THE EFFECT OF FREEZE-THAW CYCLES ON THE MECHANICAL PRPOPERTIES OF PROTON EXCHANGE MEMBRANES

by

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ABSTRACT

Fuel cells could potentially provide a clean source of power for automotive uses. However, their durability needs to be increased in order to become commercially viable. A key component of increasing the durability of Proton Exchange Membrane Fuel Cells (PEMFCs) is characterizing the behavior of the proton exchange membrane at the heart of the fuel cell. This research investigates how the mechanical properties of these membranes are influenced by repeated freezing and thawing in conditions approximating those inside a fuel cell.

A stack consisting of Nafion® 211 membrane held between Toray Carbon paper and bipolar plates was alternatingly placed in -20°C and room temperature conditions. After 50, 75, 100 freeze-thaw cycles the membranes were removed from the simulated stack set-up and a tensile test was performed on them. Membranes were tested in conditions of 25°C, 30% relative humidity and 80°C, 90% relative humidity. After testing the membranes the properties such as Young's modulus, proportional limit stress, break strain, and swelling strain were analyzed and compared with results from previous work on membranes that had not undergone freeze thaw cycles.

The results showed little change in the mechanical properties at conditions of 25°C and 30% RH. There appeared to be some effect on break strain, however, coming to any conclusions is difficult due to a large scatter and low sample size. Results for tests at 80°C and 90% RH show a slight decrease in stiffness, but the low magnitude of the change and no discernible trend with the number of freeze thaw cycles suggest this is more likely due to experimental scatter than the freezing treatment. Swelling results similarly show little impact of freeze thaw cycling. A small decrease in swelling due to changes in temperatures is noted, but swelling with changes in humidity seemed unaffected.

Chapter 1

INTRODUCTION

1.1 Proton Exchange Membrane Fuel Cells

As oil and gas prices rise the demand for alternative energy sources is increasing and fuel cells are a promising technology in this field. In general fuel cells take advantage of chemical reactions to produce an electric current. Proton Exchange Membrane Fuel Cells (PEMFCs) are a type of fuel cell that use a polymer as the electrolyte and hydrogen as the fuel. PEMFCs are of particular interest for use in fuel cell powered vehicles since they could provide a clean alternative to the gasoline-powered engines in use today. For automotive uses, PEMFCs stand out as particularly promising, due to their relatively low operating temperatures, quick start up, and high energy density [1].

PEMFCs produce electricity by combining hydrogen and oxygen to create water. Inside the fuel cell the hydrogen and oxygen are separated by a Membrane Electrode Assembly (MEA), consisting of the Proton Exchange Membrane (PEM) coated with porous electrodes containing a catalyst. On the anode side, the catalyst facilitates the splitting of the hydrogen atoms into electrons and protons. The PEM conducts the protons across the membrane while remaining impermeable to the electrons. On the cathode side, the protons combine with oxygen and electrons, from the external circuit creating an electric current, highlighted in Figure 1.

The chemical reactions that take place inside the fuel cell can be summarized:

Anode Reaction: $2H_2 \rightarrow 4H^+ + 4e^-$

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

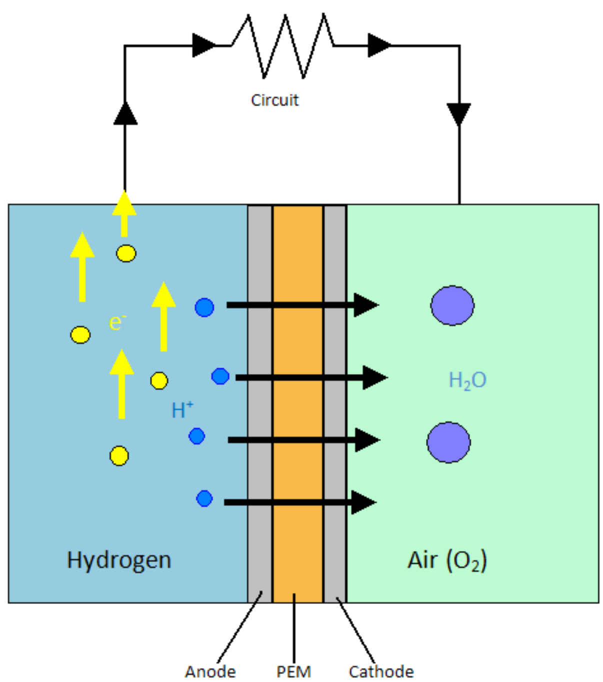


Figure 1: Schematic of PEMFC reaction

One obstacle facing the widespread adoption of fuel cells is their durability [2]. For fuel cells to become commercially viable it is necessary to improve the operating lifetime of PEMFCs; the Department of Energy has set a goal of a 5000 hour operating life by 2015[3]. The PEM plays a key role in determining the lifetime of a fuel cell since membrane failure is a major cause of cell failure [4, 5]. Apart from acting as a proton conductor the membrane also serves to separate the hydrogen and oxygen [6]. These two roles make the integrity of the PEM essential for the operation of the fuel cell. Any cracks or holes in the membrane allow the hydrogen to pass through without creating the desired electricity. As a fuel cell is used the membrane gradually degrades as these kinds of defects develop, causing the efficiency of the cell to drops, and eventually causing complete failure of the fuel cell. This degradation is caused by both mechanical stresses and chemical effects [6].

The mechanical stresses are caused by the membranes' response to changes in temperature and humidity during the operation of the fuel cell. Chemically, the membranes investigated in this work are a Perflourosulphonic Acid (PFSA) membrane. They consist of a Polytetrafluoroethylene (also known as PTFE or Teflon®) polymer backbone with side chains, containing sulfonic acid. The resulting membranes have hydrophilic regions, meaning they absorb water, suspended throughout the hydrophobic (water-repelling) polymer backbone structure. In fact, the membranes must be hydrated to function effectively. Even when not in use, the membranes absorb water from the air causing swelling and a decrease in the stiffness of the membrane as the relative humidity increases [1]. As with almost any material the membranes also expand with temperature. The byproducts of the chemical reaction in the fuel cell are heat and water which lead to significant swelling in the membranes. However, the membranes are constrained by the surrounding materials inside the fuel cell causing compressive stresses to develop as the membrane tries to expand [7]. If the stresses are high enough, plastic deformation can occur and tensile residual stresses can develop as the membranes contract when they cool or become dehydrated. The stresses that develop as the membranes swell and contract cause fatigue loading, which over time can cause mechanical degradation in the membrane.

