such as hydrogen could be employed as an energy carrier. Unlike fossil fuels, which

have to be gathered from natural resources, hydrogen could be produced from a variety of energy sources. As a form of chemical storage, hydrogen has many of the same benefits as fossil fuels. It is transportable and has a high energy density. Hydrogen is more energy dense on a weight basis than any other substance; however, its volumetric energy density is very small.[2] Storing large amounts of hydrogen is made more difficult by its volume, but safe and economical ways to store compressed hydrogen are being developed.

Fuel cell technology can be used to convert the chemical energy stored in hydrogen into electrical energy. Inside the cell, the hydrogen molecule is split into its component proton and electron. While the molecule is separated, the proton is allowed to travel through a membrane, forcing the electron to travel through a wire in order to maintain charge equilibrium. This movement of the electrons creates an electrical current, which can be used as electrical energy. This technology can reach efficiencies of up to 50 %, a value much greater than that of an internal combustion engine at 25 %.[2] When the excess heat produced by the fuel cell is used by a heat engine, the total efficiency could reach 80 %.

One of the major advantages of the fuel cell is its lack of byproducts. Unlike combustion processes, the basic hydrogen fuel cell reaction produces no products other than water. A study recently found that switching all cars in the United State to hydrogen fuel cell vehicles would decrease carbon monoxide levels from 1900 ppbv to 900 ppbv and NO_2 from 63 ppbv to 35 ppbv. It also estimated that the switch would save 2300 to 4000 lives per year considering all pollution-related health problems.[3]

The ability to store, transport and use energy without access to the grid has several useful applications. The largest is mobile power sinks, such as cars, which cannot be attached to an electrical line while operating. Another application is transporting energy from secluded renewable energy sources. Several renewable technologies are best used in regions where there is little to no human habitation, and thus no transmission lines. If a reasonable way to produce

hydrogen from these sources were established, it could form the basis for a transportation economy based on the renewable resources.

Hydrogen Production Methods

Unfortunately, since hydrogen is not naturally available in a readily harvestable form, it instead needs to be extracted from other substances. 96% of hydrogen is created through the direct conversion of hydrocarbons to hydrogen.[4] The most common method to do this is steam reformation. Many hydrocarbons can be reformed through this method, but methane is most frequently used. Methane reformation requires two steps:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

As can be seen from these chemical reactions, this method produces a substantial amount of carbon byproducts along with the hydrogen. Conversion of methane to hydrogen produces 7.33 kg CO_2 per kg H_2 while converting larger hydrocarbons, such as naptha, produces around 9.46 kg CO_2 per kg H_2.**Error! Bookmark not defined.** These byproducts negate any positive effects of supplying the steam energy from renewable sources. A way to efficiently produce hydrogen without simultaneously producing large amounts of pollutants must be developed before hydrogen could be used as an energy carrier.

Another way to produce hydrogen is water electrolysis. Although electrolysis can produce hydrogen without unwanted byproducts, it requires a large amount of electricity to do so. When this electricity is provided by renewable sources, the process produces no pollutants. However, this process is characterized by low efficiencies. When water electrolysis is used in conjunction with nuclear power, only efficiencies of around 24% can be achieved.[5] Thus ways to increase the process efficiency using increased temperature or pressure are being explored. One

promising option is using a thermochemical cycle. Thermochemical cycles involve more complicated reactions than basic water electrolysis, but have a higher efficiency at high temperatures, requiring less electricity to produce the same amount of hydrogen. However, the process is less expensive only if the thermal energy required to heat the cell is cheap compared to the cost of electricity used in conventional electrolysis. Certain cycles, such as the Cu-Cl cycle could run at lower temperatures, thus becoming less expensive.

The Copper Chlorine (Cu-Cl) Thermochemical Cycle

Cheap sources of heat with temperatures around 400-600 °C are prevalent. Cycles operating at these temperatures can gather heat from solar or nuclear technology. The Argonne National Lab selected eight thermochemical cycles for continued research and development based on their potential for commercial use. One of these cycles was the Cu-Cl cycle.

The copper chloride cycle only requires moderate temperatures, and uses inexpensive chemicals. Theoretically, it could reach efficiencies up to 40%. The chemicals go thorough a series of reactions, including an electrolysis, hydrolysis and decomposition processes. When these processes are combined, the only chemical input to the cycle is water, while the products are H_2 and O_2 alone. The Cu and Cl are cycled through the processes. More information about the complete cycle is provided in Chapter 2.

The electrolysis step is shown in Figure 1. On the anodic side of the proton-exchange membrane, CuCl(s) dissolved in HCl(aq) is electrochemically oxidized to $CuCl_2$(aq), while on the cathodic side H_2O may be used and protons are electrochemically reduced to molecular hydrogen. A system was built to determine the efficiency and workability of this step, and to test different membranes and catalytic materials for use in the cycle.
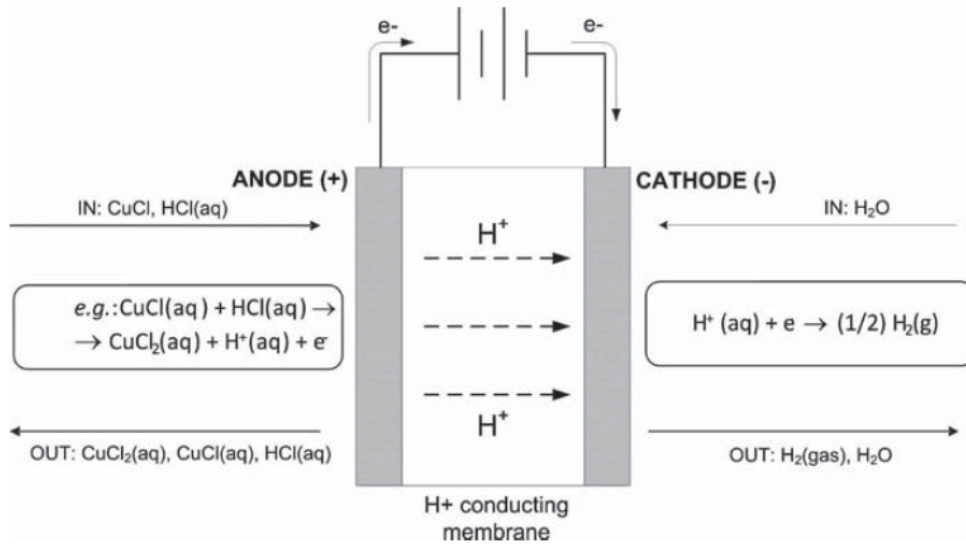
Figure 1: Electrolysis step of CuCl cycle[6]

Membrane Characterization

The characteristics of the proton-exchange membrane used in a thermochemical cell affect the efficiency and longevity of the cell itself. The membrane allows protons to travel from the anode of the cell to the cathode. Their recombination with electrons at the cathode can produce hydrogen. Measuring the membrane conductivity is a way to determine how well the membrane will allow a proton to transfer. This value should be as high as possible, so that the electrolysis efficiency can be maximized.

Another important value is the diffusivity of the membrane. Since there is copper on one side of the membrane, but not on the other, there is a concentration gradient between the two sides. Because of this gradient, the membrane might allow some of the copper to travel through to the cathode side. The rate with which the copper permeates through the membrane and travels to the far side is shown by the membrane's permeability.

Having copper pass through the membrane causes problems that could affect the longevity of its components. At a minimum, the copper that is being lost needs to be replaced on the anodic side of the system. In addition, once the copper starts to travel through the system, could be deposited in the tubes and pipes connecting regions of the system, creating blockages.

In order to address these problems, three systems were developed. The first system measured the through-plane conductivity of the membrane, the second one measured the in-plane conductivity of the membrane, and the third cell measured the permeability of the membrane. This thesis primarily addresses the second two cells, as these were the testing methods needed to properly characterize the membranes of interest. Once the systems were calibrated on Nafion, other membranes for potential use in the CuCl electrolyzer were tested.
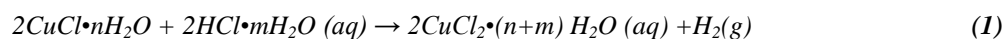
Chapter 2

Literature Review

The Copper Chlorine Electrolytic Cycle

The Cu-Cl cycle is an example of a thermochemical process, meaning it uses a combination of thermal and chemical energy to split water into its compositional parts. Additional chemicals are added to the water to lower the decomposition potential, but are not used up over the course of the reaction. "Pure" thermochemical cycles require no electrochemical step. The Cu-Cl cycle is a "hybrid" cycle, and does require a voltage in order to complete the process.[7] Theoretically, such cycles could be used with nuclear or solar heat sources, to produce a chemically stored energy from renewable sources.

The Cu-Cl cycle is being considered because of its moderate temperature, inexpensive chemicals, and potentially high efficiency. A Nuclear Hydrogen Initiative identified a series of the most promising thermochemical cycles. Most of them required temperatures above 850°C, while the Cu-Cl cycle only requires a maximum heat of 530°C.[8] Heat at this level could be provided by several types of second generation reactors or a solar tower structure.[9] Compared to other chemicals being used in electrochemical cycles, CuCl is fairly inexpensive at $7200/metric ton. The efficiency has been theoretically calculated at around 43%, using LHV and realistic heat exchange values.[10] If the system is hooked up to a Generation IV nuclear reactor with 42% efficiency, the total efficiency could be around 30%.**Error! Bookmark not defined.** It consists of four primary steps:

$$2CuCl \cdot nH_2O + 2HCl \cdot mH_2O \ (aq) \rightarrow 2CuCl_2 \cdot (n+m) \ H_2O \ (aq) + H_2(g) \qquad (1)$$

electrolysis (25-80 °C)

$$CuCl_2(aq) \rightarrow CuCl_2(s) \qquad (2)$$

drying (100 °C)

$$2CuCl_2(s) + H_2O(g) \rightarrow CuCl_2 \cdot CuO(s) + 2HCl(g) \qquad (3)$$

hydrolysis (310-375 °C)

$$CuCl_2 \cdot CuO(s) \rightarrow 2CuCl(s) + (1/2) \ O_2 \ (g) \qquad (4)$$
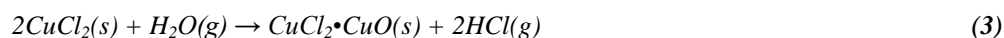
decomposition (450-530 °C)

These take place along with 4 common processes.

$$H_2O(l) \rightarrow H_2O(g) \qquad (5)$$

evaporation

$$2CuCl(s) + nH_2O(l) \rightarrow 2CuCl \cdot nH_2O(aq) \qquad (6)$$
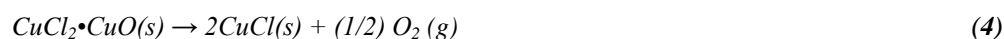
dissolution

$$2CuCl_2 \cdot (n+m)H_2O(aq) \rightarrow 2CuCl_2(s) + (n+m)H_2O(l) \qquad (7)$$

crystallization

$$2HCl(g) + mH_2O(l) \rightarrow 2HCl \cdot mH_2O(aq) \qquad (8)$$
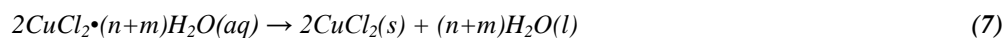
dissolution

Equation 1 was proved by Atomic Energy of Canada, Ltd, while 2 and 3 were proved at Argonne National Laboratory (ANL). ANL has completed research concerning the hydrolysis reaction, but found that very little was known about the electrolysis step.**Error! Bookmark not defined.** Atomic Energy of Canada Limited has successfully run an electrolyzer for several days.**Error! Bookmark not defined.** Argonne National Lab and Pennsylvania State University are collaborating to develop a similar electrolyzer in order to study the effects of different membranes.

