OUT OF PLANE EXPANSION OF PFSA MEMBRANES

FOR FUEL CELL APPLICATIONS

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Bachelor of Mechanical Engineering with Distinction

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ABSTRACT

A critical element of a hydrogen fuel cell is the proton-exchange membrane. Its unique properties allow it to conduct the protons of hydrogen atoms, while excluding the electrons to create an electrical charge. A fuel cell’s overall durability and conductivity is in large part determined by the properties of the membrane. This research involves the use of perfluorosulfonic acid (PFSA) membranes, a common type of proton-exchange membranes.

When any material is heated or cooled, it typically expands or contracts and, if this dimensional change is constrained, it causes a stress in the material. This stress, when applied cyclically over a period of time, leads to damage and eventual failure of the material. Hence over time as the membrane of a fuel cell is subjected to changes in temperatures, the membrane experiences a decrease in its durability and conductivity. Also, in order for these membranes to properly function, a certain level of hydration is needed. PFSA membranes are hydrophilic, and easily absorb water from the chemical reaction it sustains and from the atmosphere. Thus the absorption of the water causes the membrane to swell and result in dimensional changes in its thickness and in-plane dimensions. Similarly to thermal expansion, when this swelling strain is constrained, it causes a stress in the material, and ultimately results in damage or failure when applied cyclically over time. Therefore the goal of this research is to understand how PFSA membranes expand and contract over a range of temperatures from -40° C to 105° C, as well as with varying humidities in the range of 30% to 100%.

In these experiments there are two types of PFSA membranes used, Nafion® membrane and Membrane A. Nafion® membrane is used since it is an industry-standard fuel cell membrane. Most other polymer membrane materials, such as Membrane A, are
variations of Nafion® membrane’s basic structure. The membrane samples are analyzed using a TA Instruments Thermomechanical Analyzer, which controls the temperature in a small chamber and measures changes in thickness with an error of ± 15 nanometers. This makes it ideal for experimentation since the membranes have a thickness of approximately 20 to 59 micrometers. The TMA has been adapted with a V-Gen Humidity Generator, which allows humidified air to be funneled into the chamber of the TMA. With a miniature humidity probe inside the chamber as well, we can accurately control and measure the humidity. This is an important part in the measuring of the membrane thickness changes, since it depends on both the changes in temperature as well as humidity.

Our research to date has found extensive data regarding a specific type of Nafion® membrane - Nafion® 112 membrane. Data has been compiled for both Nafion® 112 membrane and Membrane A with regard to their thermal expansion. Also data regarding the thickness change due to water absorption via humidified air for Nafion® 112 membrane has been documented.
Chapter 1

INTRODUCTION TO P.E.M. FUEL CELLS AND PFSA MEMBRANES

In the search for “green” energy, hydrogen fuel cells provide clean power conversion for many applications. Currently, hydrogen fuel cells are replacing the internal combustion engine in prototypes for the “car of the future” since they do not release harmful byproducts into the atmosphere. Below, Figure 1 shows the basic operation of a hydrogen fuel cell, specifically a Proton Exchange Membrane Fuel Cell (PEMFC).

![Image of PEMFC Basic Operation](Figure 1: PEMFC Basic Operation (Courtesy of M. Lugo, University of Delaware))
In a PEMFC, hydrogen combines with oxygen from the air to create water and electricity. The key component which allows this process to occur is the Proton Exchange Membrane. The catalyst and the membrane allows for the protons in the hydrogen atoms to split from their electrons. While the protons are allowed to travel across the membrane, the electrons are conducted across a circuit and thus create electrical power. The chemical reactions of this process are shown in Figure 2 below.

**CHEMICAL REACTIONS**

**Anode Side:**

$$2H_2 \rightarrow 4H^+ + 4e^-$$

**Cathode Side:**

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

**Net Reaction:**

$$2H_2 + O_2 \rightarrow 2H_2O$$

Figure 2: Chemical Reactions in PEMFC (Courtesy of M. Lugo, University of Delaware)

However during this reaction, approximately 0.7 volts of electricity are generated\(^1\). Thus to increase the total voltage fuel cells are generally “stacked”, meaning many are placed in series to each other in a block as shown in Figure 3. This allows for a much greater voltage output, which is equivalent to the sum of each individual voltage.
The focus of this research is on the membrane of the PEMFC. With its fundamental property which allows protons to pass through while insulating against electrons, it is the most important component in a fuel cell. Thus the overall durability and life cycle of a fuel cell is often dependant on the quality and integrity of the membrane. When any material is heated or cooled, it typically expands or contracts. Since heat is a byproduct of a fuel cell (as shown in Figure 3), the membrane is often subject to changes in temperature. Thus if this dimensional change is constrained, it causes a stress in the material. When such a stress is applied cyclically over a period of time, it will lead to damage and eventual failure of the material.