To improve the operating life of PEMFCs it is necessary to understand the hygro-thermal-mechanical response of the membrane. Characterizing of the mechanical behavior of the PEMs used in fuel cells allows for accurate models of fuel cells to be produced which, in turn enables longer lasting fuels to be designed [5]. For most materials the mechanical properties can be measured under ambient conditions. However, the unique chemical composition of PEMs causes the properties of the membrane to change, depending on the environmental conditions (temperature and relative humidity) to which they are exposed.

This research is focused on characterizing the mechanical behavior of these membranes, specifically Nafion® 211 membrane[1], following exposure to multiple freeze-thaw cycles. Nafion® membrane was chosen because it is a standard membrane used in industry. Knowing how repeated freezing and thawing affects the properties

[1]Nafion® is a registered trademark of E.I. Dupont

of membrane is important if the PEMFCs are going to be used in an automobile where the membranes will be exposed to a wide range of temperatures.

Previous work investigating the mechanical properties and the mechanisms behind them, of these membranes has been conducted. Tang et al. [1] have studied the mechanical properties, such as Young's modulus and the proportional limit stress (PLS), of the membranes across a wide spectrum of temperatures and humidity in order to characterize the behavior of the membranes. It has been observed that membranes generally become stiffer and more brittle at lower temperatures and humidity. The temperature has a large effect on the stiffness and strength of the membranes while the humidity largely determines the swelling [1]. McDonald et al. [8] have conducted research on the effect of freeze thaw cycles on both the mechanical properties and chemical properties of the membranes. After cycling membranes between -40°C and 80°C, 385 times, they observed a dramatic decrease in percent elongation to failure and changes in water swelling behavior. The effect on Young's Modulus and yield strength were investigated but not reported due to a large uncertainty in the data. It has also been suggested that the freezing and thawing of the membranes could cause rearrangement on a molecular level that would explain changes in break strain, ultimate strength and swelling after the membranes have undergone freeze thaw cycling [8]. In a similar vein, this research investigates the changes in the mechanical properties of the membranes after undergoing freeze thaw cycling by conducting a tensile test on the membranes. Membranes were constrained in a manner approximating *in-situ* conditions during the cycling. The testing investigated properties of the Young's Modulus, proportional limit stress, and break strain.

Chapter 2

HYPOTHESIS AND GOALS

If fuel cells are to become widespread for use in the automotive industry their durability must be increased. By better characterizing the mechanical behavior of the polymer electrolyte membranes, fuel cells can be designed to account for the changes the membranes undergo as their environment changes. In turn this should help in the design longer lasting fuel cells [5].

A fuel cell that is used in a car will be exposed to a wide range of environments, and these changes in environment will cause the membrane in the fuel cell to swell and contract. Because the membrane is constrained, differences in expansion between the membrane and its surroundings will lead to stresses developing in the membrane. Due to the nature of the membranes expansion can be caused by changes in temperature or humidity, while for most of the other components in the fuel cell thermal expansion is the only concern.

The membranes are constrained between two bipolar plates and a gas diffusion layer (Figure 2). The bipolar plates are typically graphite and the GDL is typically a form of carbon paper. The bipolar plates are grooved to allow the gasses to be distributed across the area of the membrane.

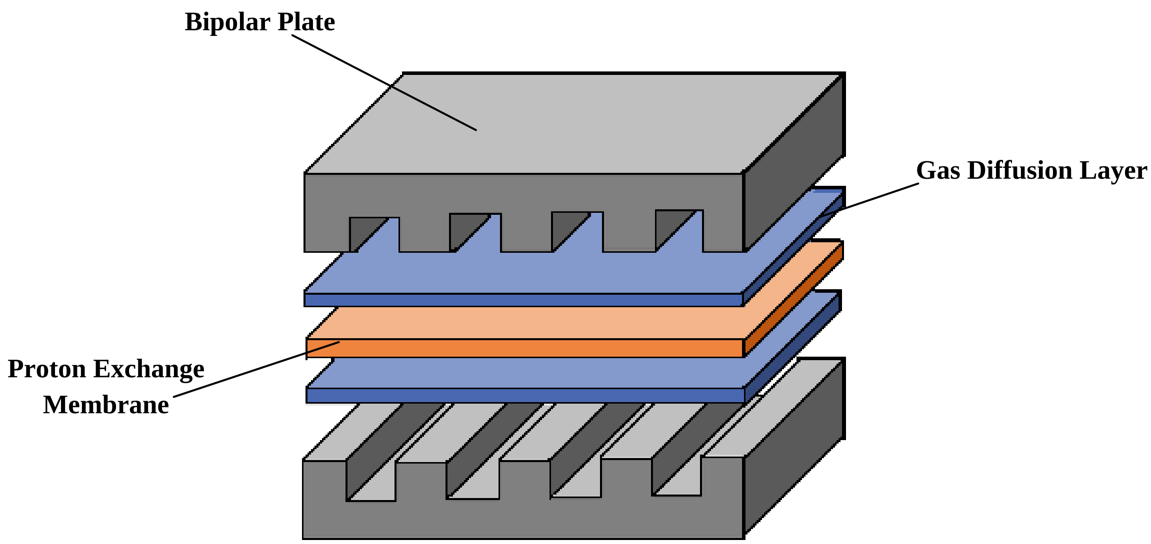


Figure 2: Schematic of Stack Set-Up

This geometry means the stresses caused by differences in expansion will not be uniform over the membrane, leading to gradients in stress and with them, the potential for more damage to the membrane. Although the exact geometry of the bipolar plates is variable depending on the design of the fuel cell, the current experiments use a geometry where the grooves in the fuel cell are in line with each other (as opposed to crisscrossed).

