Effect of Cations on the Modulus of Immersed Nafion® Film by DMA

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ABSTRACT

Nafion® film is used as the proton exchange membrane (PEM) in many fuel cell designs. Cations are known to change the modulus of dry Nafion films. This paper will present data on the modulus of Nafion while immersed in water containing different metal ions.

INTRODUCTION

Ionomer films, such as Nafion®, have been the subject of much research investigation lately. These films have a unique diffusion characteristic. Protons can diffuse through but electrons cannot. This property makes ionomer film ideal for use in electrolytic fuel cells. A typical Fuel cell construction is shown in Figure 1. The ionomer film is in the middle and separates the two, hydrogen and air, sides of the fuel cell. The catalyst on the left side of the membrane splits the proton and electron. The electron leaves the fuel cell through an external circuit to do work. The proton diffuses through the ionomer membrane to reach the air side of the fuel cell. The proton combine, with the aid of a catalyst, with a half molecule of oxygen and the electron as it returns from the external circuit. This completes the electrical circuit. The hydrogen, oxygen and electron combine to form water. This completes the chemical reaction.

The proton exchange membrane (PEM) is a critical component of the fuel cell. The rate-limiting step of current production is the diffusion rate of protons across the membrane. A thinner membrane will transmit protons faster. But thinner membranes are more susceptible to brittle failures such as small pinholes. Even the smallest hole, which allows the hydrogen gas to diffuse through the membrane, will create a 'hot spot' due to the reaction of hydrogen and oxygen. This 'hot spot' will cause the thermal degradation of the PEM and eventually a complete failure of the fuel cell. So knowing the modulus of the ionomer film and how it is affected by fuel cell conditions is of great importance to people who make PEMs.

EXPERIMENTAL

All experiments were performed on the Tritec 2000B, Figure 2, controlled stress DMA using the tension clamping geometry. No purge gas was used. The sample was Nafion® film

0.007 inches thick. The Nafion® films were manufactured by Dupont. The sample was 10 mm long, 9.1 mm wide and 0.18 mm thick. The sample was oscillated with 1 Hz frequency with 0.05 mm amplitude for a strain of 0.5 %. The same specimen of film was used for all experiments. The film was presoaked in distilled water prior to mounting in the DMA. The fluid bath was used with the glass liner. The solutions in the liner were replaced as needed for the experiment.

RESULTS AND DISCUSSION

The results of the first experiment are shown in Figure 3. In this experiment the modulus versus temperature is compared between a sample run in dry air and a sample immersed in distilled water. Let's look first at the sample run in dry air. There is an onset to a glass transition starting at about 20 °C. The modulus then starts to increase again at about 30 °C. This increase is due to the Nafion® film stiffening as it's native water is evaporating. When the water is completely gone (about 70 °C) the film goes through the glass transition one would expect for dry Nafion® film. By comparison, the immersed sample shows a glass transition between 35 and 55 °C. The modulus of an ionomer film is different when it is immersed, like in a fuel cell, than when it is run in dry air.

The acidity of the immersion fluid has a significant effect on the modulus of an ionomer film. Figure 4 shows the DMA of a Nafion® film in both acid and base. Ionomer films used in fuel cell applications are in the protonated form. This means that the DMA results in pH = 1 solution are similar to actual fuel cell conditions. Notice the dramatic increase in modulus with the higher pH. The side chains of the Nafion® are less mobile when the sulfonate groups of the Nafion® become the sodium salt. The ionic attraction of the sodium sulfonate side chain is stronger than the covalent (or even hydrogen bonding) attraction of the hydrogen sulfonates side chain. It is important that the ionomer film not be exposed to high pH when used in a fuel cell application.