During the electrolysis step, copper(I) chloride is oxidized in the presence of hydrochloric acid to produce hydrogen ions. The copper(I) is oxidized to copper(II) at the anode, while hydrogen ions are reduced to hydrogen at the cathode. It is assumed that most of the

copper remains on the anodic side, and does not permeate through to the cathode. If it does

permeate across, it is reduced to metallic copper, which then congests the system. Thus, the

membrane needs to be studied to determine the degree to which it allows hydrogen ions and

copper ions to travel across it. These are affected by the conductivity and permeability of the

membrane.

In developing methods to measure the conductivity and permeability of membrane, a

standard needed to be used to determine the accuracy of the methods. The most logical

membrane to test as a standard is Nafion, as is it one of the most commonly used membranes in

electrochemical cells.

Nafion

Nafion is a sulfonated tetrafluorethylene copolymer, with a chemical formula of

$$-[(CFCF_2)(CF_2CF_2)_m]-$$
$$OCF_2CFOCF_2CF_2SO_3H$$
$$CF_3$$

(9)
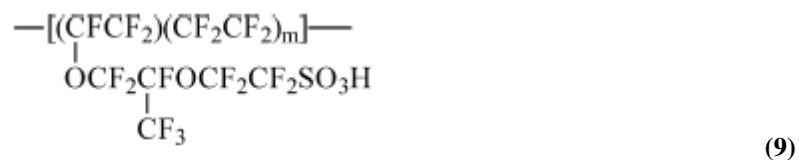
Its mechanical and thermal stability are useful in high-temperature environments, like

thermochemical cells. A Nafion membrane transfers cations, without transferring anions or

electrons, thus is defined as a proton exchange membrane (PEM). This characteristic is essential

for electrochemical processes where the separation of hydrogen is desired. The proton is allowed

to travel through the membrane, where it meets an electron to form a hydrogen atom.

Nafion is frequently described by a three digit code such as 117. The first two digits

show the equivalent weight (EW), which is the grams of dry Nafion per sulfonic group. So

Nafion 117 has an EW of 110 grams. The EW can also be used to determine how many CF_2 units

are in between each sulfonic acid group. The final digit of the code describes the thickness of the

film in English units, so a 117 film has a thickness of .007 inches.[11] This translates to a thickness

of .118 in mm.

Conductivity

Concept

An electrochemical conductivity is related to the movement of ions in a solution. These

ions create a current within the solution as they move. When dealing with conductivity through a

membrane, these ions must also be able to travel through the membrane. The mobility of these

ions is defined as $v_{max} = u*|E|$, where $|E|$ is the magnitude of the electric field

The conductivity depends not only on the concentration of the electrolyte and in the

solution, but also on the dissociation of that electrolyte. Higher concentrations with higher

dissociations produce higher conductivities. Increasing the charge of the ions does not

necessarily increase the conductivity, due to increased hydration of the ion. The ion both forms a

solvation sheath of water attracted to the ion as well as forming associations with other ions in the

solution. This increased hydration leads to a larger total radius, as the solvation sheath must

move along with the ion. Similarly, ions with the same charge, but larger size might have a lower

conductivity, as they interact with more molecules as they travel through the solution.

The conductivity, L, can be geometrically calculated from the ionic conductivity, κ,

which is defined as:

$$\kappa = \frac{lL}{A} \tag{10}$$

$$\kappa = e_0(n^+z^+u^+ + n^-z^-u^-) \tag{11}$$

where l is the length of the system, A is the area, L is the conductance, ze_o is the charge of the ions, n is the number of ions, and u is the mobility. Ionic conductivity measurements are frequently made using a cell of known width and volume allowing Equation 10 to be simplified by referring to l/A as the cell constant k_{cell}.[12]

It would be convenient to assume that the cell would respond linearly with the electric potential. However, this is only true if the potential is greater than the decomposition potential. For a lower potential, the interface between electrode and electrolyte creates a non-ohmic resistance, which dominates the conductivity.

If an AC voltage is used instead of a DC potential to create the differential, these non-Ohmic effects can be avoided. As a DC potential is applied to the system, the interface between the electrode and the electrolyte starts to act like a capacitor, storing up positive and negative charges on either side. B. Ershler determined this action early in the research of electrode reactions.[12] However, if an AC potential is instead applied, the charge of the electrode will switch between positive and negative, constantly reversing the potential across the system. This avoids the capacitance effect across the interface, as the charge is continually being discharged.

If $\omega \gg (1/RC)$, the interface impedances will become small compared to the resistance of the electrolyte solution itself. Thus a valid measuring technique is to use an alternating potential at very high frequency and extrapolate to infinite frequency. At very high frequency stray inductances can affect the impedance and produce an inaccurate measurement.

Electrochemical Impedance Spectroscopy

Impedance Spectroscopy is the use of small electrical signals to measure the linear response of a system or material. Impedance spectroscopy is most commonly used for electrochemical measurements.[13] Electrochemical Impedance Spectroscopy (EIS) is specifically

the measurement of materials whose characterization is dominated by ionic conduction. An accurate potentiostat with three or four electrodes should be used to create a known potential across the region of interest. Electrochemical impedance is usually measured by applying an AC potential, creating a current signal in response

Before modern EIS instrumentation was developed, E_t was plotted against I_t to produce a "Lissajous Figure" on an oscilloscope.[14] This figure has an oval shape which can be analyzed to find the magnitude and phase shift of the impedance. In current techniques, there are two types of plots used to present EIS data: a Nyquist plot, and a Bode plot. The Nyquist plot, the real part of the impedance is plotted on the X-axis, while the imaginary part is shown on the Y-axis. Each point on this graph represents a different frequency. With this plot, the impedance can be presented as a vector with magnitude $|Z|$ and angle from x axis φ. The major shortcoming of the Nyquist plot is that it does not show the frequency of each point. The Bode plot shows the log of frequency on the x-axis and simultaneously the magnitude and phase shift of the resistance on the y-axis.

If you look at a small enough segment of the current-voltage curve, it can appear to be linear. In a linear system, the current signal will contain no harmonics of the excitation frequency. This can help distinguish a linear system from a non-linear one. Some researchers intentionally use larger amplitude potentials so that they can analyze the harmonics and determine the current-voltage curve from them. For most standard EIS analysis tools, it is essential that the system be in a steady state. If any aspect of the system is in flux, all of the above assumptions of linearity will be false, creating an inaccurate result.

The data received from electrochemical impedance spectroscopy is frequently translated by creating an equivalent circuit out of basic circuit elements such as resistors, capacitors, and inductors. Creating such a model allows a prediction of the system's reaction to AC potentials.

Standard Equivalent Circuits

The resistance of the electrolytic solution itself is a reasonable starting point in modeling an electrochemical system. Most modern potentiostats consider the resistance of the solution in their calculations, but it must still be modeled in the equivalent circuit. The resistance of the system can be used to calculate the conductivity of the membrane.

$$R = \rho * \frac{l}{A} = \frac{l}{\kappa A} \qquad\qquad (12)$$

where ρ is the solution resistivity, κ is the solution conductivity, l is the length of the system, and A is the area of the system.

The double layer between the electrode and the electrolyte is the next part to be modeled. As a potential is applied to the electrode, a charge forms near the surface of the electrode. At the same time, ions in the solution shift to create an opposite charge at a very small distance away from the electrode. Thus a natural capacitor is formed, with two walls of opposite charge separated by a gap. As an estimate, this capacitance can be modeled as 20 to 60 µF per 1 cm^2 of electrode area.[15] This capacitor is placed in parallel with a Warburg impedance, symbolized as a box.
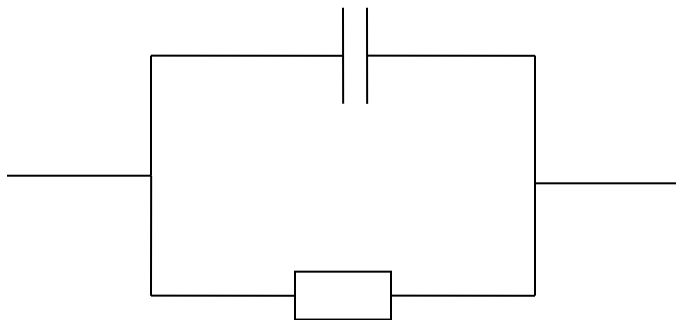

Figure 2: Basic diagram of electolyte behavior

One of the first equivalent circuits applied to membrane conductivity was the one developed by J.E.B. Randles. He combined the basic diagram above with an additional resistance

symbolizing the membrane resistance, along with placing the Warburg impedance in series with the capacitance.[16]
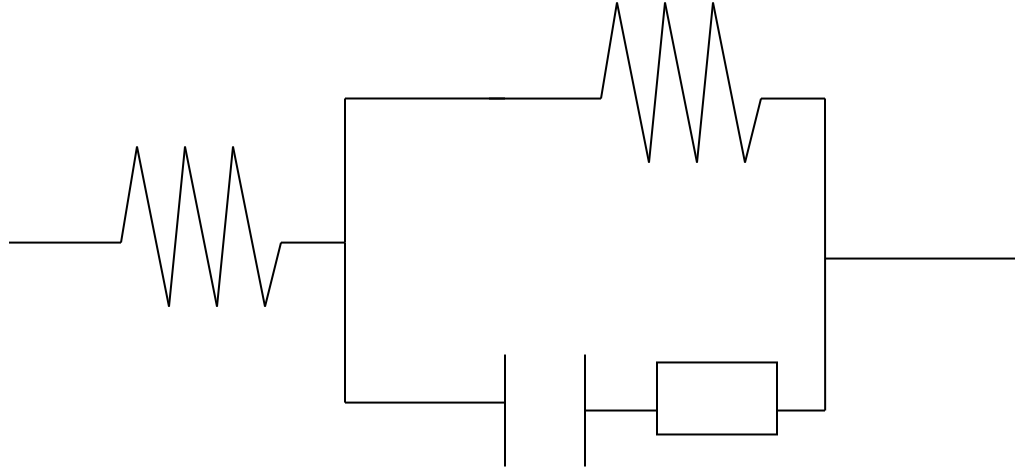
Figure 3: Randles circuit

Application

The conductivity of Nafion has been well established. The through-plane conductivity has been measured by trapping a membrane between two electrodes. Alberti et al. studied the effects of temperature and humidity on Nafion 117 and S-PEEK-2.48 membranes.[16] In-plane conductivity has been measured using both two-electrode and four-electrode systems. It is thought that four-probe EIS eliminates contact impedances. Two-probe measurements record conductivies 0.01 S cm^{-1} higher than four-probe measurements. Four-probe measurements often show Nafion conductivities of 0.070 to 0.086 S cm^{-1}. Proton Exchange Membrane Fuel Cells (PEMFC) have frequently been modeled using a form of Randles equivalent circuit. Several circuits are set in series with one another in order to model planar catalyst forms, and several circuits are set in parallel to model porous catalysts.[15] However, these models are intended to represent an entire fuel cell, not just the membrane.