Not only do these membranes expand due to changes in temperature, but also to water absorption via humidified air. With its hydrophilic properties, proton-exchange membranes readily absorb water or water vapor. Thus a change in the saturation levels of the membrane will cause a dimensional change, subsequently inducing stresses to the material.
Understanding exactly how PFSA membranes react to changes in temperature and humidity are of utmost importance when trying to improve the durability of a fuel cell. One PFSA membrane used in these experiments is Nafion® membrane, which was initially developed by DuPont in 1967[2] and is an industry standard membrane. The majority of PFSA membranes, including Nafion® membrane, have similar chemical compositions which involve Polytetrafluoroethylene as a chemical backbone. Polytetrafluoroethylene, more commonly known as PTFE or Teflon®, has a high resistance to chemical degradation, thus this property is important in membranes. While PTFE is strongly hydrophobic, these polymers are subsequently “sulphonated.” The sulphonation process involves adding a side chain of polymer which is attached to sulphonic acid ions(HSO₃), giving it hydrophilic properties. This is an important step, because the membranes need to be saturated with water to function properly. These sulphonated membranes are now called perfluorosulfonic acid membranes, or PFSA for short.

Over the last several decades, DuPont has developed new types of Nafion® membrane while also improving its chemical properties and overall durability. This research involves the use of Nafion® membrane 112; the designation “112” represents certain properties of the specific type of Nafion® membrane. The first two digits represent the equivalent weight of the polymer, which is the number of grams of dry polymer per mole of sulphonic acid (in the case of 112, the 11 represent 1100 EW). The third digit represents the thickness of the membrane, which is denoted by thousandths of an inch. Therefore Nafion® membrane 112, hereafter referred to as “Membrane 112”, has an average equivalent weight of 1100 grams of dry polymer per mole of sulfonic acid, and is 0.002” (50.8 micrometers) thick.
Another membrane which has shown considerable promise in mechanical durability is Membrane A, which is manufactured by W.L. Gore and Associates\textsuperscript{[3]}. While similar in basic structure and thickness to Nafion\textsuperscript{®} Membrane, Membrane A is a proprietary product to W.L. Gore and consequently the details of its chemical composition and manufacturing process are confidential. Thus Membrane A will also be tested as a comparison to Membrane 112.
Chapter 2

HYPOTHESIS AND GOALS

The primary goal of the research is to analyze the thermal and swelling effects due to water vapor uptake on Membrane 112 and Membrane A. However in order to achieve this goal, the necessary equipment needs to be configured and calibrated. Consequently one must create an apparatus capable of reliably and accurately measuring these effects, while also performing experiments which will yield data regarding thickness changes due to the thermal and swelling effects.

In understanding the basic principles of thermal expansion, these effects are generally minor under relatively small temperature changes. The thermal expansion experiments have a temperature range of 145° C, which represents a change from 105° C to -40° C. As a comparison, Table 1 below shows how selected materials would expand from an increase of 145° C. Results are displayed as percent elongation, which is the change in length divided by the original length.

<table>
<thead>
<tr>
<th>Material</th>
<th>$a \times 10^{-6}$ (per degree C)</th>
<th>Percent Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>23.6</td>
<td>0.342</td>
</tr>
<tr>
<td>Steel</td>
<td>11.7</td>
<td>0.170</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.59</td>
<td>0.009</td>
</tr>
</tbody>
</table>
Based on previous research, the underlying hypothesis is that the swelling due to water vapor uptake will be greater than the effects of thermal expansion. It is also expected that the out-of-plane swelling strain should be similar to the in-plane swelling strain. Previous results from our experimentation has shown a 6% elongation in the in-plane direction for Membrane 112 when the relative humidity increases from 30% to 90%[5]. To investigate the swelling of the membranes in the thickness direction, it is first necessary to modify the existing equipment to include humidity control in addition to temperature control.
Chapter 3

METHODS AND MATERIALS

3.1: Constructing the Testing Apparatus

The testing apparatus consists of four main components which are as follows:

a) The TA Instruments Thermomechanical Analyzer (TMA)
b) Mechanical Cooling Assistant (MCA)
c) The Instruquest V-Gen Humidity Generator
d) The E+E Humidity Probe

3.1.1: The Thermomechanical Analyzer and Mechanical Cooling Assistant:

The Thermomechanical Analyzer, or the TMA, is the main component of the testing apparatus and can be seen in Figure 4.