We expect to see some degradation as the number of freeze-thaw cycles increased. This could be observed as a decreased Young's Modulus, yield strength or break strain. We also expect these changes to be more visible when testing at lower temperature and humidity (25°C 30% RH) because the membranes behave in a more brittle manner than at high temperature and humidity (80°C 90% RH). (Figure 3)

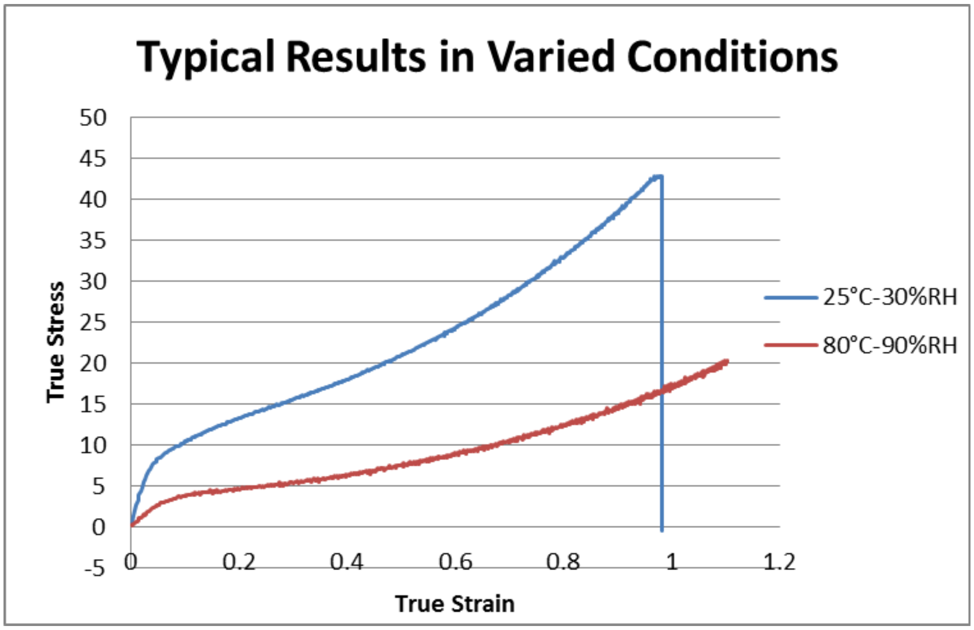


Figure 3: Typical stress-strain results at two environmental conditions

This change in mechanical response motivates the decision to test the membranes in two sets of environmental conditions. It's possible that the effect of the freeze thaw cycles is more pronounced at one set of conditions and not the other. By testing in both 25°C-30% relative humidity and 80°C-90% humidity, any impact of changing conditions should be visible.

By exposing the membranes to alternately freezing and room temperature conditions we can simulate the conditions that the membrane would be exposed to in a vehicle, over the course of a winter. The membranes can then be tested to investigate if there are any changes in the mechanical properties caused by damage due to the exposure to freeze thaw cycling.

An important part of this work was coming up with a method to test how these freeze-thaw cycles affected the mechanical properties of the Nafion® 211 membrane. The approach that was decided on was to develop a system to simulate the constrained conditions as in Figure 2. The membrane will be sandwiched between the GDL and the bipolar plate while it undergoes freeze-thaw cycling. Although it would be more accurate to use the MEA for these tests the membrane is used because its behavior is better understood, and any changes in the mechanical properties can be more easily determined.

Chapter 3

METHODS AND MATERIALS

Equipment List

- EdgeStar® 1.5 Cu. Ft. Medical Freezer
- Espec Environmental Chamber (custom designed)
- MTS Alliance^{TM} RT/5 material testing system
- 4 Poco Graphite Blocks (Bipolar plates)
- Toray Carbon Paper TGP-H-060

3.1 Experimental Set-Up

The goal of this research is to investigate the effects of repeated freezing and thawing on the mechanical properties of PEMs. In order to test these effects, samples of Nafion® 211 membrane will be alternately subjected to freezing conditions and room temperature conditions. After 50, 75 and 100 of these freeze thaw cycles a tensile test will be performed on the samples to determine important properties such as Young's Modulus and proportional limit stress of the membrane.

The central goal is to determine how freezing and thawing effects membranes in an actual fuel cell. To do this it was necessary to simulate the mechanical constraint conditions that would be present in a fuel cell assembly while the freezing and thawing cycles were performed. An assembly was designed to constrain the membranes similar to the way they are when part of a fuel cell.

This assembly consisted primarily of two graphite bipolar plates machined with one millimeter wide channels to simulate the grooves in an actual fuel cell for the gasses to be distributed across the membrane. There is a 50mm by 50mm area on the bipolar plates covered with the channels. It is largely the mechanical effect that these channels have on the membrane during freezing and thawing that we are interested in studying.

Figure 4: Bipolar Plate

Two 50mm by 50mm sheets of Toray Carbon paper were placed over the channels to simulate the gas diffusion layer and 120mm by 50mm sheets of the membrane were then sandwiched between the plates and carbon paper (Replicating Figure 2). The length of 120mm was used to provide area for the membrane to be gripped during testing of the 50mm area between the pieces of carbon paper. The membrane was marked to ensure that the correct area was tested after the freeze thaw cycles were completed.

The entire stack was held together using a wooden clamping assembly. This was designed to prevent the bipolar plates from moving and to apply a consistent force holding the stack together. All contact to the membranes, occurred along the grooved area of the bipolar plates. The entire assembly was alternately frozen and thawed for the desired number of cycles using an EdgeStar® lab freezer for freezing and laboratory ambient conditions for thawing.

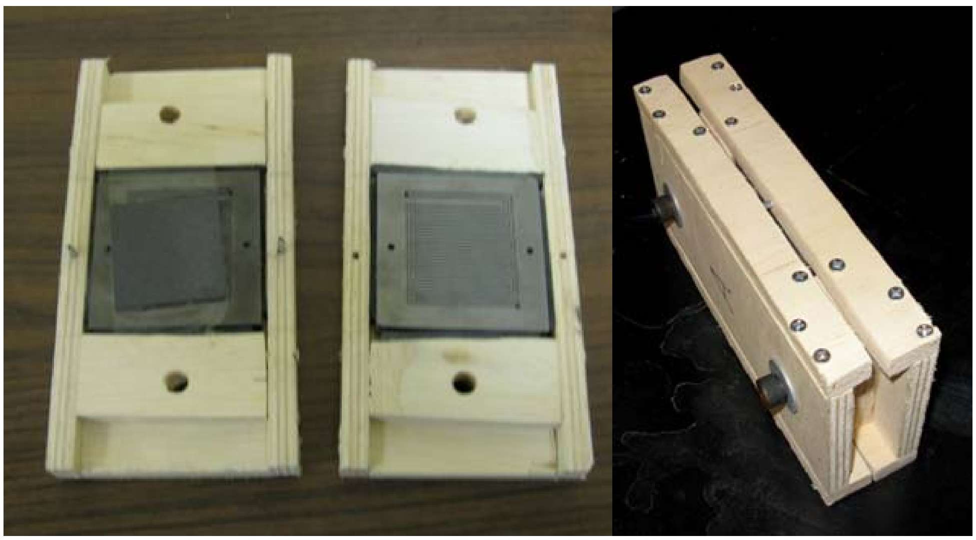


Figure 5: Clamping set-up, open and closed

For the purposes of this work a freeze-thaw cycle consisted of storing the clamping set-up in a lab freezer for at least three hours and then storing in the ambient conditions for at least three hours. Preliminary testing revealed that it took the clamping set-up about two hours to return to room temperature after being stored at -20°C overnight. The three hours cycle time was chosen to ensure that the membrane would be completely thawed or frozen before the conditions were changed.