<center>**Permeability**</center>

Concept

The permeability of the membrane also has an effect on the efficiency of the reaction. If any of the copper travels across the membrane, it could clog up the downstream piping or pump. The permeability of the membrane is most easily measured as the diffusion of certain elements across the membrane. Diffusion is the movement of a substance from a region of high concentration to a region of lower concentration. It is driven by entropy, leading the two sides toward a state where both have the same concentration. However, it is a rate driven process, and thus is governed by a certain constant, called the diffusivity of the material. A material with higher diffusivity will allow more of the substance to pass through it.

The basic principles for testing diffusion are well developed and defined. Two liquids are kept separate by a membrane. Both liquids must be continuously stirred to maintain their homogeneity. A specified time is allowed to elapse, during which liquid from one side of the membrane diffuses to the other side, in order to restore equilibrium between the two liquids.

If it is assumed that the membrane has a linear concentration distribution, and side B has no initial concentration, it can easily be determined that the concentration on either side of the membrane will be defined by equations 13 and 14.

$$v = \frac{1}{2} v_0 \left(1 + e^{-2\lambda kt/a2}\right) \qquad\qquad\qquad (13)$$

$$w = \frac{1}{2} v_0 \left(1 - e^{-2\lambda kt/a2}\right) \qquad\qquad\qquad (14)$$

where v is the concentration on side A, w is the concentration on side B, v_0 is the initial concentration of side A, $\lambda = a/b$, and k is the diffusivity.[19]

Equation 14 can also be expressed as Fick's equation:

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x}(k\frac{\delta c}{\delta x}) \qquad (15)$$

where c is concentration, t is time, x is distance, and k is the diffusivity.

When the concentration distribution inside the actual membrane is neglected, the permeability, k, is calculated instead of the diffusivity. For the specific application of permeation across a membrane, Fick's equation can simplified to equation 16, where k is the permeability, not the diffusivity.

$$k = \left(\frac{lV_{sample}}{At_{exp}}\right)\ln\left(\frac{C_{Cu}}{C_{Cu}-C_2}\right) \qquad (16)$$

l is the thickness, A is the area of the membrane, V is the volume of the sample, C_{Cu} is the concentration on the side with initial copper and C_2 is the concentration in the compartment with no initial copper.[8]

Application

Three types of membranes have already been considered as part of the ANL/PSU project characterizing membranes. First, ANL has been physically modifying Nafion to develop a less permeable membrane with similar conducting properties to Nafion. Nafion chains were inter-wound with sulfonic acid groups to develop a cross-linked polymer matrix. This membrane has not yet been tested.

Second, polysolfone membranes have been developed at PSU from Radel NT-5500, available from Solvay advanced polymers. The Radel NT-5500 base is characterized by low ion diffusion rates, so it was hoped that these membranes would prevent more Cu crossover than Nafion. Initial tests in AECL's electrolyzer showed higher copper diffusion with these membranes than with Nafion, however separate permeability test results showed permeation rates 1/10 that of Nafion.[8] These membranes require further testing in order to rectify this discrepancy.

Since these tests the membranes have been modified with varying amounts of cross-linking to improve thermal stability and provide a way to vary conductivity.

The third set of membranes has been provided by the Gas Technology Institute (GTI). According to GTI, these membranes have very low metal ion diffusion, high proton conductivity, high thermal stability, and high stability under reductive and oxidative conditions. These membranes are very economically promising, as they only cost \$1 per square meter.[8]

All of these membranes are being tested simultaneously at ANL and PSU. At ANL, these membranes were tested at 80°C in a diffusion set-up with 10 mol/L HCl on both sides of the membrane, and 1 mol/L CuCl2 on one side. UV-vis spectroscopy was used to measure the concentration of CuCl2 in the compartment that initially contained no copper. The permeability was then calculated using equation 16. The tests showed that many of the commercial membranes from GTI had very high permeabilities at 80°C, and that placing two layers of Nafion into the system actually had the lowest permeability.

As part of this thesis, this research was continued, and the permeability of Nafion and PSU-CEM membranes was measured.

Chapter 3

Materials and Methods

Conductivity

In-Plane Conductivity Cell

A Bekktech conductivity cell was used to measure the in-plane conductivity. The cell consisted of four electrodes crossing a region where a membrane was held. The membrane was first cut into a thin rectangular shape that crossed all four electrodes, and then was placed between two panels. These panels were then screwed together to hold the membrane securely across the electrodes. The entire system was immersed in DI water, and the electrodes were used to apply and read electric signals. Bubbles occasionally formed around the electrodes, requiring tapping to remove.
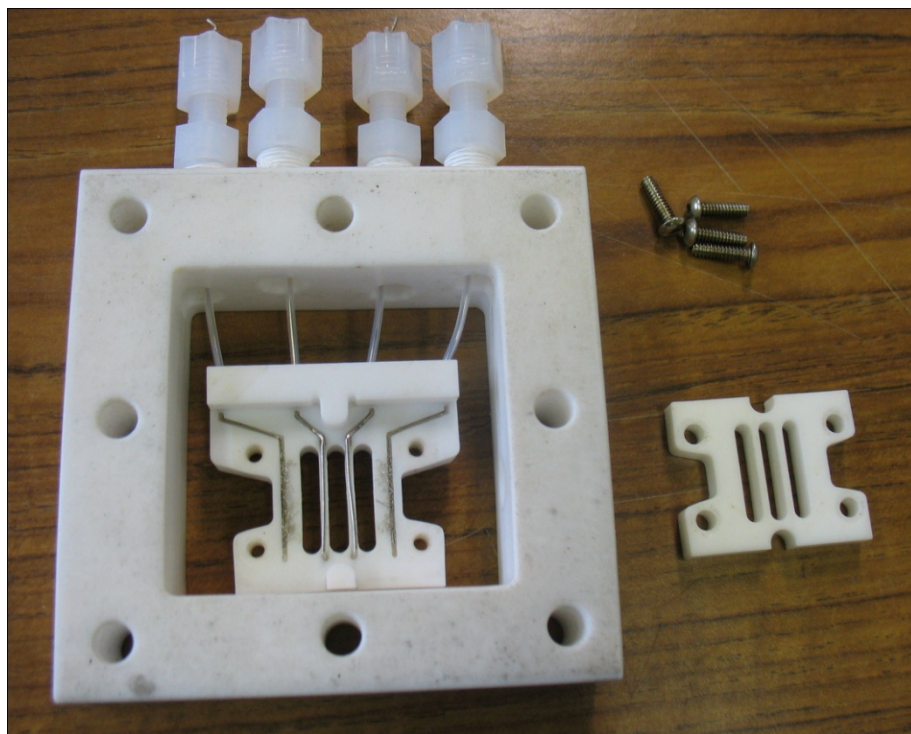
Figure 4: BekkTech conductivity cell

DC Measurements

A Gamry EIS Potentiostat[14, 21] was used to measure the resistance of the system. Originally, the system was being used to provide a DC voltage across the membrane. When a DC voltage is applied, the voltage must cause a reaction to occur in the system, or the membrane resistance will not be measured. The current measured across the system was graphed against the voltage applied to the system. The results were fit to a linear regression, and the slope of that regression was taken to be the resistance of the system. If the system behaved independent of frequency, this slope would have been constant showing that the resistance is linear. It was assumed that the usual interface problems do not occur when measuring in-plane conductivity, since the system is in water, instead of an electrolyte, and the electrodes are tightly fastened to the

membrane. In practice, however, it can be seen in Figure 5 that the resistance is not constant over frequency, so the current vs. voltage graph is not linear.
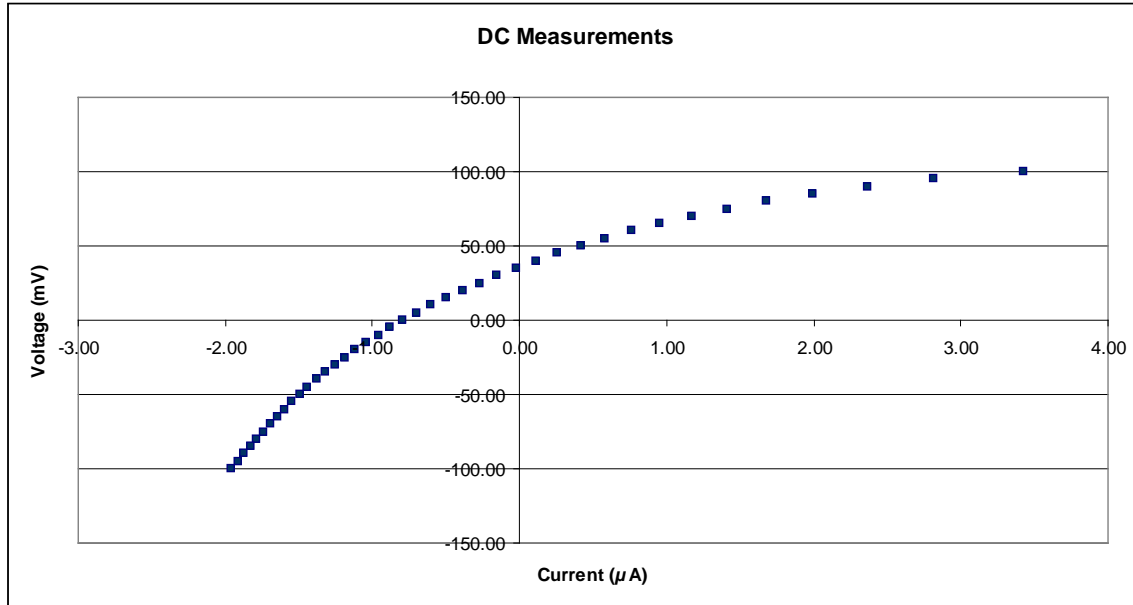
DC Measurements

Figure 5: Voltage vs. current for conductivity cell

AC Measurements

Instead of the above DC measurement system, an AC system needed to be established. When the Gamry EIS system is used as a potentiostat, it provides an AC voltage across the system, and changes the frequency over time. The results of the potentiostat can be presented in two ways: as a Nyquist plot, and as a Bode plot. The Nyquist plot shows the impedance of the system with the imaginary portion on the y axis and the real portion on the x axis. As it doesn't show the frequency, the way the impedance is changing over a frequency is not very well seen. A Bode plot is needed to show the impedance over frequency.