Copper ions are absorbed by Nafion® ionomer and increases the film modulus as shown from 70 to 160 minutes in Figure 5. Also of interest is the kinetics of adsorption and desorption. The copper is absorbed faster than it is released in the presence of acid (pH=1) solution. Magnesium ions have a similar affect on the film, Figure 6, but with a smaller changes in modulus. The desorption of magnesium ions is also slower. Cobalt ions are absorbed by the ionomer film as well, Figure 7. The rate of adsorption and desorption of cobalt appear to be very similar. Iron (+2) ions by far (except for sodium) have the largest affect on the modulus of the ionomer film, Figure 8. The film is in water from 0 to 50 minutes. The solution is changed at 50 minutes to 0.1 N NaOH and the modulus increases dramatically. At 100 minutes the bath is changed to 0.1 N H_2SO_4 and the modulus decreases again as the sulfonate side chains are protonated. At 140 minutes the solution is changed to 0.1 N $FeSO_4$ solution and the modulus increases as the iron ions are bound inside the ionomer membrane.

All the results are presented in Figure 9. The results were normalized to the same starting modulus value for ease of interpretation. Sodium has the largest effect on the modulus. Iron ions have the second largest effect. Magnesium, cobalt and copper all have much smaller effects. These tests indicate that Nafion® films should not be exposed to basic solutions and iron ions. Additional tests, not reported here, have indicated that once the ionomer film has adsorbed ions, such as iron, water is not acidic enough to remove the ions from the membrane. So the adsorption of ions by the film, in use in a fuel cell, is cumulative and could be a possible cause of premature failure of the fuel cell. The Tritec 2000 DMA has proved to be a great tool in the analysis of ion adsorption by ionomer films.

REFERENCES

1) NAFION® is a registered trademark of E.I duPont deNemours, Inc.

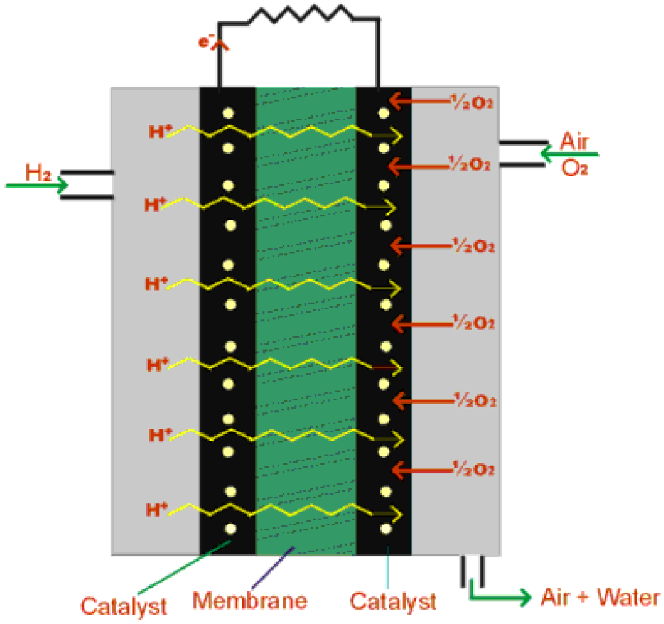

Figure 1: Typical electrolytic fuel cell

Figure 2: Tritec 2000 DMA with fluid bath.