3.2 Testing Procedure

The testing was conducted using a MTS Alliance RT/5 material testing system, specially fitted with an Espec environmental control chamber. This set-up allows the tensile testing to be performed in an environment where the temperature and relative humidity can be controlled.

Figure 6: Environmental Chamber Fitted with Materials Testing System

After the samples had been subjected to the desired number of freeze-thaw cycles testing was performed. The piece of membrane in the clamp was a 50mm by 120mm sheet, which was cut into 5 samples each 10mm by 120mm for testing. The width and thickness of the samples was measured before they were placed in the fixtures inside the environmental chamber (Figure 7).

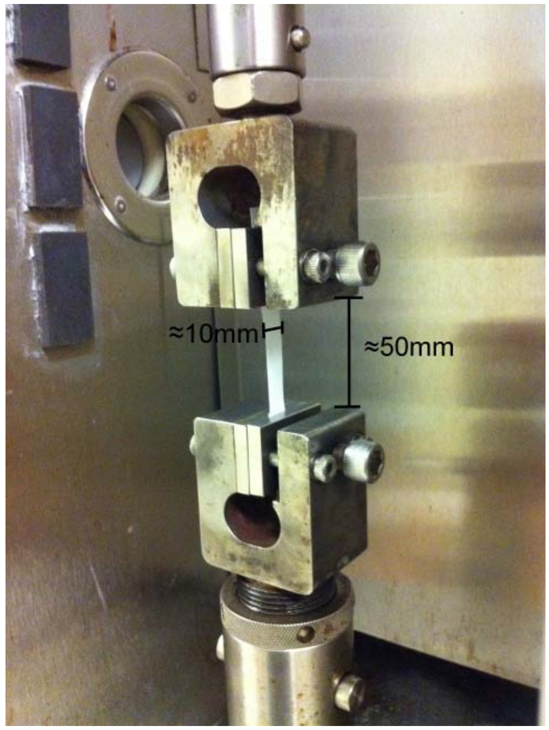


Figure 7: Grips used for testing
(Note: A piece of paper represents the membrane for visibility)

The initial gage length was then measured and the chamber set to 25°C and 30% relative humidity. These conditions were used to establish the length of the membrane in a known environment. If the membrane was to be tested at 25°C 30% it was tested once equilibrium was reached. For tests at 80°C and 90% humidity, the conditions in the environmental chamber were gradually increased. First the temperature was increased to 45°C, 60°C, and 80°C. Then the humidity was increased to 50%, 70%, and 90%. Before each change in conditions, the length of the membrane was measured. This allowed data on the swelling behavior to be collected. Once the desired conditions were reached, and the environment stabilized, the membrane was tested at a rate of 10mm/min until failure.

3.3 Analysis

The tensile test provides data in the form force versus displacement, which is easily converted into stress-strain data using the measured width, thickness, and gage length. The stress-strain data can then be analyzed to reveal important information about the mechanical properties of the membrane. The properties of interest in this research were Young's Modulus, proportional limit, break strain and swelling behavior, and in particular, changes in these properties due to the freeze thaw cycling

Stress-Strain: a Note on Area

The average stress in an object loaded in uniaxial tension is calculated as the total force over the cross sectional area. In the case of these experiments, the cross-sectional area is simply the width of the membrane sample multiplied by the thickness. These values are measured at the beginning of the experiment, before the membrane is inserted into the environmental chamber. Once the chamber reaches the desired environmental conditions there is no way to measure the thickness or the width with the present equipment. This makes it impossible to know the true width of the membrane at the time of testing. However, the length can be measured by adjusting the crosshead of the MTS. Assuming the membrane's swelling behavior is isotropic (this assumption is currently being researched), we can use the measured change in length to predict the change in the thickness and width, thereby obtaining a more accurate value of the cross sectional area and the stress.

Young's Modulus

Young's Modulus is a material property that characterizes the stiffness of a material. The modulus is calculated by finding the slope of the stress-strain curve in the elastic region, the initial linear region.

Proportional Limit Stress

The proportional limit stress is a measure of when the material exhibits nonlinear stress strain behavior or when it yields. Here it defined as the intersection of the extension of the linear elastic region and the extension of the strain hardening response (See Figure 8).

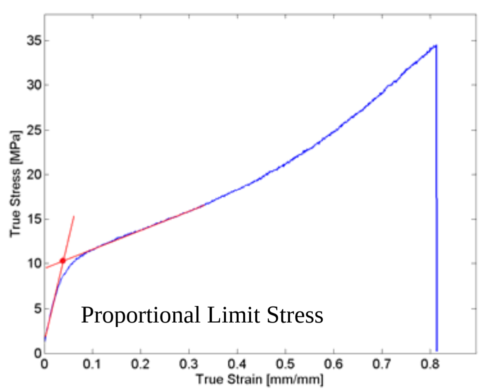


Figure 8: Definition of Proportional Limit Stress

Break-Strain

Break-strain is defined simply as the strain at which the material fails to carry load. Results for break strain of the membrane materials have proven difficult to interpret for two reasons. The first reason is that there is a large scatter in the results. In past testing of the membranes, break strains have varied largely and inconsistently among samples tested under the same conditions. The other is the limited stroke length of the testing system. At high temperatures and humidity the crosshead will often reach its upper limit before the membrane fails. Despite these challenges it is worth looking at break strain to see if any notable pattern emerges.

Swelling Strain

The swelling strain is the amount the membrane swells at the set temperature and humidity before being tested. For these tests, the membranes initial length is taken as its length at 25°C and 30% relative humidity.