The data with a very high frequency is the most relevant, as the interface capacitance has the smallest effect in this region. The real resistance of the system as the imaginary resistance

approaches zero in the high frequency region is considered to be the resistance of the membrane. Thus, for through-plane conductivity measurements, the resistance is taken to be the lowest value of resistance on the Bode plot. However, when in-plane conductivity is measured, the line does not actually come to a minimum. Instead it continues decreasing over frequency. Since the minimum could not be taken, equivalent circuit models needed to be used to calculate the resistance. In order develop an accurate value for the resistance of the membrane, an equivalent circuit representing the physical aspects of the cell with electrical components.

The equivalent circuit that was developed is shown in figure 6. The resistance of the solution and the resistance of the membrane are split into two separate resistors, *Rs* and *Rm* respectively. There are also two capacitors intended to represent the effects of the interface between the membrane and the solution. The CPE is a constant phase element. It works with the capacitors to create a more accurate fit.

_____   _____

Figure 6: Equivalent circuit for in-plane system

Figure 2 shows how accurate the fit is on a Bode graph. The fit falls much closer to the data around the high frequency area, while it has a good deal of error around the lower frequency region.
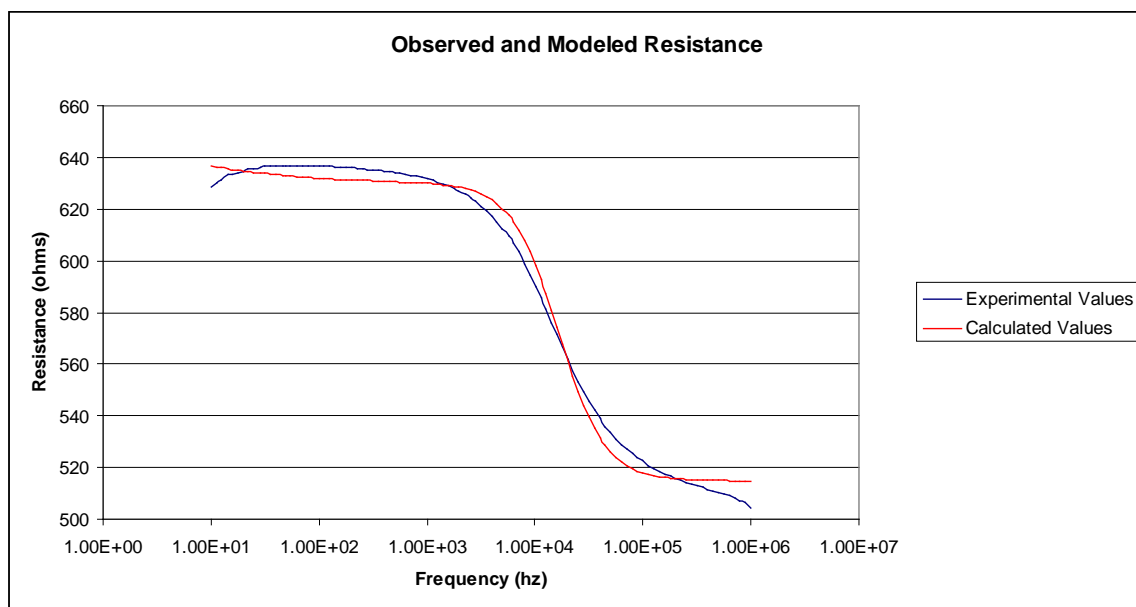
Observed and Modeled Resistance

Figure 7: Comparison between measured resistance values and those calculated using the model

Permeability

In order to test the permeability of a membrane, an experimental system was developed that creates copper concentration differential across the membrane. This forced the copper to permeate through the membrane. In order to determine the rate of this permeation, the concentration of copper in the side of the membrane without any initial copper was tested at proscribed times. This concentration was tested using complexometric titration.

Complexometric titration uses a molecule that forms a complex with the chemical to be tested. In this case, murexide, $NH_4C_8H_4N_5O_6$, was used as an indicator. It is a purple salt, but turns yellow in the presence of metals. EDTA, or Ethylenediaminetetraacetic acid, was used to complex with the copper ions and prevent them from reacting with the murexide. Thus, the amount of EDTA required to return the indicator to its purple color can be used to determine the copper concentration in the solution.

Initial Set-Up

The permeability cell consisted of two identical glass compartments, two magnetic stirrers, four caps, two o-rings, and a clamp. As shown in Figure 7, the membrane is held between the two o-rings which are in turn between the two compartments. This membrane is pre-treated as desired, then cut into a roughly circular shape following a template slightly larger that the openings in the compartments. The whole system is held together with a clasp attached to the wide openings of the compartment next to the membrane. A very small magnetic stirrer is placed in each compartment. The openings on the ends of the compartments are covered with caps.
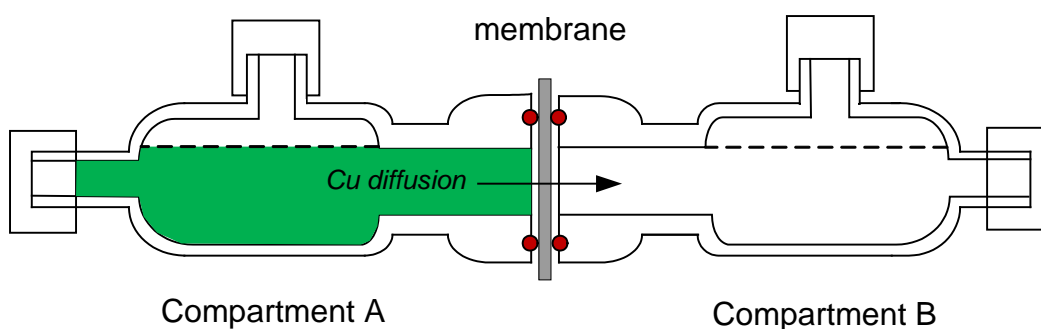

Figure 8: Diffusion set-up

The two compartments are each filled with solution. One compartment is filled with a solution of 1 mol/L $CuCl_2$ and 3.32 mol/L HCl(aq). The other side is filled with 0.5 mol/L

HCl(aq). These two solutions are similar to those actually inside a CuCl electrolytic cell. Care must be taken to insure that there are absolutely no bubbles in the solution. Such bubbles commonly appear next to the membrane, and can decrease the permeability of the membrane, as the entire surface of the membrane is not covered with solution.

Initial Procedure

1.) Assemble the clip cell with the piece of membrane carefully placed between the two o-rings in between Compartments A and B. Make sure that the membrane area is greater than that of O-rings for proper seal.

2.) Place 17 mL of 1 mol/L $CuCl_2$ in 3.32 mol/L HCl solution in compartment A. Put 17 mL of distilled water in compartment B.

3.) Check for bubbles and remove any by closing the system and moving it around.

4.) Put one magnetic stirrer in each compartment.

5.) Place system on the hot plate stirrer, and turn the knob controlling the stirrer to setting "2".

6.) Take a 2-mL sample from compartment B

7.) Add 6 drops of Murexide indicator

8.) Titrate using ethylenediaminetetraacetic acid (EDTA)

Problems with Initial Procedure

Although the initial procedure did measure the permeability of the membrane, it was not very accurate due to several issues with the procedure. One of the purposes of this thesis work was to change the procedure in order to make it more reliable.

Overflow of Compartment A

One of the problems faced with the system was the overflow of liquid in Compartment A. Because there was a higher concentration of acid in compartment A than in compartment B, water traveled across the membrane to correct the imbalance. As it did so, the total volume of compartment A rose. Since the compartments were almost completely filled, this caused a problem with the compartment overflowing. Thus copper was lost out of the system, decreasing the total concentration available to diffuse across the membrane.

This problem was remedied by changing the procedure in two ways. First, both compartments were only filled with 10 mL of solution instead of 17 mL. This provided enough solution to cover the entire membrane, while allowing more room for water to diffuse to the left. Although this did help with the overflow problem, it also made it more difficult to prevent bubbles from forming near the membrane, since the water levels in the compartments were lower. However, this merely made the initial set-up more time intensive, as the process to eliminate bubbles was still effective.

The second change was to switch the composition of the liquid in the second compartment so that it contained 0.5 mol/L HCl. This decreased the concentration gradient between the two compartments, decreasing the impetus for water to travel to the left. This change did adjust the cell so that it did not mimic the electrolysis cell as closely, since the original cell only has water on the cathodic side. However, the acidity of the cell may not significantly affect the movement of the Cu ions through the membrane, so this was deemed to not be too effectual.

Change in Total Volume

Another problem with the original procedure was that it called for measuring the concentration several times over the course of the experiment. Each time the concentration was measured, 2 mL of liquid was removed from compartment B. This decreased the total volume in the compartment, as well as the total amount of copper in the system. Both of these facts decreased the accuracy of the measurements, although the volume loss could be accounted for as it was a specific amount.

By running separate tests for each period of time, the inaccuracies due to withdrawing a sample could be avoided completely. The new procedure specifies that the entire system should be reset each time a measurement is taken. This did require more time for each test, and meant that the different times didn't overlap. In addition the typical time spans for each test were expanded from 1, 3, and 6 hours to 6, 12, and 24 hours, respectively.

