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# Student Laboratory for Synthesis and Characterization of Proton Exchange Membranes

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## Introduction

Fuel cells (FCs) are electrochemical devices that use the chemical energy of a fuel, such as methanol or hydrogen, and oxygen to produce electrical energy. In a FC, hydrogen is supplied to the anode side, and oxygen is supplied to the cathode side. At the anode, electrons are stripped from hydrogen atoms and the produced protons pass through a proton-conducting electrolyte, where the electrons are directed through an external path, powering an attached device and leading to the cathode, reducing oxygen. At the cathode, the protons are combined with oxygen, forming water. Overall, the FC combines hydrogen and oxygen to produce water and electricity.[1]

Proton exchange membrane (PEM) FCs are considered the optimum FC for applications such as backup power sources, power sources for portable electronics, distributed power generation, and electric vehicles. PEM FCs use a solid polymer membrane that is permeable to protons when saturated in water. Many important PEM fuel cell features depend upon the properties of the PEM. Nafion is the benchmark in the industry for PEMs. The benefits of Nafion are that it has a high proton conductivity, acts as a superacid catalyst, provides high proton conductivity and moderate water swelling. Some issues however are that it is high cost, high methanol permeability, functions poorly at elevated temperature and at low humidity. An alternate to Nafion is Polyetheretherketone (PEEK), which is a Poly(arylene ether)-Based PEM. It is low cost, has low methanol permeability, high mechanical strength, excellent chemical and thermal stability, high water absorption, excellent organic solvent resistance, and is used in medical, electronic, automotive, and aerospace fields. PEEK PEMs can be compared to Nafion PEMs using characterization methods such as water uptake testing, percent sulfonation, and electrochemical impedance spectroscopy.[2-5]

The primary goal of this research was to improve the current PEM Synthesis and Characterization laboratory exercise for CHEM 411-Synthesis and Characterization of Materials.[6] Improvements to this lab included measuring conductivity of the PEM by finding the best procedure for creating the conductivity cell through both research and experiments in order to add electrochemical impedance spectroscopy to the methods of characterizations for the lab.

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## Results

24 Hour Water Uptake Testing:

| | 09FEB23 Initial | 09FEB23 Final | 21NOV22 Initial | 21NOV22 Final |
|---|---|---|---|---|
| Mass (g) | 0.127 | 0.144 | 0.195 | 0.261 |
| Percent Difference | 12.5% increase | | 28.9% increase | |
| Length (cm) | 5.9 | 6.0 | 5.1-5.2 | 5.7 |
| Percent Difference | 1.7% increase | | 10.1% increase | |
| Width (cm) | 1.7-1.8 | 1.8 | 3.5-3.7 | 3.7-4.0 |
| Percent Difference | 2.8% increase | | 6.7% increase | |

Percent Sulfonation:

| | 09FEB23 | 21NOV22 |
|---|---|---|
| Titration 1 | 54.1% | 78.4% |
| Titration 2 | 54.5% | 78.8% |
| Average | 54.3% | 78.6% |

$$Percent\ Sulfonation = \frac{Moles\ of\ acid\ x\ 288}{Sample\ Mass - (Moles\ of\ acid\ x\ 80)}$$

Electrochemical Impedance Testing:

| | 09FEB23 | 21NOV22 | Nafion |
|---|---|---|---|
| Resistivity (Ω) | 2250 | 1610 | 1160 |
| Width (cm) | 1.8 | 1.9 | 2.0 |
| Thickness (cm) | $9x10^{-3}$ | $9x10^{-3}$ | 0.018 |
| Conductivity (1/Ωxcm) | 0.0823 | 0.109 | 0.0718 |
| Ion Exchange Capacity (mmol/g) | 2.24 | 1.64 | 0.92 |