Figure 4: The TA Instruments Thermomechanical Analyzer (TMA)
Its main purpose is to either heat or cool the specimen to a specified temperature, while measuring its thickness change. As shown in Figure 4 there are several key parts to the TMA, of which the Furnace Assembly, Probe Assembly, and Stage are most important. When performing an experiment, the furnace lowers over the stage and uses electrical coils to heat the chamber. When the specimen expands or contracts, the expansion probe measures the change in thickness with an accuracy of ± 15 nanometers.

![Image of TMA Stage Setup]

**Figure 5: TMA Stage Setup**

The expansion probe rests on the stage; both components are made of quartz, which has a very low coefficient of thermal expansion (see Table 1). When setting up an experiment, the specimen is placed between the stage and probe. Also note the metal thermocouple next to the stage which measures temperature.

In order to achieve temperatures below ambient conditions, the Mechanical Cooling Assistant is required. The MCA covers the furnace and works with the TMA to achieve temperatures as low as -70° C; see Figure 6.
3.1.2: The V-Gen Humidity Generator

While the combination of the TMA and MCA allows for the complete range of temperatures necessary for experimentation, the apparatus still lacks humidity control. Thus, the V-Gen Humidity Generator and E+E Humidity probe were purchased to create an environment in which the user can control the relative humidity inside the chamber. However the TMA is not designed to have a humidified air input. Consequently a method to have the humidified air funneled into the chamber was designed; this is discussed in Section 3.2.
3.1.3: The E+E Elektronic Humidity Probe

In order to measure the humidity inside the chamber, a humidity probe was needed to meet the specifications for the project, which are:

1) Accurately measure relative humidity from 0% to 100%
2) Withstand temperatures from at least -40° C to 105° C
3) Have a maximum thickness of 5mm

While many humidity probes satisfied the first two requirements, only the E+E probe had a small enough diameter to fit inside the chamber. Below Figure 7 shows a picture of the probe:

![Figure 7: E+E Humidity Probe](image)

3.2 Development of the Testing Apparatus:

While all of the components individually satisfy the specific requirements for the project, the next step is to integrate them together to create an apparatus which can accurately measure thickness chambers on a micrometer scale, while controlling and measuring the temperature and humidity inside the chamber.
3.2.1: First Design

A first design was to connect the output of the V-Gen to the liquid nitrogen input on the TMA. Liquid nitrogen could be used to cool the chamber as an alternative to the MCA. An adapter was machined from aluminum and designed with a tolerance to allow an air-tight fit into the TMA’s nitrogen input; see Figure 8.

![Image of the first design of attachment of the V-Gen to the TMA](image)

**Figure 8: First Design of Attachment of the V-Gen to the TMA**

Initial testing at room temperature showed that a full range of humidities could be reached, however problems were encountered when the temperature was increased. High humidity values (above 50%) could not be sustained with an increase in temperature (generally above 60° C). Upon further analysis the root of this problem was due to the low volumetric flow rate into the chamber; the nitrogen input tube has a very small cross sectional area, thus
limiting the amount of humidified air that is delivered into the chamber. Therefore an alternative method of inputting the humidified air needed to be designed.

3.2.2: Second Design

With a special thanks to Tom Cender, a second design was implemented. The process was three-fold; redesign the base, redesign the quartz stage, and design an input to allow a direct flow of humidified air in the chamber. The first two steps were important to ensure that all of the necessary components can fit inside the chamber.

Figure 9 below shows the difference between the designs of the old base against the new one. Note the additional slots to allow space for the humidity probe and output of the V-Gen.