Oxidation of Indicator

While water was flowing to the left to counter the difference in pH between the two compartments, the pH of the right hand compartment was rising. Thus, when samples were taken from the chamber, they were very acidic as well as containing copper. This didn't affect the concentration of copper in the samples, but did affect how that concentration could be measured.
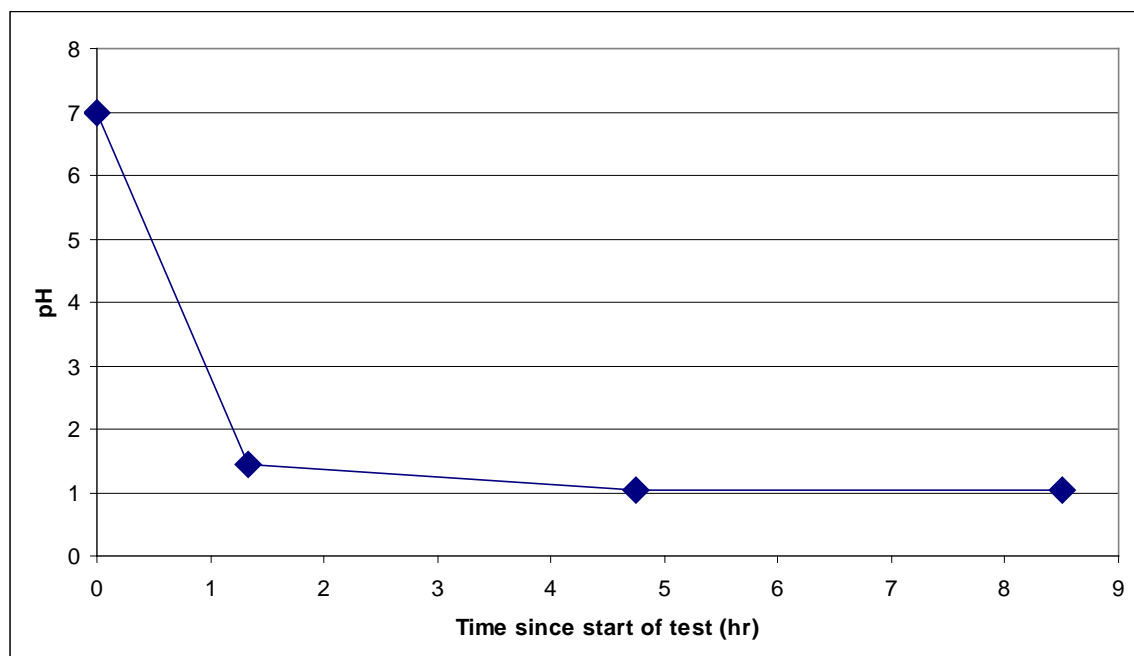
Figure 9: Acidity of solution in compartment B over time

There were two problems with using the complexometric titration in an acidic medium. The first was the color of the indicator. When the indicator was used in a very acidic solution, the indicator's color faded over time from a light yellow to clear. The second was that the rate of the reaction allowing EDTA to complex with metal ions can be affected by high acidities in the solution. EDTA contains several loosely bonded hydrogen atoms, which need to break off to allow the metal to complex. This occurs best in a slightly basic environment.

In order to ensure that the titration was accurately measuring the concentration, the solution was made more basic by adding NH_4OH until the solution turned slightly blue. At this point the solution was basic enough to produce accurate results in a series of standard solution tests.

Final Procedure

Assembly Procedure

1.) Assemble the clip cell with the piece of membrane carefully placed between the two o-rings in between compartments A and B. Make sure that the membrane area is greater than that of O-rings for proper seal.

2.) Place 10 mL of 1 mol/L $CuCl_2$ in 3.32 mol/L HCl solution in compartment A. Put 10 mL of 0.5 mol/L HCl solution in compartment B.

3.) Check for bubbles and remove any by closing the system and moving it around.

4.) Put one magnetic stirrer in each compartment.

5.) Place system on the hot plate stirrer, and turn the knob controlling the stirrer to setting "2".

6.) After the desired amount of time, usually 6 hours, use the unlabeled pipette to remove 3-2 mL samples from compartment B and determine the concentration of Cu^{2+} using titration procedure described below.

7.) Carefully pour out the solutions, being sure to save the magnetic stirrers. Remove the caps and rinse out the system with DI water, without actually removing the membrane.

8.) Repeat steps (2)-(7) for different exposure times until all desired measurement have been taken. The recommended method is three tests: one at 6 hours, one at 12 hours, one at 18 hours and one at 24 hours.

Titration Procedure

1.) Using a pipette, take 2 mL of test sample and place in a beaker or vial.

2.) If the test was 6 hours or less, use the labeled 1 mL pipette to add 4 mL of NH_4OH. If the test was longer, when you add the first mL of NH_4OH, look for a temporary blue color before the solution mixes. If you see a color change, you should add NH_4OH until the sample turns slightly blue. If you do not see a color change, just add 4 mL.

3.) Add 6 drops of Murexide indicator. Note color change. If the color changes to yellow, the concentration of Cu is substantial. If color changes to red/pink, concentration of Cu is at the detection limit. If there is no visible color change, copper concentration is negligible so do not titrate and proceed to text for a longer time.

4.) Fill 250 μL syringe with the standard .01 mol/L concentration EDTA solution. Slowly, drop by drop, add the standard solution to the sample. Stir the sample after every addition. At the equivalence point, the yellow color will change drastically to the original purple color of the indicator. The red color will slowly change, so the sample must be frequently compared to the color of the standard vial found near the system. Record the volume of the standard EDTA solution used at the equivalence point.

5.) Use the recorded amount of EDTA for calculation of the Cu concentration in the sample.

6.) Repeat the procedure steps (1) through (5) at least twice for each exposure time.

Chapter 4

Results

Conductivity

DC Polarization

With the four-electrode system, two electrodes can be used to apply a voltage across the length of the membrane and measure the produced current. The remaining two electrodes should be used to measure the potential difference. This can create a graph as shown in figure 10. The slope of the graph of voltage vs. the current should be constant and should provide the resistance.
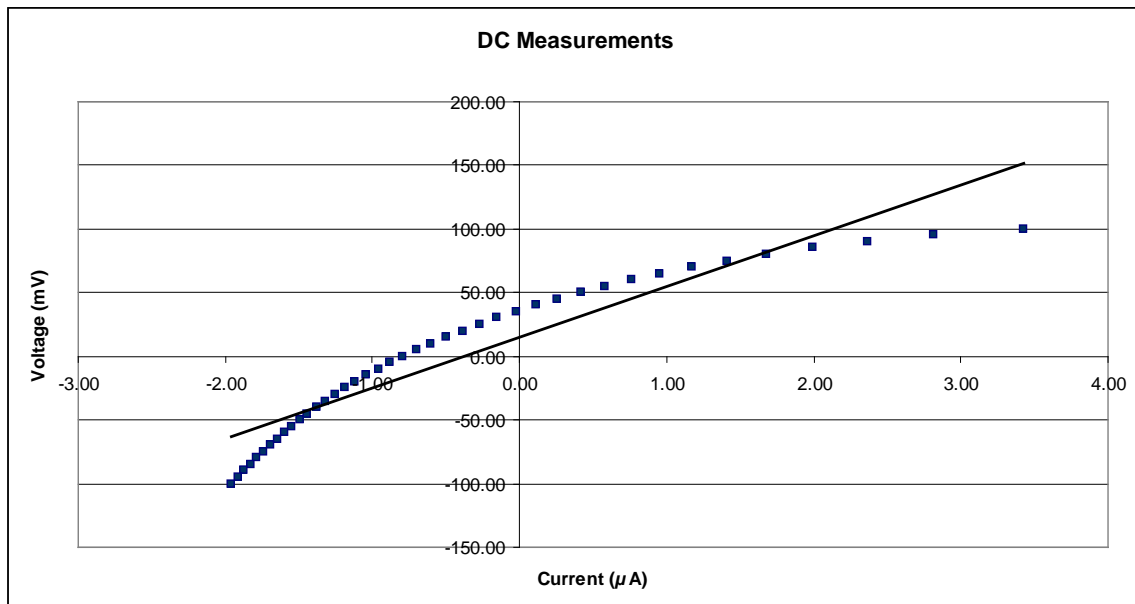

Figure 10: DC plot of voltage vs. current with linear approximation

When this method was used with a gaseous environment, this curve was very close to being perfectly linear. Unfortunately, when the system was placed in distilled, de-ionized water, a graph shown in Figure 10 was produced. Although the shape of the graph is roughly linear, it does not have a consistent slope. This would seem to show that there is some element in the system that is not acting as a pure resistor. The results obtained from these tests were also much lower than would be expected, at a max of 0.043 S/cm.

Table 1: Conductivity values obtained from DC method

Time (min)	Resistance (Ω)	Conductivity (S/cm)
4	881.2	0.04315
15	1100	0.03456
25	1271	0.02991
35	1371	0.02773
40	1391	0.02733
46	1430	0.02659
50	1489	0.02553
56	1473	0.02581
61	1395	0.02726
65	1392	0.02731
70	1399	0.02718

This non-linear effect is most likely caused by the interactions between the electrode, membrane, and solution.[12] The interfaces between the electrode and the electrolyte especially can act as capacitor, storing charge over time. This can be avoided by switching to an alternating current method. As the voltage switches from positive to negative, this interface switches between charging and discharging.

Calculating Conductivity

In the BekkTech conductivity cell used, the distance between the two voltage electrodes is 0.425 cm.[16] The formula for the relationship between resistance and resistivity is:

$$R \;=\; \rho * \frac{L}{A} \;=\; \frac{(\rho * L)}{W * T} \qquad\qquad (17)$$

where L is the distance between voltage measurement electrodes, A is the area of the plane traveled by the ions, W is the width of that area, L is the length of the area, and T is the thickness of the membrane. Conductivity is the inverse of resistivity, so first the equation is solved for resistivity, then the formula is inverted.