Chapter 4

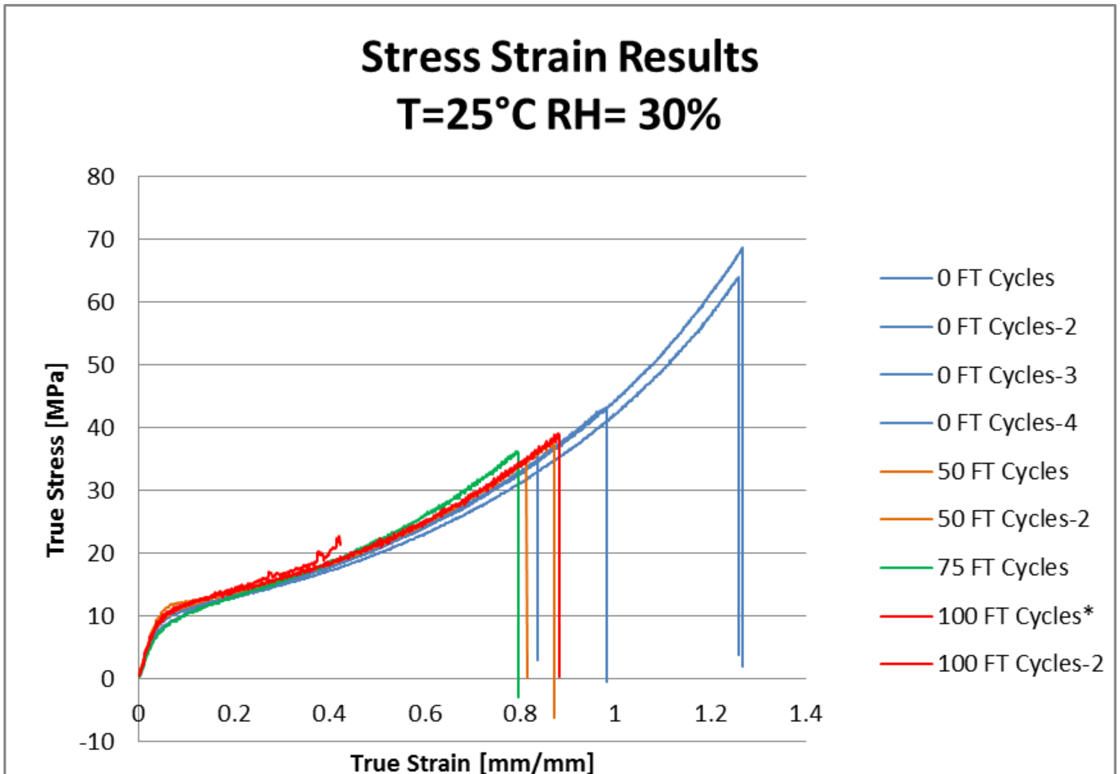
RESULTS

4.1 Notation

After 50, 75, and 100 freeze-thaw (FT) cycles the Nafion® membrane samples were tested in conditions of 25C-30% relative humidity and 80C-90% relative humidity. The tests have been grouped by the conditions and labeled based on the number of freeze thaw cycles the sample was subjected to. The notation "X-FT Cycles-#" is used to specify the sample. Here X represents the number of freeze thaw cycles the sample was exposed to and # is the test number for those conditions. For example 50-FT Cycles-2 refers to a sample that went through 50 freeze-thaw cycles and was the second such sample tested in the given conditions.

4.2 Results for 25°C 30% Relative Humidity

After undergoing freeze thaw cycles, the membranes were tested at conditions of 25°C and 30% relative humidity. The results are shown in Figure 9:



*Due to an error in the load cell data for this test is inaccurate after 0.4 mm/mm and not shown

Figure 9: Tensile Test Results at 25°C and 30%RH

Figure 9 shows stress strain test results performed after freeze thaw cycles compared with results obtained with no freezing and thawing. Simply by looking at the curves it can be seen that there is little difference between the specimens that underwent freeze thaw cycling and those that did not. These similarities show up after a closer analysis as well. Looking at the modulus, PLS, and break strain shows that the effect of freezing and thawing up to 100 cycles is minimal. (summarized in Table 1)

Table 1: 25°C 30%RH Average results

FT Cycles	Modulus [MPa]	PLS [MPa]	Break Strain [mm/mm]
0	219.86	8.125	1.0865
50	224.65	9.05	0.8435
75	194.4	6.9	0.796
100	212.625	8.727	0.884
Standard deviation (0 FT cycles)	14.8	0.68	0.21

For the specimens that underwent no freeze thaw cycling, the average modulus was 219.9 MPa with a standard deviation of 14.8MPa. After 50 freeze thaw cycles, the average modulus was 224.65MPa, this falls within one standard deviation of the specimens with no freeze thaw cycles suggesting that the difference is likely due to experimental scatter rather than any effect of the cycling. The average value of the modulus for 100 cycles is 212.6MPa, this also falls within one standard deviation of the value for the membranes with no freezing or thawing. For 75 cycles the modulus is still within two standard deviations of the unfrozen membranes. The break strains of the specimens that were subjected to freeze thaw cycling seem considerably lower than the 0 cycle specimens. However, due the large scatter all the values fall within two standard deviations of the break strain for membranes with no freezing.

4.3 Results for 80°C 90%RH

The Nafion® membrane being investigated has a dramatically different mechanical response depending on the environmental conditions (Figure 3). Because of these changes in response the membranes were tested at conditions of 80°C and 90% humidity as well as 25°C and 30% relative humidity. Figure 10 shows the results from test at 80°C and 90% relative humidity