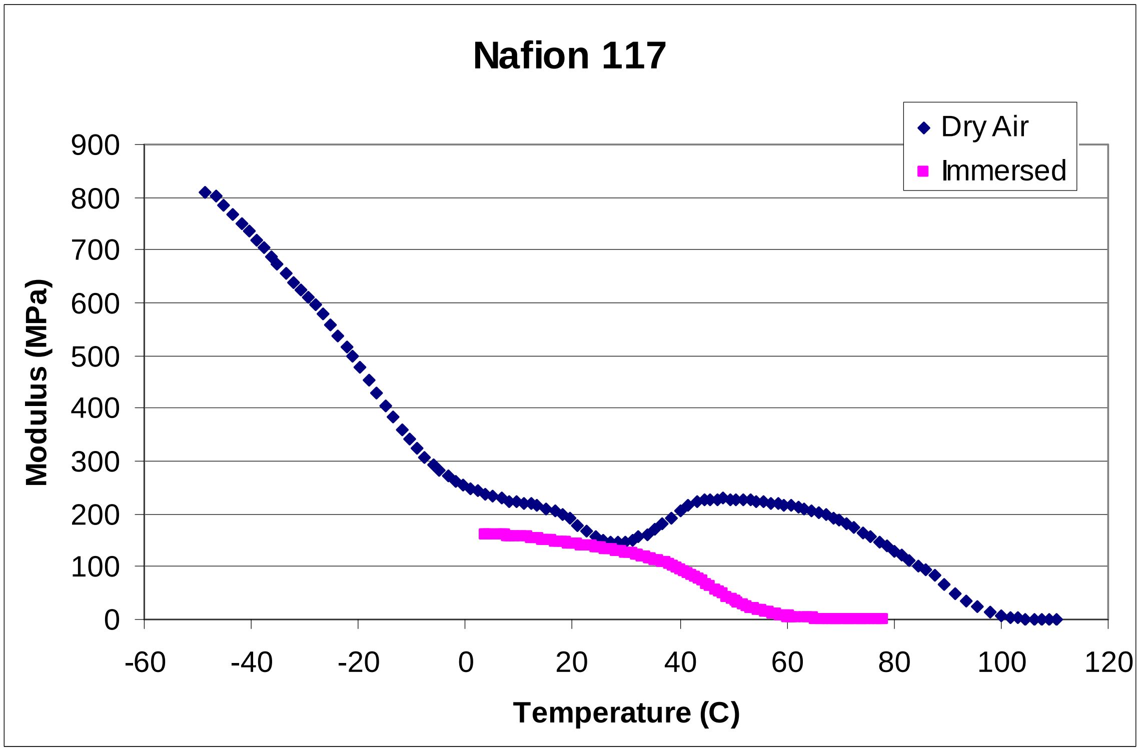

Figure 3: DMA for Nafion 7 mil film in tension mode.