$$\rho \;=\; \frac{(R * W * T)}{L} \qquad\qquad (18)$$

$$\sigma \;=\; \frac{1}{\rho} \;=\; \frac{L}{R * W * T} \qquad\qquad (19)$$

Obtaining Resistance

Bode Graph

The Bode graph shows the correlation between the log of frequency and log of the impedance magnitude as well as the relationship between the phase angle and the log of frequency. When the AC method is used on a through-plane system, the Bode graph usually reaches a minimum at some point before the end of the test. This minimum is taken as the impedance value for the membrane. When the Bode graph was used for treating the in-plane data, the graph never reached a minimum, as can be seen in Figures 11 and 12. The darker set of data is the impedance, while the lighter set is the phase angle.
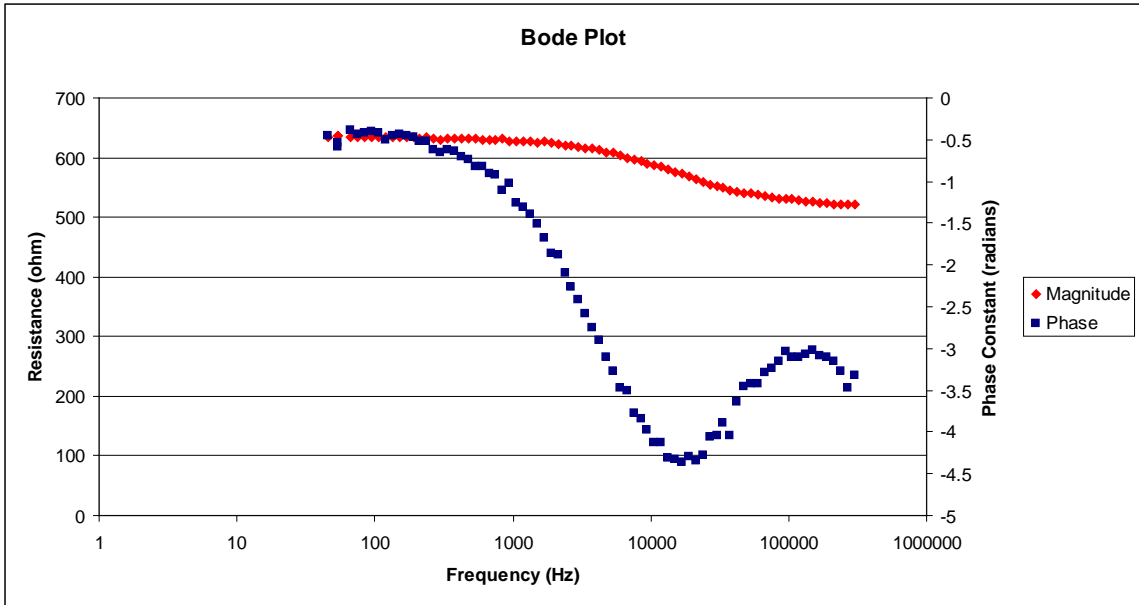
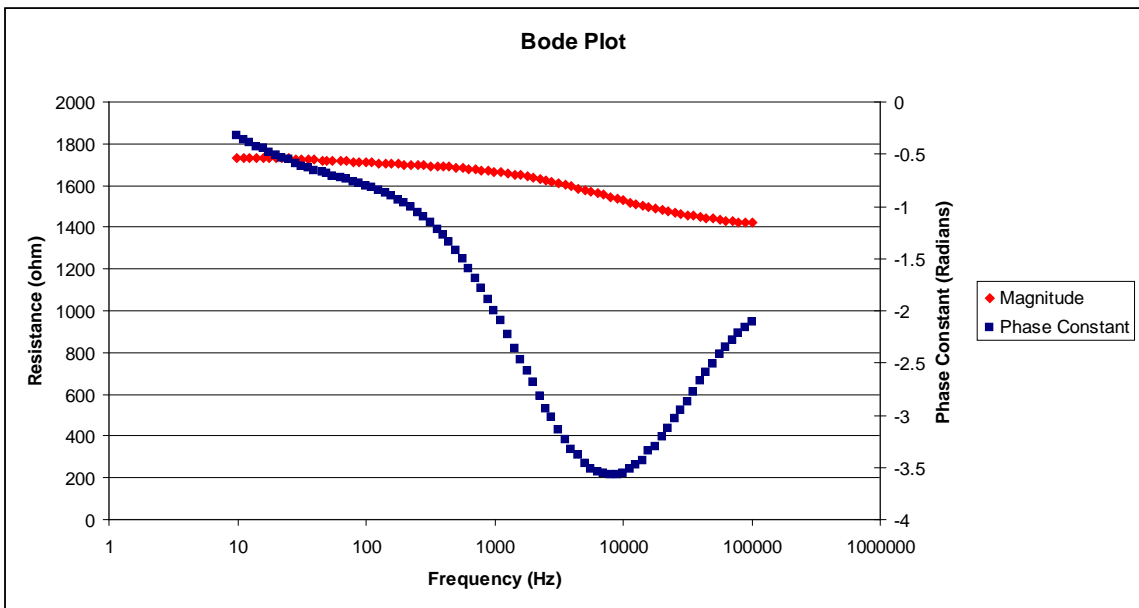**Bode Plot**

Figure 11: Bode plot of Nafion 117

Bode Plot

Figure 12: Bode plot of PSU-CEM

As well as the classic Bode plot produced by the Gamry EIS, the resistance is often graphed in a log(z) vs. log(f) chart. In the following figures, the lack of minimum resistance is even more obvious.
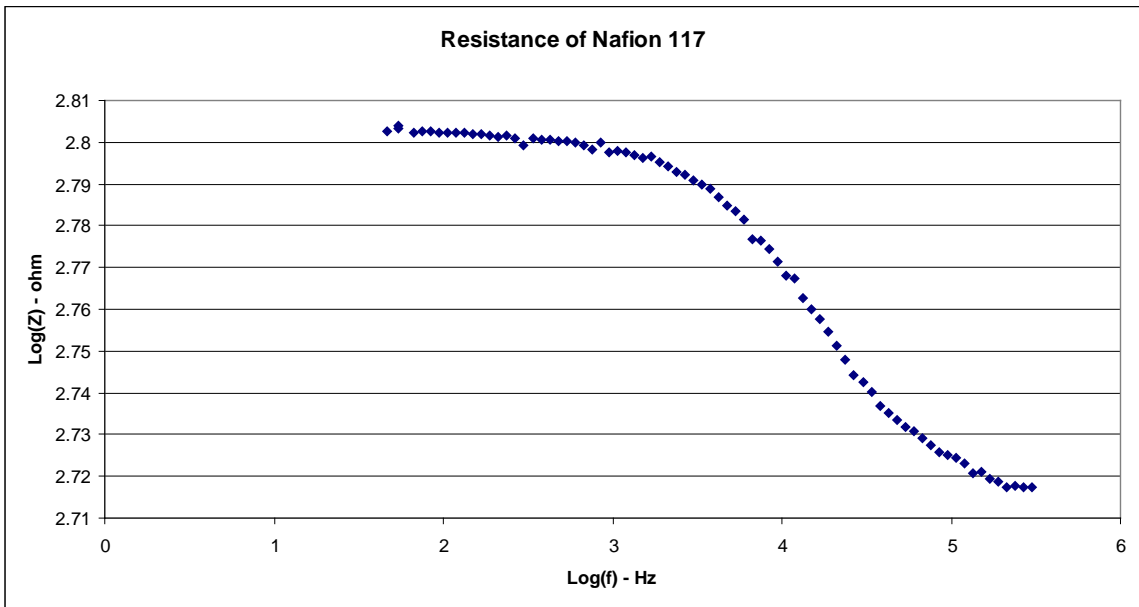
Figure 13: Log(z) vs Log(f) graph for Nafion 117
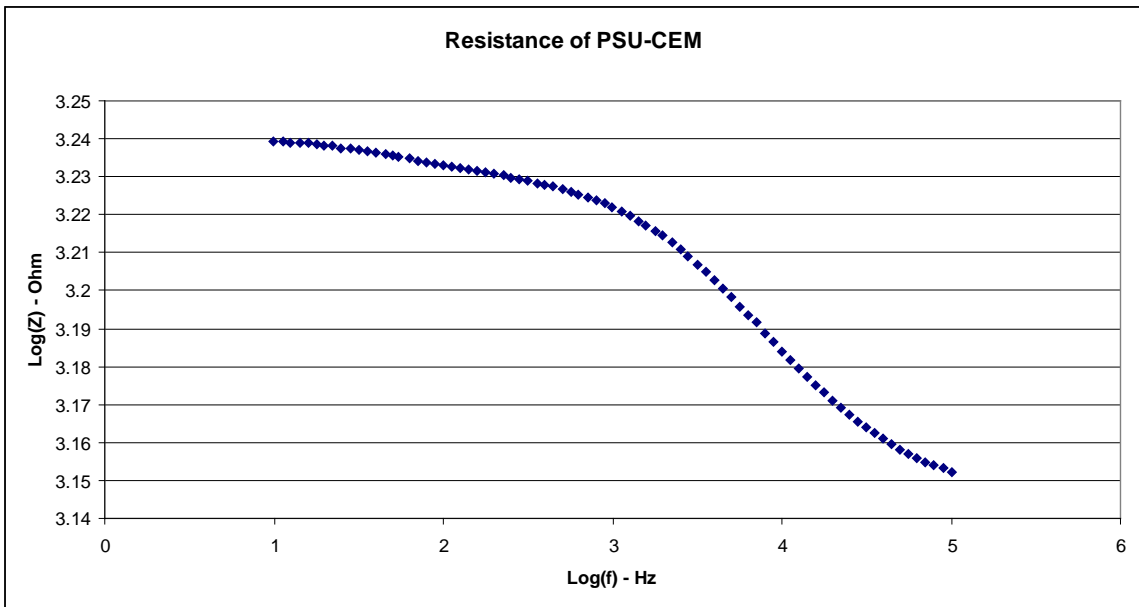

Figure 14: Log(z) vs. Log(f) graph for PSU-CEM

Nyquist Graph

The Nyquist graph shows the imaginary part of the impedance vs. the real part of the impedance. The resistance was taken from the Nyquist graph as the point where the imaginary part of the impedance is zero. The graph approaches by does not actually reach the x-axis.
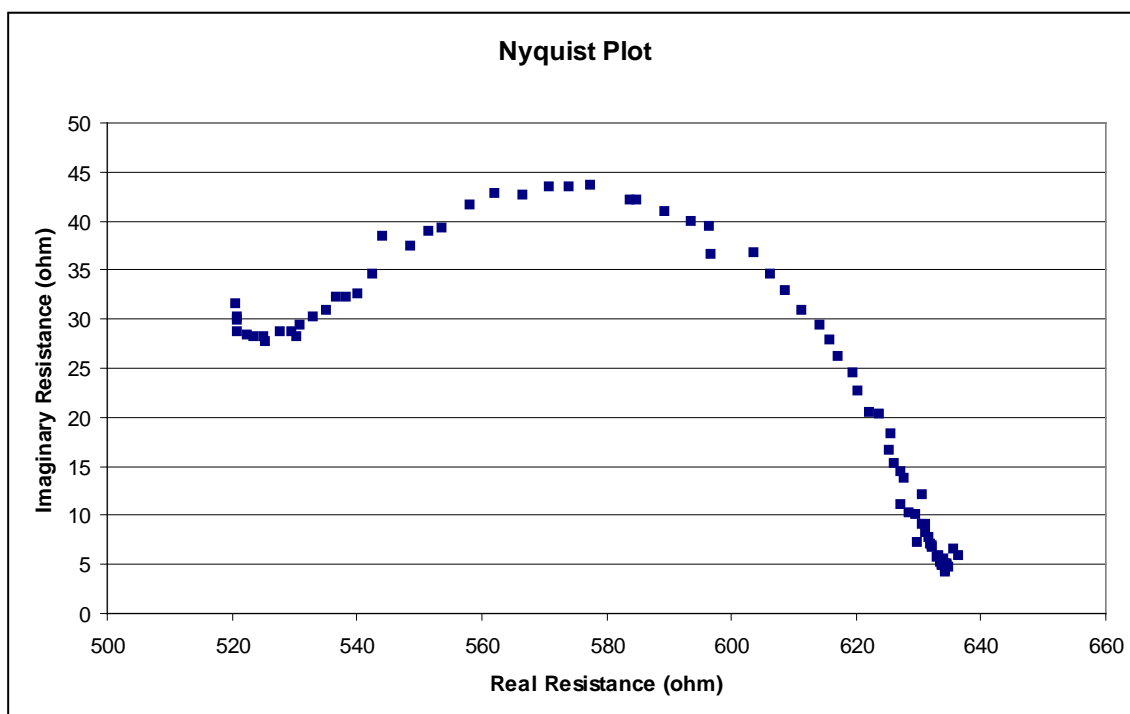