![Figure 9: TMA Base Redesign (Right) Compared to Initial Design (Left)](image)

The first model was constructed out of aluminum for ease of machining, but this created a problem during experimentation. The aluminum base acted as a heat sink, causing a gross inaccuracy in the E+E probe humidity readings. This led to issues in maintaining and measuring the humidified air in the chamber. Subsequently the base was recreated out of Delrin® (polyoxymethylene plastic).
Redesigning the quartz stage was extremely important to efficiently use the space inside the chamber. The goal was to make the stage smaller in diameter, while allowing space for the humidity probe, expansion probe and V-Gen output to all fit inside the chamber. When designing the quartz stage, issues arose regarding manufacturability. The material selected for construction needed to be quartz due to its low coefficient of thermal expansion, which minimizes any error when measuring a thickness change. Quartz is difficult to machine, and is fragile by nature. However a final design was chosen, and was outsourced to a third party for construction. Below Figure 10 shows the difference in the two stages:

![Figure 10: TMA Stage Redesign](image)

Note how the design of the new stage incorporates a smaller diameter, as can be seen by the top of the stage. Thus with the quartz stage redesigned, all of the components fit inside the chamber and allow for proper experimentation.
3.3: Testing Methods

Before performing any experimentation, Membrane 112 needs to be chemically pretreated to remove organic and ionic impurities. This is a standard process[6], and consists of putting the material in the following boiling solutions in succession for one hour each:

1) 3% Aqueous H₂O₂
2) Distilled and deionized (DI) water
3) 0.5 M H₂SO₄
4) Distilled and deionized water

The material is then kept in room temperature DI water until needed for experimentation.

3.3.1: Thermal Expansion Experimentation

In order to properly test for thermal expansion, water vapor absorption needs to be isolated from the experiments. Therefore each sample was heated to 105° C for an hour to ensure it is thoroughly dried. Several experiments were done to verify that the relative humidity inside the chamber was less than 5%, as well as having all of the water evaporated from the membrane. Also, 105° C is a temperature that is used often in literature when predrying a sample.[7]

Once the sample was heated for an hour, it was cooled to -40° C, and then brought back to room temperature. The relevant information that is obtained is how the specimen’s thickness changes from 105° C (after the hour) to -40° C.
3.3.2: Water Vapor Absorption Experimentation

Similar to the thermal expansion experimentation, one variable needs to be controlled while the other is varied. Here the TMA will fix the chamber at a certain temperature, while the V-Gen will vary the relative humidity inside the chamber. For a given temperature, the humidity will increase from 30% to 90% in increments of 20%. At each increment, the specimen will sit for an hour to equalize with the change in humidity and fully absorb the water vapor.
Chapter 4
DATA AND RESULTS

4.1: Membrane 112

4.1.1: Membrane 112 Thermal Expansion Results

After performing twelve successful experiments, the thermal effects on Membrane 112 have been characterized. Figure 11 below displays how the thickness of Membrane 112 varies from 378 to 230 Kelvin (105° to -40° C). It is important to note that this data reflects the expansion after the specimen is heated to 105° C, as explained in Section 3.3. With the relative humidity less than 5%, this gives a true test of the thermal expansion with minimal variability from water vapor absorption.

![Nafion 112 Thermal Expansion graph](image)

**Figure 11: Membrane 112 Thickness vs. Temperature Change**
One key piece of data to extract from Figure 11 is the overall change in thickness from any two temperatures. Table 2 below shows this change from 105° to -40° C.

**Table 2: Thickness Change in Membrane 112**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Thickness Change (µm) from 105°C to -40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.448</td>
</tr>
<tr>
<td>2</td>
<td>-2.436</td>
</tr>
<tr>
<td>3</td>
<td>-2.362</td>
</tr>
<tr>
<td>4</td>
<td>-2.281</td>
</tr>
<tr>
<td>5</td>
<td>-2.529</td>
</tr>
<tr>
<td>6</td>
<td>-2.629</td>
</tr>
<tr>
<td>7</td>
<td>-2.685</td>
</tr>
<tr>
<td>8</td>
<td>-2.854</td>
</tr>
<tr>
<td>9</td>
<td>-2.488</td>
</tr>
<tr>
<td>10</td>
<td>-2.542</td>
</tr>
<tr>
<td>11</td>
<td>-2.377</td>
</tr>
<tr>
<td>12</td>
<td>-3.020</td>
</tr>
<tr>
<td>Average</td>
<td>-2.560</td>
</tr>
<tr>
<td>St. Dev</td>
<td>0.206</td>
</tr>
</tbody>
</table>