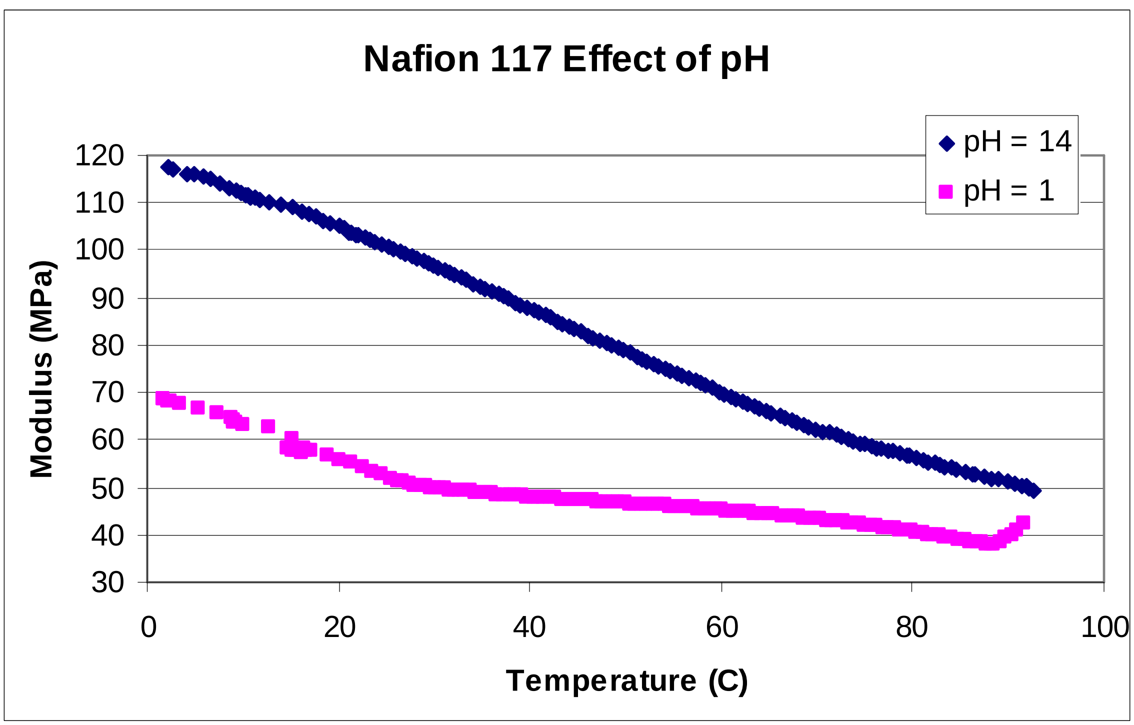

Figure 4: DMA for Nafion. Effect of pH.

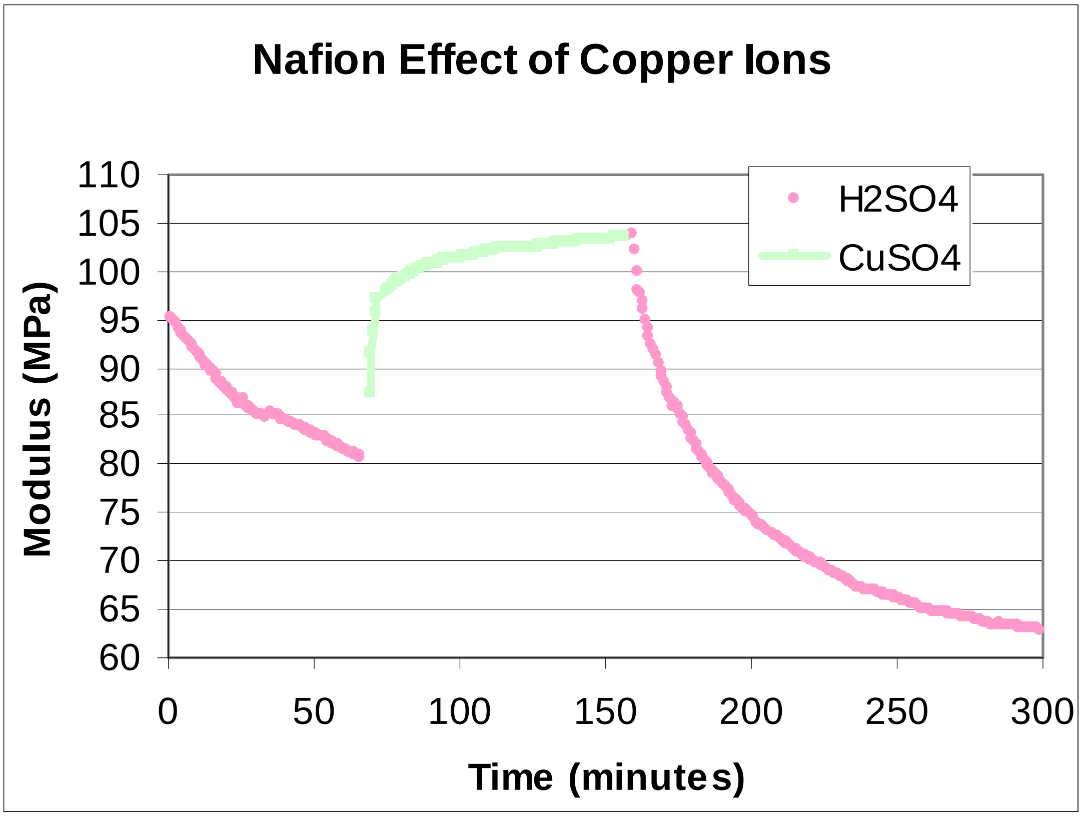

Figure 5: DMA of Nafion. Effect of copper ions.