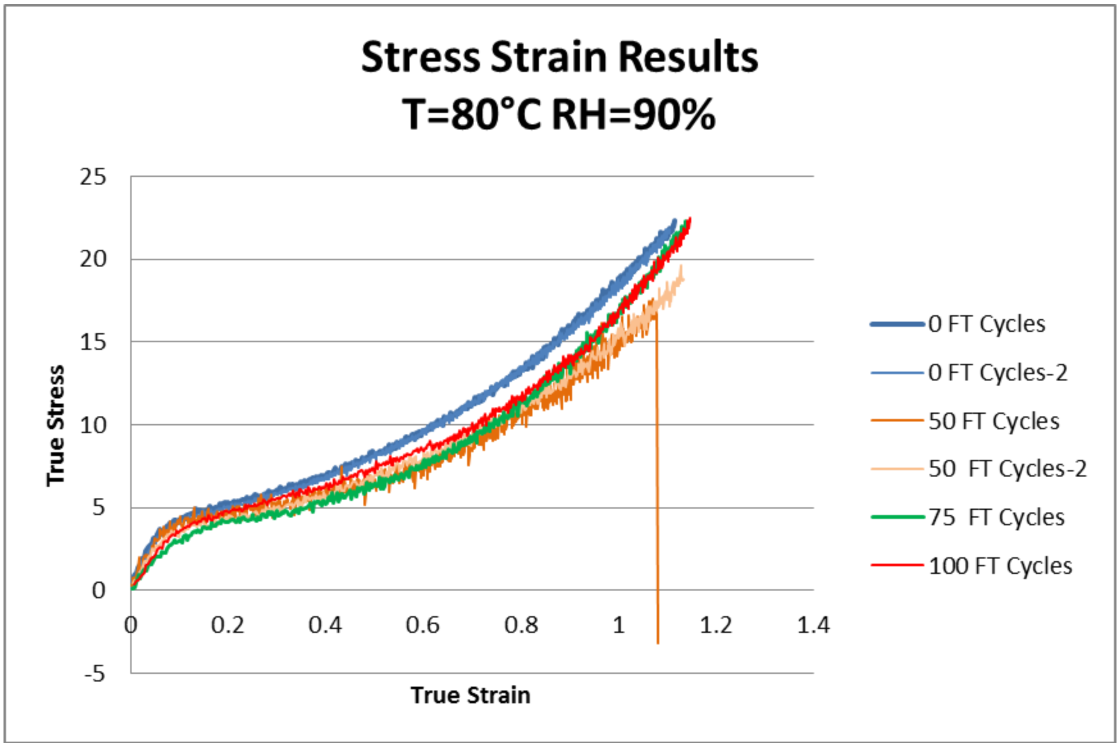


Figure 10: Tensile Test Results at 80°C and 90%RH

The results of the membranes at 80°C and 90% (Figure 10) relative humidity are generally consistent with the results from 25°C and 30% relative humidity. The membranes that had been frozen appear to be slightly less stiff than membranes that were not cycled, however the difference is slight and there is no trend with increasing the number of cycles. The sample with the lowest stiffness had been through 75 freeze-thaw cycles, and the sample after 100 cycles had a stiffer response. This lack of any trend as the cycles increase suggests that the slight difference were due to experimental scatter rather than any effect of the freeze thaw treatment. Again, looking closer at the mechanical values of Young’s Modulus and Proportional Limit stress confirms this analysis.

Table 2: 80°C 90% RH results

Specimen	Freeze Thaw Cycles	Young's Modulus [Mpa]	PLS [Mpa]
1	0	50.879	3.2
2	0	51.264	2.8
3	50	45.59	2.9
4	50	38.13	2.6
5	75	32.58	1.7
6	100	41.04	2.6

The cycled membranes have lower moduli and Proportional Limit Stresses than the membranes that were not cycled in all cases, indicating a slight change in response.

However, the lack of a trend stands out, with specimen 3 having a higher PLS than specimen 2, and specimen 6 having a higher modulus than specimen 4.

4.4 Swelling Results

As the environmental conditions change in the chamber before a tensile test is conducted, the change in length of the membrane is recorded at various points. This change in length is due the swelling in the membrane, by measuring the change in length we can measure the in-plane swelling of the membrane due to changes in temperature or humidity.

The swelling of membrane is caused by both thermal expansion and water uptake, so the swelling has been measured by holding the humidity constant while changing the temperature and changing the humidity at a constant temperature. Due to differences in the initial length of the membrane specimens the data has been normalized to the length of the specimen at conditions of 25°C and 30% relative humidity.

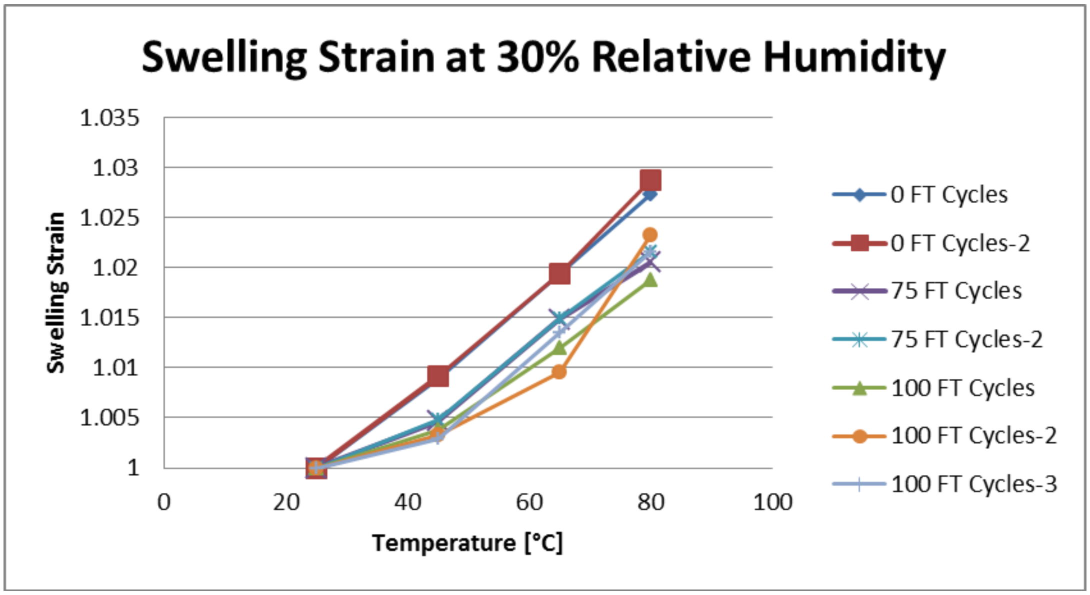


Figure 11: Swelling Strain at 30%RH

The swelling in membranes appears to have been slightly effected by the freeze thaw cycles. When held at a constant humidity the membranes that had been frozen show a decreased swelling strain compared to the membranes that were not cycled. Comparing the percent elongation from 25°C to 80°C shows this drop.