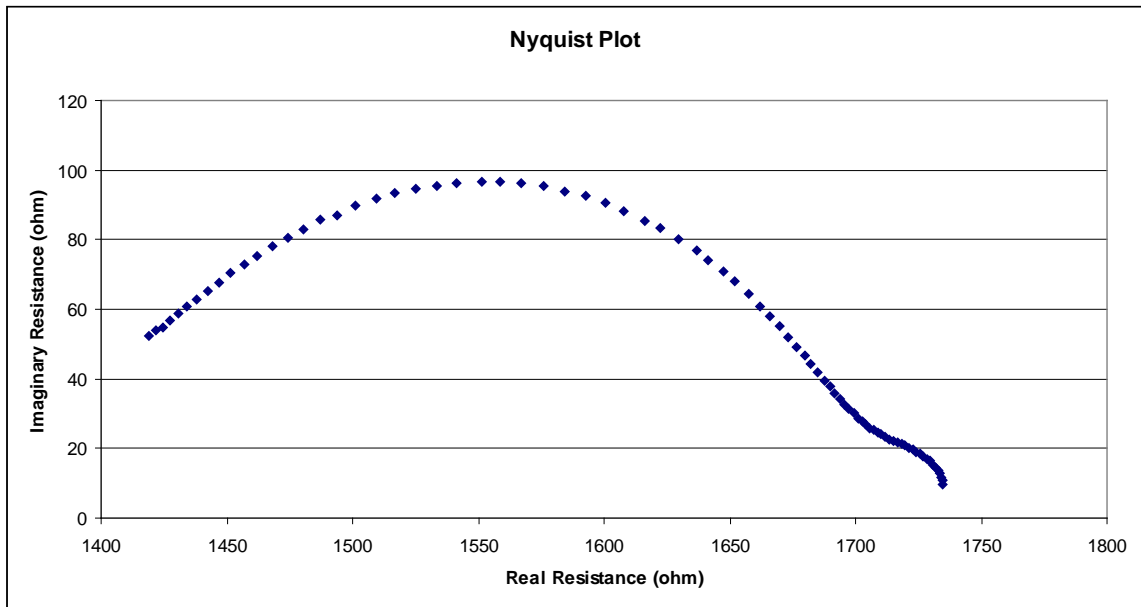Figure 15: Nyquist Plot of Nafion 117

Figure 16: Nyquist Plot of PSU-CEM

Equivalent Circuit

The equivalent circuit shown in Figure 6 was used as a model to predict the resistances outside of the range of the Bode and Nyquist graphs. Usually the difference between the point obtained from the two graphs and the equivalent circuit model was only around 10 ohms.

Two different Nafion 117 membranes were tested, one was completely untreated, while the other was treated in DI water for 2 hours, acid for one hour, and DI water for another hour. Using the circuit model, the completely untreated membrane had a resistance of 552.3 Ω with an error of 12.36 Ω which translated into a maximum conductivity of (0.075±0.02) S. The treated Nafion had a resistance of 418.4 Ω, which was calculated to be a conductivity of (0.095±0.02) S. One of the PSU-CEM membranes was also tested, and was found to have a conductivity of (0.047±0.02) Siemens. See Tables 2-4 for full data.

Table 2: Conductivity of untreated Nafion

Time (min)	Resistance (Ω)	Conductivity (S/cm)
0	554.2	0.07
8	536.9	0.072
16	533.7	0.073
39	521.7	0.075
47	520.7	0.075
55	515.7	0.075
63	514.1	0.075

Table 3: Conductivity of treated Nafion

Time (min)	Resistance (Ω)	Conductivity (S/cm)
4	412.4	0.096
33	416.5	0.096
40	417.5	0.095
49	418.4	0.095

Table 4: Conductivity of PSU-CEM

Time (min)	Resistance (Ω)	Conductivity (S/cm)
5	1409	0.048
11	1414	0.048
20	1423	0.048
29	1430	0.047
44	1442	0.047

Permeability

The permeability of the membranes was calculated from the change in concentration in compartment B over time. (See Figure 7) The actual concentration of Copper was calculated from the concentration of EDTA required to neutralize all of the copper using the equation:

$$C_{EDTA}V_{EDTA} = C_{Cu}V_{Cu} \qquad (20)$$

Where C_{EDTA} is the concentration of EDTA in the titration solution in M, V_{EDTA} is the volume of titration solution used to neutralize all of the copper in mL, C_{Cu} is the concentration of copper in mol/L, and V_{Cu} is the volume of the sample taken from the compartment in mL.

From this value, the permeability can be calculated using equation 21

$$k = \left(\frac{lV_{sample}}{At_{exp}}\right) ln\left(\frac{C_{Cu}}{C_{Cu} - C_2}\right) \tag{21}$$

where l is the thickness of the wet membrane in cm, V_{sample} is volume of solution in each of the compartments in cm³, A is the surface area of the membrane exposed to the solution in cm², t_{exp} is the duration of the test in seconds, C_{Cu} is the initial concentration of Cu^{2+} in the left-hand compartment and C_2 is the concentration of Cu^{2+} measured in the sample from the right-hand compartment at $t=t_{exp}$.

Four different membranes were tested: Nafion and PSU-CEM with three different forms of cross linkage. A PSU-CEM with 2.5 Cross-links was also tested while dry and after pretreatment. Relevant data appears in Table 5 and Figures 17-20.

Table 5: Permeabilities of four membranes in cm²/s

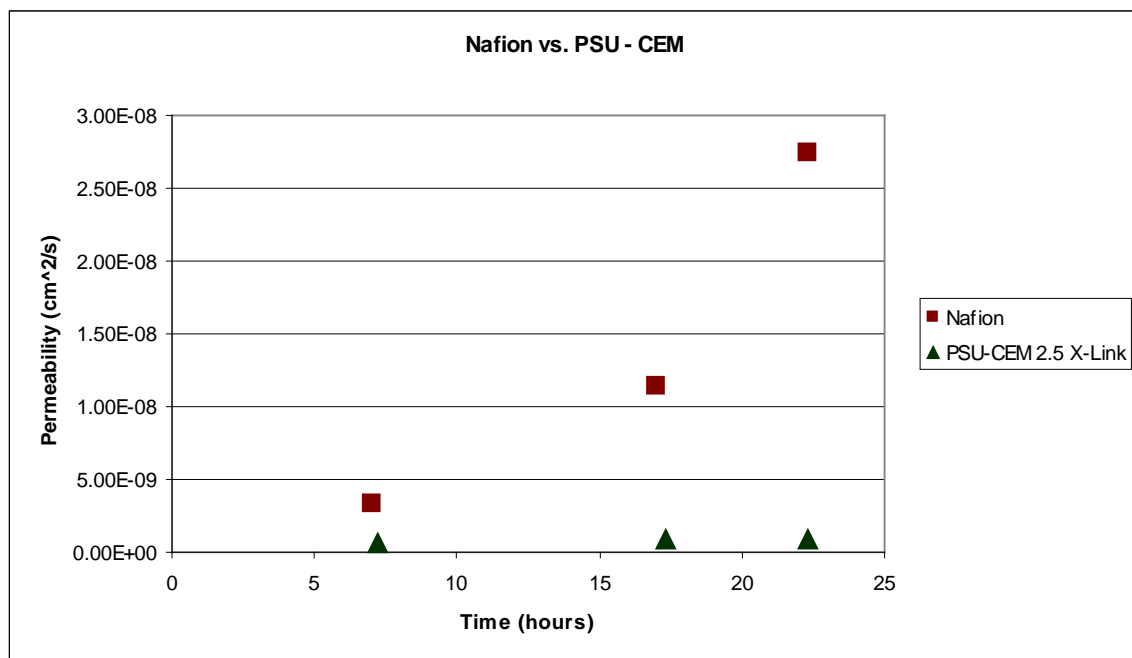| Hours	Nafion	PSU-CEM 2.5 X-Link	PSU-CEM 2.0 X-Link	PSU-CEM1.5 X-Link
7	3.33E-09	6.74332E-10	4.67E-09	3.0609E-08
17	1.14E-08	8.78E-10	2.60E-09	2.35808E-07
23	2.75E-08	8.76E-10	4.64E-09	9.60E-08

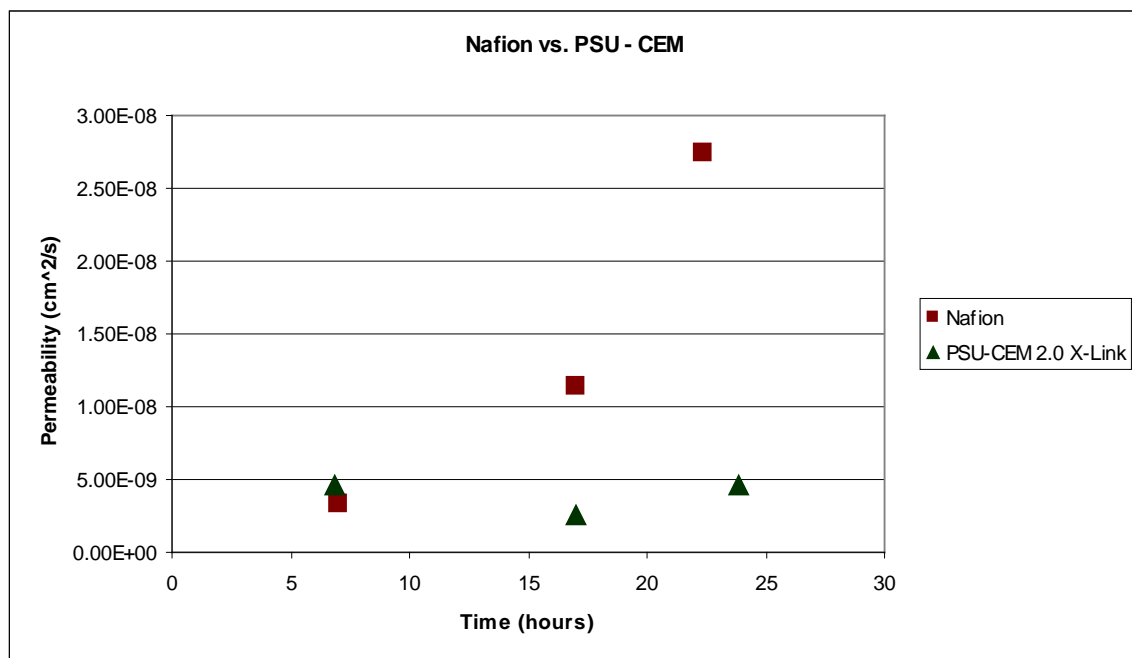Figure 17: Permeability of 2.5 x-link PSU-CEM
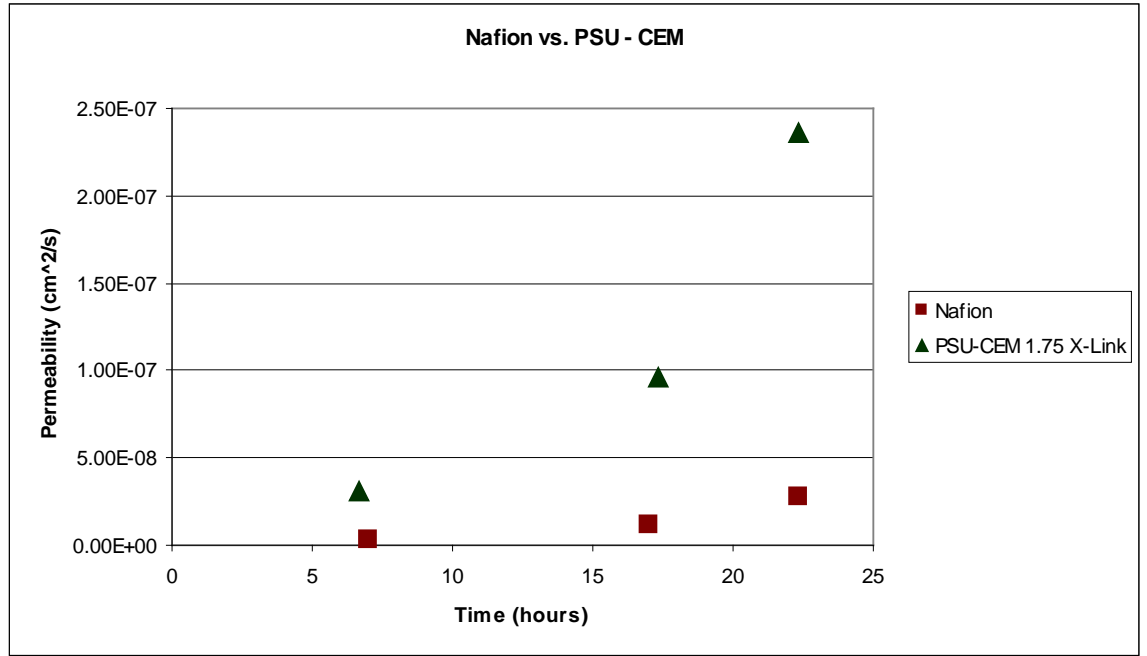