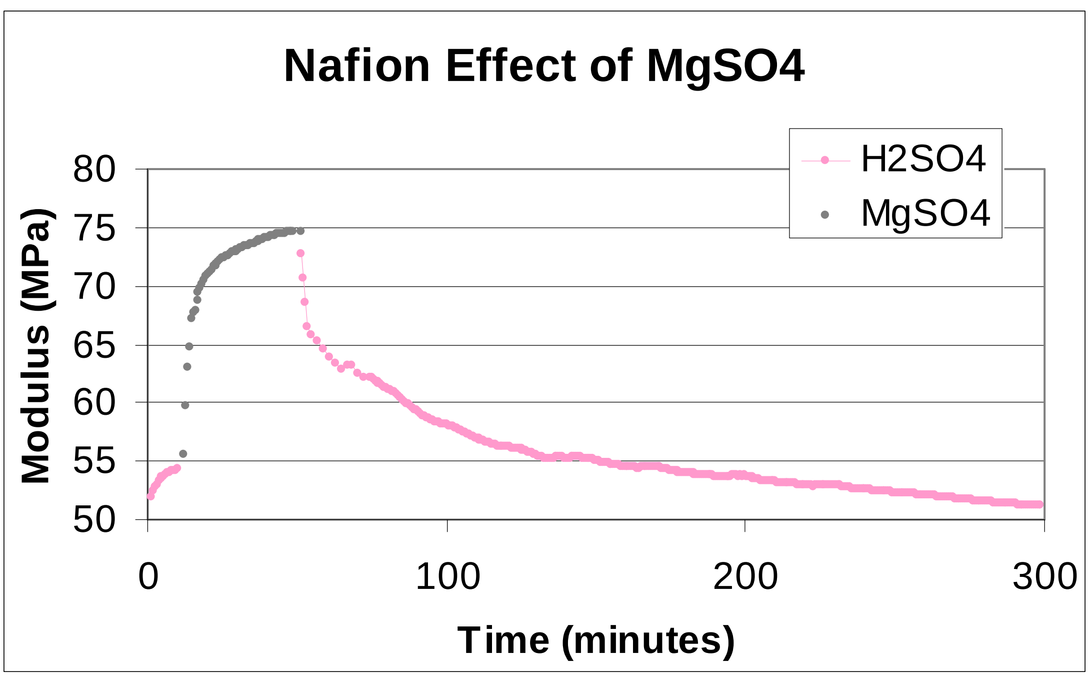

Figure 6: DMA of Nafion. Effect of copper ions.