Table 3: Swelling Strain at 30% RH results

Cycles	Average Percent Elongation at 80°C
0	2.8
75	2.11
100	2.12

The average swelling decreased from 2.8% for the membranes with no freeze thaw cycles to 2.11% and 2.12% for the membranes after 75 cycles and 100 cycles respectively. Although this change is a 25% decrease in the swelling due to changes in temperature, the actual magnitude of the change is quite small. For specimens that are about 50mm long the 0.7% drop in percent elongation is represents only a change in length 0.35mm. It is also worth noting that changes in humidity tend to have a larger impact on the swelling. Increases of between around 5-7% were found in going from 30% relative humidity to 90% at a temperature of 80°C.

The swelling caused by changes in humidity was investigated by changing the humidity while keeping the temperature constant at 80°C. The results of the tests are shown below.

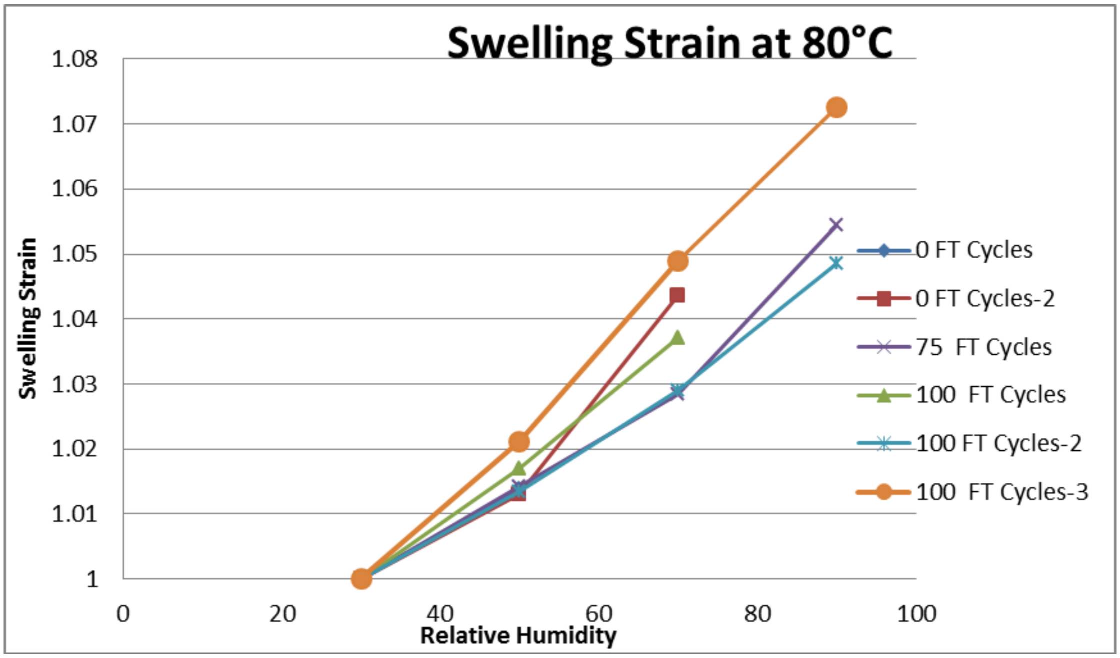


Figure 12: Swelling Strain at 80°C

Here the initial lengths were taken as the length at 80°C and 30% relative humidity to eliminate differences in swelling caused by thermal expansion. Unlike in Figure 11 (changing the temperature) there is apparently no impact on the swelling from the freeze thaw cycles. The samples that swelled the most and the least were both exposed to 100 freeze thaw cycles, the rest of the results fall in between the scatter provided by the 100 freeze thaw cycle samples. Looking at the swelling at 70% relative humidity we can see that there is no consistent effect; from greatest swelling strain to least swelling strain the samples had been exposed to 100, 0,100, 100, and 75 cycles. This shows that the number of freeze thaw cycles a sample was exposed to has no consistent effect on the swelling do to the humidity.

Chapter 5

DISCUSSION AND CONCLUSIONS

5.1 Conclusions

After testing membranes that had been exposed to 50, 75, and 100 freeze thaw cycles in conditions of 25°C and 30%RH it appears that simply freezing and thawing in a clamped state has little effect on the mechanical properties of the membrane. Both the modulus and proportional limit stress remained unchanged within the experimental scatter found in the testing of the membranes that were not exposed to freezing. It appears that there may be a reduction in the break strain of the membranes. This is consistent with the findings of other researchers; however, further investigation is needed to verify this preliminary observation, due to the large scatter found in break strain throughout the tests.

The tests conducted at 80°C and 90% humidity show similar results. The membranes that had undergone freeze thaw cycling had slightly more compliant mechanical response than the membranes that had not. At all numbers of cycles both Young's Modulus and the proportional limit stress were lower in the freeze thaw treated membranes than the other ones. Although this could be a sign of some degradation caused by the cycling, the differences are small. If the cycling caused this degradation we would expect to see the effect magnified with increased numbers of freeze thaw cycles, for these test no such trend emerges. The minimal change and the lack of a trend in increasing the number of freeze thaw cycles suggest that the differences are due to the scatter in the experiments rather than the effects of freeze thaw cycles, or perhaps the clamping of the membrane.

Results from measuring the swelling in the membranes again show little to no effect of the freeze thaw cycling. The changes in length due to changes in temperature decreased minimally for the membranes that had been frozen, but, as with the high temperature tensile tests, there is no change with increasing number of freeze thaw cycles. The decrease in thermal expansion is worth noting, but the small magnitude and lack of a trend suggest that any effect of the freeze thaw cycles was small. The swelling due to changes in the relative humidity showed no apparent differences between the samples that had been frozen and those that had not.

The lack of change in mechanical properties suggests that freezing and thawing alone, for up to 100 cycles, does not cause significant mechanical damage to the membrane.

5.2 Potential Future Work

While this work showed little change in the properties of the PEM after the freeze thaw cycles there are several questions that still worth exploring. One such issue is the rate of thawing. In a fuel cell the membranes will be rapidly thawed by the heat produced in the fuel cell. It is possible that thawing at a faster rate will produce a different effect on the properties of the membranes. Another area that is worth looking into is the addition a heating portion to the freeze-thaw cycles. PEMFCs typically operate at around 80°C, so by storing the membranes at 80°C instead of room temperature for the thawing would provide a closer approximation of the conditions inside a fuel cell. The addition some kind of heating element would enable both the effect of thawing rate and higher temperatures to be tested, although it would require modifying the equipment used in this work.