It is also important to consider this data in a normalized form, to account for the differences in initial thickness. Figure 12 shows thermal strain vs. temperature, where thermal strain is defined as $\Delta L/L_0$. Here $L_0$ is defined as the thickness after heating the specimen for one hour. This is in essence the thickness of a dry membrane.
From this data the coefficient of thermal expansion (α) can be extracted. α is defined by:

$$\alpha = \frac{1}{L_0} \frac{dL}{dT} \quad (1)$$

Where $dL/dT$ is the change in length due to a change in temperature. Figure 11 shows explicit data regarding how the length $L$ (in this case the thickness of the material) varies with temperature; this yields $L(T)$. Thus knowing $L(T)$, as well as the initial thickness, one can explicitly calculate the thermal coefficient $\alpha$. In order to obtain $L(T)$, this relationship must be in the form of an equation which is differentiable. Thus curve fits were applied to each of the twelve specimens. After trial and error the optimal fit was determined to be a second-
degree polynomial, which is of the form \( Ax^2 + Bx + C \), where \( A, B \) and \( C \) are constant coefficients. Table 3 below shows each specimen and its coefficients.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000010</td>
<td>-0.04254</td>
<td>51.55</td>
</tr>
<tr>
<td>2</td>
<td>0.000011</td>
<td>-0.04780</td>
<td>52.89</td>
</tr>
<tr>
<td>3</td>
<td>0.000010</td>
<td>-0.04464</td>
<td>52.70</td>
</tr>
<tr>
<td>4</td>
<td>0.000010</td>
<td>-0.04224</td>
<td>50.56</td>
</tr>
<tr>
<td>5</td>
<td>0.000012</td>
<td>-0.05930</td>
<td>54.95</td>
</tr>
<tr>
<td>6</td>
<td>0.000008</td>
<td>-0.02809</td>
<td>49.54</td>
</tr>
<tr>
<td>7</td>
<td>0.000007</td>
<td>-0.02531</td>
<td>49.17</td>
</tr>
<tr>
<td>8</td>
<td>0.000009</td>
<td>-0.03255</td>
<td>52.78</td>
</tr>
<tr>
<td>9</td>
<td>0.000009</td>
<td>-0.03763</td>
<td>52.43</td>
</tr>
<tr>
<td>10</td>
<td>0.000007</td>
<td>-0.02483</td>
<td>47.95</td>
</tr>
<tr>
<td>11</td>
<td>0.000008</td>
<td>-0.03431</td>
<td>48.02</td>
</tr>
<tr>
<td>12</td>
<td>0.000007</td>
<td>-0.01919</td>
<td>46.27</td>
</tr>
<tr>
<td>Average</td>
<td>0.000009</td>
<td>-0.03654</td>
<td>50.73</td>
</tr>
<tr>
<td>St. Dev</td>
<td>1.65E-05</td>
<td>0.01143</td>
<td>2.58</td>
</tr>
</tbody>
</table>

Using the averages as the coefficients, the explicit form of thickness as a function of temperature, \( L(T) \), is as follows;

\[
L(T) = 0.00009T^2 - 0.03654T + 50.73 \quad (2)
\]

Differentiating \( L(T) \) yields the following:

\[
\frac{dL}{dT} = 0.00018T - 0.03654 \quad (3)
\]
Finally substituting the above value into Equation 1 yields the following, where \( L_0 \) is in micrometers, and \( T \) is Kelvin.

\[
\alpha = \frac{1}{L_0} (0.00018T - 0.03654) \quad (4)
\]

Next \( \alpha \) can be substituted into Equation (1) to predict the thickness change over any temperature interval in the range of 105° to -40° C.

\[
\alpha * dT = \frac{1}{L_0} dL
\]

\[
\frac{1}{L_0} (0.00018T - 0.03654) dT = \frac{1}{L_0} dL
\]

\[
\int_{T_t}^{T_f} (0.00018T - 0.03654) dT = \int_{T_i}^{T_f} dL
\]

\[
L_F = L_0 + \int_{T_t}^{T_f} (0.00018T - 0.03654) dT \quad (5)
\]

Equation (5) shows how Membrane 112 expands over any temperature interval. However to verify the usefulness of this derivation we need to compare this computed value over the same temperature interval as the experiments, which is 105° C to -40° C. Note that when inserting temperatures to Equation (5) they must be in Kelvin; this was intentional as to avoid negative temperatures for simplicity. Also all lengths are in micrometers. Therefore when substituting the appropriate values, Equation (5) reduces to:
Finally, Equation (6) explicitly states how much Membrane 112 will expand when being cooled from 105 C to -40 C. Table 4 below shows how this result compares to the observed values, as well as the percent elongation for each specimen.