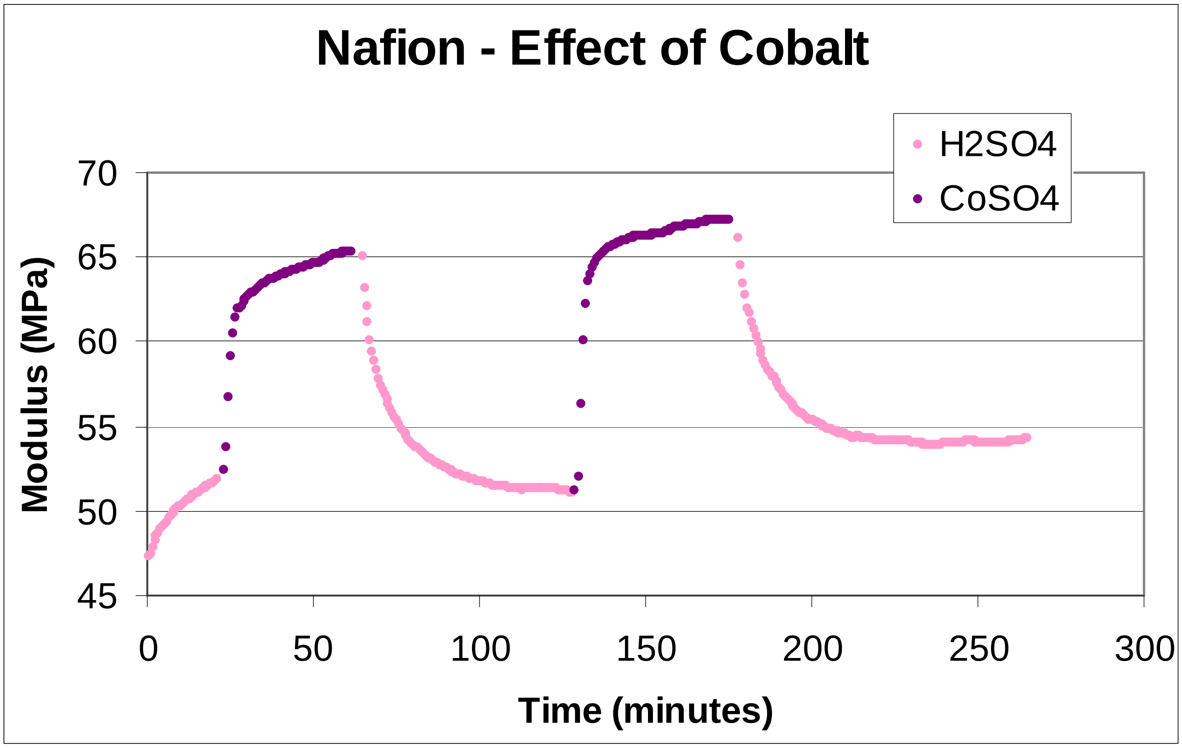

Figure 7: DMA of Nafion. Effect of cobalt ions.