A final condition that would be interesting to explore is the effect of freezing membranes in a humidified state. In these experiments the membranes were taken from room conditions before they were frozen, however, in a fuel cell they may be frozen while in a more humidified state. Water management is complex issue in fuel cell design, and investigating the effect of freezing on wetted membranes could provide important information on the issue. The impact of freezing humidified membranes could be tested running humidified air through the bipolar plates between cycles. This would have the added effect of speeding up the thawing of the membranes, which would make the freeze-thaw cycles shorter and be a more accurate simulation of a fuel cell.

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Appendix A

CODE USED TO FIND PLS

The following MatLab code was used to find the proportional limit stress for the raw data provided by the testing. This code also graphs the data and determines the modulus, however for the results shown here Microsoft excel was used to produce the graphs and determine the modulus. The code was provided by Tom Cender from his previous work.

```
Graph.m
close all;
%%========================== PLOTTING PROPERTIES...
colorDefault = [1 0 0;
    1 0 0;
    1 0 0;
    1 0 0;
   0 0 1;
   0 0 1;
   0 1 0;
    0 1 0;
    .5 .25 .5];
set(0,'DefaultAxesFontSize',14)
set(0,'DefaultLineLineWidth',1.00)
set(0,'DefaultAxesColorOrder',colorDefault)
%%
%%========================== Variables
direction = '50FT';
T = 25;
RH = 30;
specimen = [1,2,3,4,5,6,7,8];
position = specimen;
trueCurve = true;
%%Filename
base = [direction,'-',num2str(T)];
type = '.txt';
%%Axis Intitial
xMax=0;
yMax=0;
EPLS=[];
%% Set the limits for data analysis
eps_lim = 0.025;
eps_t1 = 0.03;
```

```
eps_t2 = 0.1;
%%===========================

figure;
%%
%%=======================Loop Start

for i = 1:1:size(specimen,2);

    fileName = [num2str(specimen(i)),type];

    curve = csvread(fileName);

        if trueCurve == true
           stress = curve(:,7);
           strain = curve(:,6);
        else
            stress = curve(:,5);
            strain = curve(:,4);
        end

        strain = strain - strain(1);

        if xMax < max(strain)
            xMax = max(strain);
        end
        if yMax < max(stress)
            yMax = max(stress);
        end

    %%============================
        trueStress = stress.*(strain+1);
        trueStrain = log(strain + 1);

    %%====================Modulus and Proportional Limit
    [E, PLS] = fun_EP_finder(strain, stress,
eps_lim,eps_t1,eps_t2,true);
    EPLS = [EPLS; specimen(i), position(i), E, PLS];

    %%====================PLOT

    plot(strain, stress,'Markersize',6);hold all
    %%plot(strain, stress,colorDefault(i),'Markersize',6);hold
on;

end;
%%
legend(num2str(specimen'),2);legend('boxoff');
title('Nafion 211 T=25 RH=  30%');
xlabel('True Strain [mm/mm]');
```

```
ylabel('True Stress [MPa]');
axis([0 xMax+.1*xMax 0 yMax+.1*yMax])
%%text(.1*xMax,yMax*.99,[direction, ' Dir ';num2str(T),'[C]']);
%%text(1,20,'\leftarrow 4')
csvwrite([base,'-','E&PLS.txt'],EPLS);
saveas(gca,[base,'.png']);

%%
position = EPLS(:,2);
E = EPLS(:,3);
PLS = EPLS(:,4);
figure(2)
plot(position,E,'o')
axis([(min(position)*.9) (max(position)*1.1) (min(E)-(max(E)-
min(E))*.1) (max(E)+(max(E)-min(E))*.1)]);
title('Young''s Modulus');
xlabel('Position');
ylabel('Modulus [MPa]');
%%text(min(position)*1.1,max(E)*1.05,[direction, '
Dir';num2str(T),'[C]';num2str(RH),' % ']);
saveas(gca,['Modulus-',base,'.png']);
figure(3)
plot(position,PLS,'o')
axis([(min(position)*.9) (max(position)*1.1) (min(PLS)-
(max(PLS)-min(PLS))*.1) (max(PLS)+(max(PLS)-min(PLS))*.1)]);
title('Proportional Limit Stress');
xlabel('Position');
ylabel('True Stress [MPa]');
%%text(min(position)*1.1,max(PLS)*1.05,[direction, '
Dir';num2str(T),'[C]';num2str(RH),' % ']);
saveas(gca,['PLS-',base,'.png']);

csvwrite([base,'-
','Summary.txt'],[T,mean(E),std(E),mean(PLS),std(PLS)]);


fun_EP_finder.m
function [E, PLS] = fun_EP_finder(eps_org,str_org,
eps_lim,eps_t1,eps_t2,nom2_true)
%% str_org == measured exp. stress input
%% eps_org == measured exp. strain input
%% eps_lim == limit for determining the modulus
%% eps_t1,2== first and last point for the tangent (for PLS)

%% shift epsilon values by the value of strain
%% measured at the beginning of the experiment:
%%eps = eps_org - eps_org(1);

%% ===> if nom2_true = 0, already true. Nothing changes
if nom2_true == true;
```

```
    epsx = eps_org; strx = str_org;
elseif nom2_true == false;
    epsx = log(1 + eps);          %% true strain
    strx = str_org.*(1 + eps);    %% true stress
end

%% ::: M O D U L U S

%% pick the set of data below the limiting strain
ind_lin = find(epsx <= eps_lim);
epsx_linear = epsx(ind_lin);
strx_linear = strx(ind_lin);

%% y == strx_linear, stress below eps_limit
%% x == epsx_linear, strain below eps_limit
%% a == slope, or the "modulus", i.e.
%% polyfit solves for [a, b] in "y = a*x + b"
p1 = polyfit(epsx_linear,strx_linear,1);
E = p1(1);

%% ::: Y I E L D   L I M I T

%% pick the set of data for the tangent
ind_tan = find(eps_t1 < epsx & epsx < eps_t2);
epsx_tan = epsx(ind_tan);
strx_tan = strx(ind_tan);

%% polyfit solves for [a, b] in "y = a*x + b"
p2 = polyfit(epsx_tan,strx_tan,1);
PLS = p1(2) + p1(1)*(p2(2) - p1(2))/(p1(1) - p2(1));
```