Table 4: Complete Data for Membrane 112

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Thickness Change (μm) from 105°C to -40°C</th>
<th>Predicted Thickness Change (μm) from 105°C to -40°C</th>
<th>Relative Error (%)</th>
<th>Initial Thickness (μm)</th>
<th>Percent Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.448</td>
<td>-2.69</td>
<td>-9.87</td>
<td>49.400</td>
<td>-4.96</td>
</tr>
<tr>
<td>2</td>
<td>-2.436</td>
<td>-2.69</td>
<td>-10.41</td>
<td>49.090</td>
<td>-4.00</td>
</tr>
<tr>
<td>3</td>
<td>-2.362</td>
<td>-2.69</td>
<td>-13.91</td>
<td>50.141</td>
<td>-4.71</td>
</tr>
<tr>
<td>4</td>
<td>-2.361</td>
<td>-2.69</td>
<td>-14.42</td>
<td>48.235</td>
<td>-4.87</td>
</tr>
<tr>
<td>5</td>
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<td>-2.69</td>
<td>-6.37</td>
<td>50.389</td>
<td>-5.02</td>
</tr>
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<td>6</td>
<td>-2.629</td>
<td>-2.69</td>
<td>-2.32</td>
<td>49.686</td>
<td>-5.29</td>
</tr>
<tr>
<td>7</td>
<td>-2.685</td>
<td>-2.69</td>
<td>-0.20</td>
<td>49.936</td>
<td>-5.38</td>
</tr>
<tr>
<td>8</td>
<td>-2.854</td>
<td>-2.69</td>
<td>-5.73</td>
<td>52.801</td>
<td>-5.40</td>
</tr>
<tr>
<td>9</td>
<td>-2.456</td>
<td>-2.69</td>
<td>-8.10</td>
<td>50.933</td>
<td>-4.00</td>
</tr>
<tr>
<td>10</td>
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<td>-2.69</td>
<td>-5.81</td>
<td>48.526</td>
<td>-5.24</td>
</tr>
<tr>
<td>11</td>
<td>-2.377</td>
<td>-2.69</td>
<td>-13.18</td>
<td>46.988</td>
<td>-5.06</td>
</tr>
<tr>
<td>12</td>
<td>-3.020</td>
<td>-2.69</td>
<td>10.91</td>
<td>48.369</td>
<td>-6.24</td>
</tr>
<tr>
<td>Average</td>
<td>-2.960</td>
<td></td>
<td></td>
<td></td>
<td>-5.16</td>
</tr>
<tr>
<td>St. Dev</td>
<td>0.206</td>
<td></td>
<td></td>
<td></td>
<td>0.41</td>
</tr>
</tbody>
</table>

There are two important things to note from Table 4:

1) The “Predicted Thickness Change” lies within one standard deviation from the average of the observed thickness changes. Thus, the prediction is a reliable model.

2) The average Percent Elongation is 5.16%. It is clear to see that this is much greater than the selected materials in Table 1.
4.1.2: Membrane 112 Swelling Results

After isolating the thermal expansion effects on Membrane 112, the next step was to determine how the thickness changes with varying humidities. As the relative humidity increases, the number of moles of water vapor in the air increases and the membrane will absorb the water vapor in relation to the humidity.

4.1.2.1: Temperature = 25° C

For a constant temperature of 25° C, eight sets of data were recorded which measured the thickness change due to water vapor absorption for Membrane 112. The method of experimentation was to initially set the chamber to 30% relative humidity and have the membrane rest for an hour. The humidity would then be increased in 20% intervals until 90% was reached, while allowing the membrane to sit at each interval for one hour to ensure that the membrane was in equilibrium with the additional water vapor. Figure 13 shows one set of data; all eight sets can be seen in Appendix B along with a summary.
It is clear from Figure 13 that the swelling due to water vapor is much greater than thermal expansion. Unlike the results for thermal expansion, the swelling results do not contain as much consistency. This can first be observed by measuring the total percent elongation, which is defined as the elongation as the specimen is humidified from 30% to 90%; see Table 5.
Table 5: Total Elongation of Membrane 112

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Percent Elongation (from 30% to 90%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.453</td>
</tr>
<tr>
<td>2</td>
<td>14.549</td>
</tr>
<tr>
<td>3</td>
<td>14.931</td>
</tr>
<tr>
<td>4</td>
<td>5.833</td>
</tr>
<tr>
<td>5</td>
<td>6.408</td>
</tr>
<tr>
<td>6</td>
<td>19.711</td>
</tr>
<tr>
<td>7</td>
<td>7.479</td>
</tr>
<tr>
<td>8</td>
<td>8.719</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>10.635</strong></td>
</tr>
<tr>
<td><strong>St. Deviation</strong></td>
<td><strong>5.083</strong></td>
</tr>
</tbody>
</table>