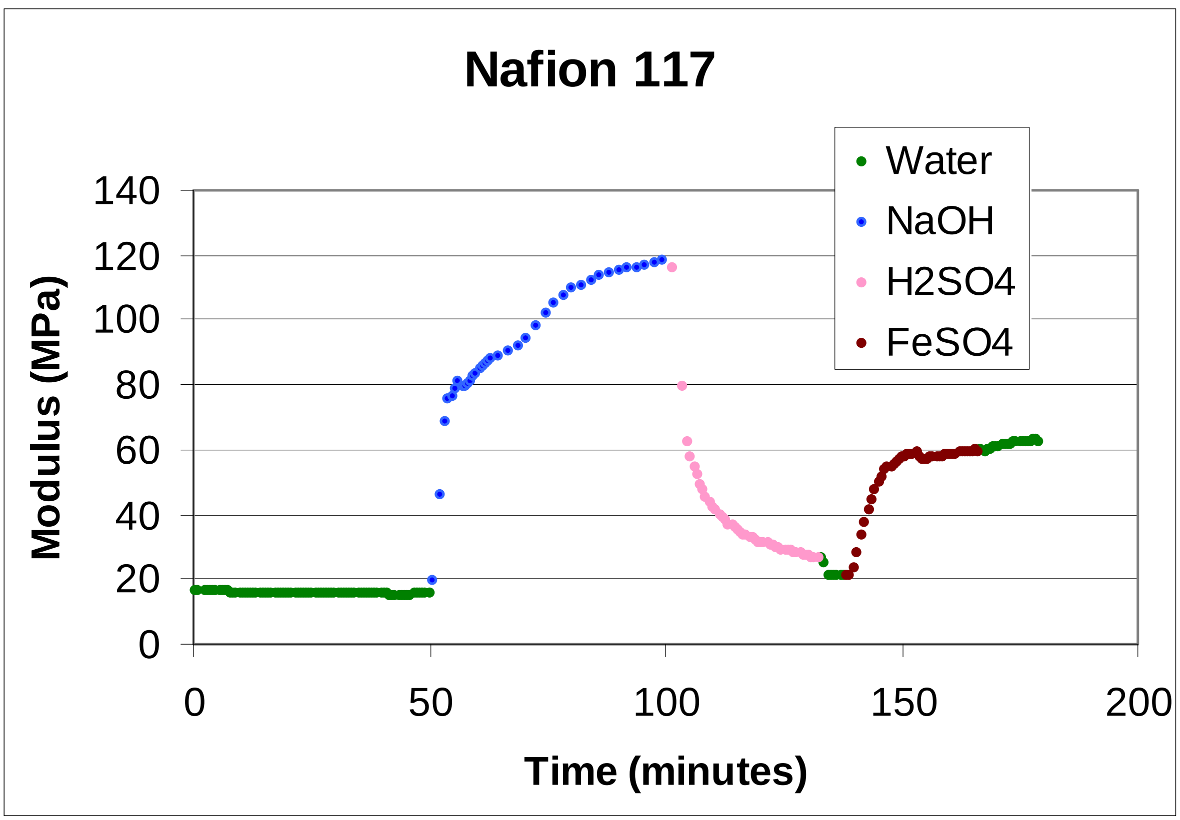

Figure 8: DMA of Nafion. Effect of iron ions.

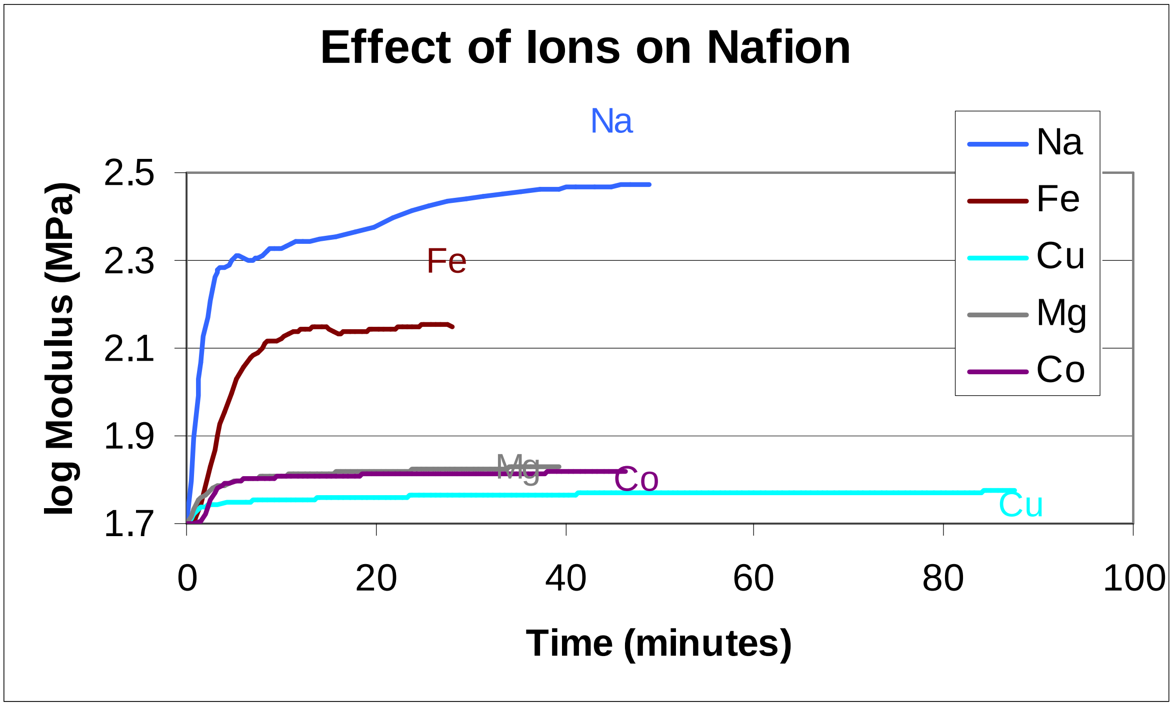

Figure 9: DMA of Nafion. These results were normalized to the same starting modulus value for ease of comparison.