Figure 18: Permeability of 2.0 x-link PSU-CEM
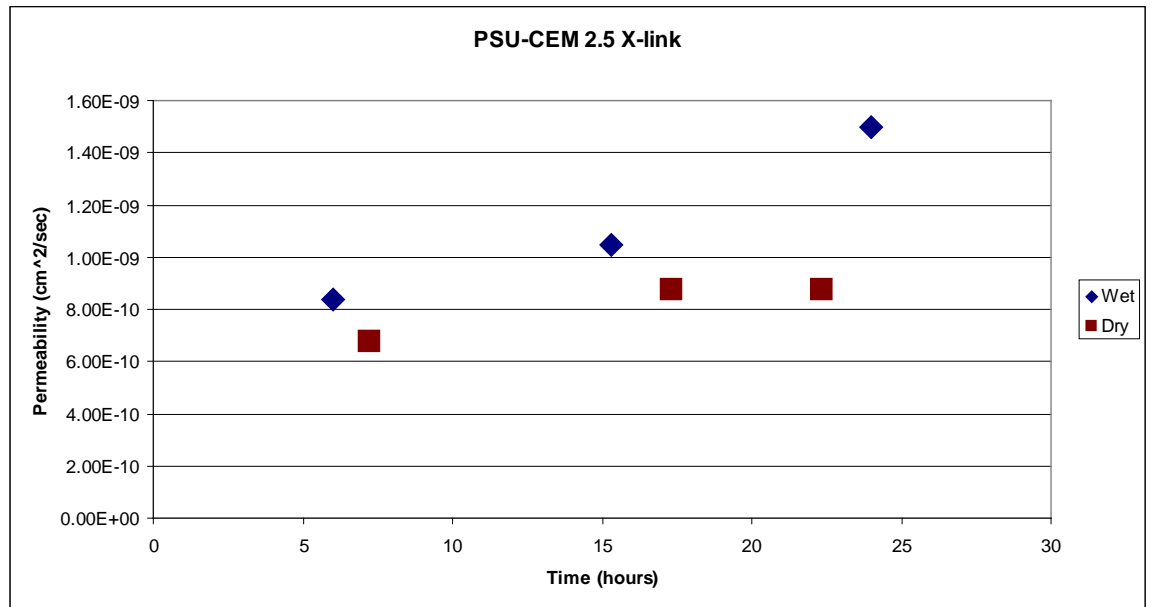
Figure 19: Permeability of 1.75 x-link PSU-CEM

Figure 20: Permeability of wet and dry 2.5 x-link PSU-CEM

Chapter 5

Discussion

Conductivity

Though the values for in-plane conductivity found over the course of the thesis are required for completeness, they are not as crucial to the characterization of the membrane as the values from the through-plane conductivity tests. However, since most membranes are polymers, their conductivity is not independent of direction. Thus, it was important to have a way to measure it accurately.

According to literature, see Chapter 2, the in-plane conductivity of Nafion is .077 S/cm. This means the in-plane measurement is close to being correct, with an error of .002 S/cm. When the Nafion is treated by boiling in water and in acid, a much higher value of .095 S/cm was achieved. The PSU-CEM membrane did not perform quite as well as the Nafion, as it had around .047 S/cm. Although this conductivity is still in the same order as Nafion's, it will produce a less efficient electrolysis process. However, if the permeability of the same membrane is low enough, it might outweigh the decreased efficiency.

The next steps in this process are to determine the conductivity of all of the individual PSU-CEM membranes with different cross-linkage. The membrane tested had 2.0 crosslinks, but membranes of 1.75 and 2.5 are also available. All of these membranes will also need to be tested for through-plane conductivity to determine the conductivity in the direction commonly used by the electrochemical cell.

The equivalent circuit as laid out in the materials and methods section is still flawed. It produces a more accurate result than simply looking at the graphs, but it does not exactly match

the data. Although it is very close in the high frequency region, which is the primary region of interest, it has a relatively large error in the low frequency region. A rationale also needs to be developed for each of the elements in the circuit.

Permeability

The permeability values found were very important to discover what the effects of leaving the membranes inside the reactor for an extended period of time were, as well as to weed out some of the membranes we were considering using. It was very clear from the results that the PSU-CEM with 1.75 cross linking did not permeate any less material than Nafion, and actually permeated more. PSU-CEMs with 2.0 and 2.5 cross links permeated less than Nafion, and thus are reasonable candidates for the electrolyzer.

The permeability data is not sufficient yet, as the values for permeability do not reach an upper plateau. During the longest test, the value for permeability is still rising rapidly. Ultimately, this value should become stable. As this point has not yet been reached, the tests should be extended till the change in diffusivity over time decreases.

The next step with the permeability procedure is to run the test at elevated temperatures. As the actual electrolyzer runs at 80°C, the permeability tests should also be run at 80°C. Performing this test requires a heater that is capable of reaching and maintaining such a temperature accurately and evenly. The initial problems with such a test were that the available oven was too large, and thus had too much of a temperature distribution inside it.

Work by Rest of Group

While this work on the conductivity and permeability of the membranes was being completed, other members of the group were perfecting an electrolysis cell capable of testing the membranes for efficiency and durability. Membranes received from the rest of the group were tested both before and after being put through the system. After the completion of this thesis, this process was continued, to the ultimate goal of simultaneously producing a high efficiency reaction and low copper permeability in the full system.

As of November 2011, the electrolyzer is being run for tests of several hundred hours without stopping. These tests provide a more accurate sense of the longevity of each of the membranes. Work is also being done on combining the permeability method with the through-plane conductivity method to produce a cell to directly calculate transport number. That work is ongoing.

Chapter 6

Conclusion

Over the course of this thesis, two methods were successfully established and tested. The In-plane conductivity method was proved with a value +/- 0.02 S/cm from the expected value. The permeability procedure produced reasonable results, but showed that the total time for the tests needed to be extended to determine the maximum permeability of the membranes. The permeability procedure also needs to be adapted for high temperature tests.

The results showed that the PSU-CEM membranes are a reasonable substitute for Nafion as far as their conductivity, and that PSU-CEM membranes with 2.0 cross-links or more allow less copper to diffuse across them than Nafion. This makes these membranes worthy of continued research and application into the CuCl electrolyzer.

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North Allegheny Senior High School (June 2007)

Publications

Sharon Falcon Miller, Justin Weber, Ben Carlson, Laura Bradley, Arwen Kandt, Bruce G. Miller, "Conducting a Bench-Scale FC Study on Oxygen-Enhanced Combustion of Coal and Coal/Biomass Mixtures", *DOE Report*, prepared for the National Energy Technology Laboratory (June 2009)

Arwen R. Kandt, Quijing Yang, Sharon Falcone Miller, Bruce G. Miller, "Effect of Process Parameters on Rheological Properties of Coal-Derived Liquids", *The Clearwater Clean Coal Conference*, (June 2010)

Qiujing Yang, Arwen R. Kandt, Sharon Falcone Miller, Bruce G. Miller, "Effect of Process Parameters on Rheological Properties of Coal Derived Liquids", *Energy Fuels,* **25** (2011) 2119-2129

Research Experience:

Research Assistant   Energy Institute, PSU   June 2008 – Present
- Presented technical paper at the Clearwater Clean Coal Conference
- Co-authored Dept. of Energy report on coal emissions
- Conducted research for and contributed to technical summary
- Dismantled and rebuilt fluidized bed reactor system
- Tested coal liquids for viscosity, surface tension, and thermal constants
- Studied the transport properties of electrolysis cell membranes

WISER Student   Energy Institute, PSU   January – May 2008

- Studied alternative catalysts for use in copper-chloride fuel cells
- Sponsored by Women in Science and Engineering Research

Work Experience:

Summer Consultant   Bates White Economic Consulting, LLC   Summer 2011
- Summarized technical reports for use in expert witness report
- Updated model for additional power in New York ISO
- Created spreadsheet to analysis market power for use in a merger case

Volunteer Experience:

Mission Trip   Peru   August 2010
- Wrote letters and set up interviews in order to raise funds
- Collaborated with non-English speaking coworkers

Community Auto   Allison Park, PA   June – August 2006
- Non-profit organization that provides cars for low-income families
- Added clients to RClient database
- Managed general office activites

Skills:

- Programming with Java, C++, Matlab, and Mathematica
- Basic knowledge of Chemkin, SolidWorks, Minitab, and MS Office
- Proficient in German

Activities:

- Sergeant in Arms - Penn State Fencing Club
- Leadership Team – DiscipleMakers Christian Fellowship
- French Horn - Concert Band