The results indicate that while the swelling due to water vapor absorption is much larger than thermal expansion (an average of 10.635% versus 5.16%), there is also a much higher variability (a deviation that is approximately 50% of the average as compared to one that is approximately 8% of the average).
4.2: Membrane A Results

After nine successful experiments, reliable data has been obtained regarding Membrane A’s thermal expansion. Figure 1 below shows thermal strain, $\Delta L/L_0$, versus temperature. Recall that $L_0$ is defined as the thickness after heating the specimen for one hour.

![Membrane A: Thermal Strain vs. Temperature](image)

**Figure 14: Membrane A Thermal Strain vs. Temperature**

From Figure 13 it is clear that there is an average trend to the thermal strain as the specimen cools. However Specimen #3 varies from this average trend; this is easily seen below in Table 6:
Table 6: Membrane A Thickness Change and Percent Elongation

<table>
<thead>
<tr>
<th>Specimen #</th>
<th>Change in Thickness</th>
<th>Strain</th>
<th>Percent Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.813</td>
<td>-0.041</td>
<td>-4.085</td>
</tr>
<tr>
<td>2</td>
<td>-0.824</td>
<td>-0.041</td>
<td>-4.122</td>
</tr>
<tr>
<td>3</td>
<td>-0.546</td>
<td>-0.028</td>
<td>-2.756</td>
</tr>
<tr>
<td>4</td>
<td>-0.714</td>
<td>-0.035</td>
<td>-3.498</td>
</tr>
<tr>
<td>5</td>
<td>-0.803</td>
<td>-0.040</td>
<td>-4.035</td>
</tr>
<tr>
<td>6</td>
<td>-0.651</td>
<td>-0.043</td>
<td>-4.340</td>
</tr>
<tr>
<td>7</td>
<td>-0.869</td>
<td>-0.040</td>
<td>-3.995</td>
</tr>
<tr>
<td>8</td>
<td>-0.772</td>
<td>-0.042</td>
<td>-4.161</td>
</tr>
<tr>
<td>9</td>
<td>-0.795</td>
<td>-0.042</td>
<td>-4.226</td>
</tr>
<tr>
<td>Avg</td>
<td>-0.754</td>
<td>-0.039</td>
<td>-3.913</td>
</tr>
<tr>
<td>St. Dev</td>
<td>0.101</td>
<td>0.005</td>
<td>0.494</td>
</tr>
</tbody>
</table>

All specimens except Specimen #3 fall within one standard deviation of the mean; Specimen #3 is beyond two standard deviations. Even though the thermal strains are similar, the changes in thickness have a greater deviation. Figure 15 below shows the thickness versus temperature for each specimen. Since there is a relatively high amount of variation from each experiment, it is difficult to create an accurate estimate of Membrane A’s coefficient of thermal expansion.

Figure 15: Membrane A Thickness vs. Temperature
Chapter 5

CONCLUSION AND DISCUSSION

As a result of experimentation the thermal and water vapor absorption effects on Membrane 112 and Membrane A are well understood. Figure 16 below shows these results in terms of percent elongation. Note that all elongations are positive for equal comparison.

![Experiment Results: Percent Elongation](image)

Figure 16: Experiment Results in Percent Elongation

It is clear from these experiments that the water vapor absorption has a much greater effect on the out-of-plane expansion than thermal effects have. There is also a much greater
amount of variability in the water vapor absorption effects. While future experimentation is required to understand the water vapor absorption effects on Membrane A, it is safe to hypothesize that it will be a much greater effect than thermal expansion. Also further experimentation will be required to understand if the water vapor absorption effects are dependent on temperature, i.e. if a higher or lower temperature will allow for more or less water vapor absorption.
REFERENCES


APPENDIX A: MEMBRANE 112 POLYNOMIAL CURVE FITS

Polynomial Curve Fit Equations

\[ y = 0.00010x^2 - 0.04254x + 51.55217 \]
\[ y = 0.00011x^2 - 0.04476x + 52.99526 \]
\[ y = 0.00010x^2 - 0.04664x + 52.89951 \]
\[ y = 0.00010x^2 - 0.04324x + 51.55700 \]
\[ y = 0.00012x^2 - 0.06930x + 54.95234 \]
\[ y = 0.00003x^2 - 0.02893x + 48.54069 \]
\[ y = 0.00007x^2 - 0.02631x + 49.15733 \]
\[ y = 0.00009x^2 - 0.03365x + 52.78169 \]
\[ y = 0.00009x^2 - 0.03753x + 52.42847 \]
\[ y = 0.00007x^2 - 0.02495x + 48.36890 \]
\[ y = 0.00005x^2 - 0.02431x + 48.01179 \]
\[ y = 0.00007x^2 - 0.04191x + 46.26539 \]
### APPENDIX B: MEMBRANE 112 HUMIDITY DATA AND PLOTS

<table>
<thead>
<tr>
<th>Nafion 112 #1</th>
<th>Displacement</th>
<th>Swelling Strain</th>
<th>Nafion 112 #2</th>
<th>Displacement</th>
<th>Swelling Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.270</td>
<td>0.650</td>
<td>0.012</td>
<td>55.880</td>
<td>1.430</td>
<td>0.026</td>
</tr>
<tr>
<td>53.920</td>
<td>0.350</td>
<td>0.006</td>
<td>57.310</td>
<td>1.910</td>
<td>0.033</td>
</tr>
<tr>
<td>54.270</td>
<td>2.970</td>
<td>0.055</td>
<td>59.220</td>
<td>4.790</td>
<td>0.081</td>
</tr>
<tr>
<td>57.240</td>
<td></td>
<td>64.010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total Displacement</strong></td>
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<td></td>
<td><strong>Total Displacement</strong></td>
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</tr>
<tr>
<td><strong>Percent Elongation</strong></td>
<td><strong>7.453</strong></td>
<td></td>
<td><strong>Percent Elongation</strong></td>
<td><strong>14.549</strong></td>
<td></td>
</tr>
<tr>
<td>Nafion 112 #3</td>
<td>Displacement</td>
<td>Swelling Strain</td>
<td>Nafion 112 #4</td>
<td>Displacement</td>
<td>Swelling Strain</td>
</tr>
<tr>
<td>55.590</td>
<td>2.300</td>
<td>0.041</td>
<td>56.750</td>
<td>0.860</td>
<td>0.015</td>
</tr>
<tr>
<td>57.890</td>
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<td>0.048</td>
<td>57.610</td>
<td>0.680</td>
<td>0.012</td>
</tr>
<tr>
<td>60.675</td>
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<td>0.053</td>
<td>58.290</td>
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<td><strong>Total Displacement</strong></td>
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<td></td>
<td><strong>Total Displacement</strong></td>
<td><strong>3.310</strong></td>
<td></td>
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<tr>
<td><strong>Percent Elongation</strong></td>
<td><strong>14.931</strong></td>
<td></td>
<td><strong>Percent Elongation</strong></td>
<td><strong>5.833</strong></td>
<td></td>
</tr>
<tr>
<td>Nafion 112 #5</td>
<td>Displacement</td>
<td>Swelling Strain</td>
<td>Nafion 112 #6</td>
<td>Displacement</td>
<td>Swelling Strain</td>
</tr>
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<td>55.710</td>
<td>0.750</td>
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<td>55.350</td>
<td>2.560</td>
<td>0.046</td>
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<td>56.460</td>
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<td>62.170</td>
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<td>0.066</td>
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<tr>
<td>59.280</td>
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<td>66.260</td>
<td></td>
<td></td>
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<tr>
<td><strong>Total Displacement</strong></td>
<td><strong>3.570</strong></td>
<td></td>
<td><strong>Total Displacement</strong></td>
<td><strong>10.910</strong></td>
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<tr>
<td><strong>Percent Elongation</strong></td>
<td><strong>6.408</strong></td>
<td></td>
<td><strong>Percent Elongation</strong></td>
<td><strong>19.711</strong></td>
<td></td>
</tr>
<tr>
<td>Nafion 112 #7</td>
<td>Displacement</td>
<td>Swelling Strain</td>
<td>Nafion 112 #8</td>
<td>Displacement</td>
<td>Swelling Strain</td>
</tr>
<tr>
<td>54.690</td>
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<td>1.300</td>
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<td>55.920</td>
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<td><strong>Percent Elongation</strong></td>
<td><strong>8.719</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Total Displacement:**
- **Average:** 5.834
- **Standard Deviation:** 2.858

**Percent Elongation:**
- **Average:** 10.635
- **Standard Deviation:** 5.083
Nafion 112 #1

Nafion 112: 25°C Humidity Test # 2