$$Conductivty = \frac{Length}{Resistivity \times Area}$$

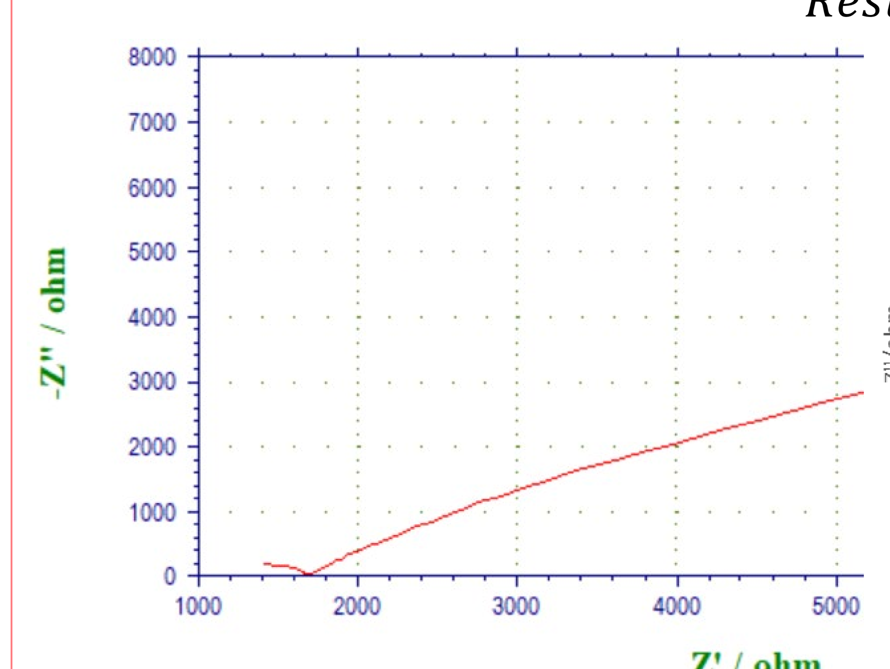



Figure 1: Nafion Nyquist Plot

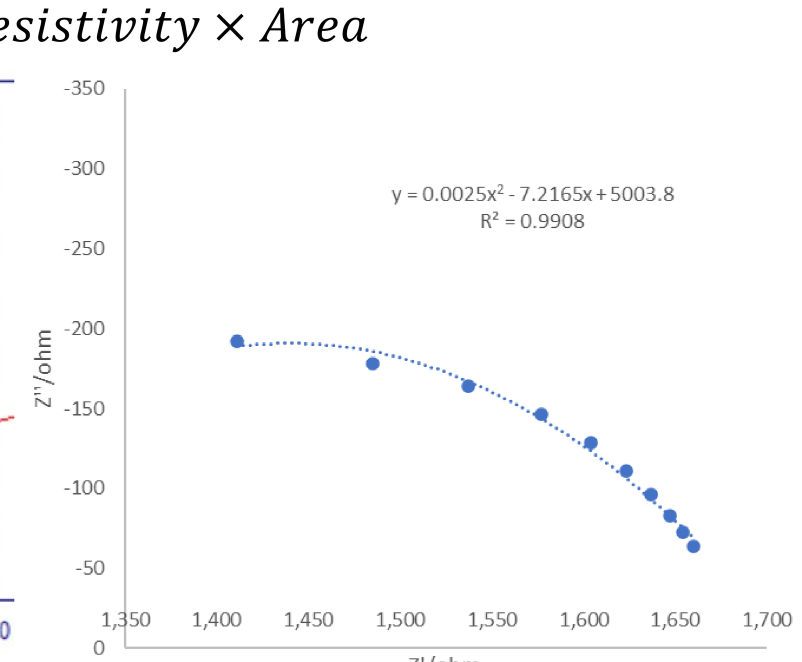



Figure 2: Nafion 1-1,00,000 Hz

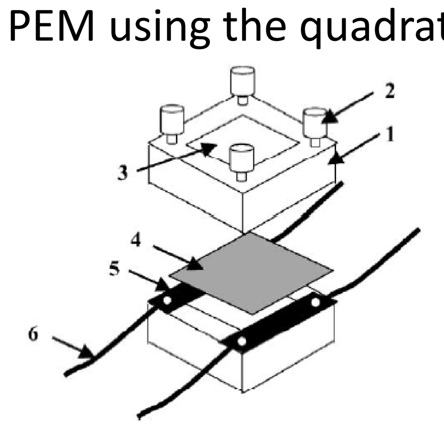
## Methods

Synthesis: The first step to synthesize PEMs to be used in the electrochemical cell is to add concentrated sulfuric acid to PEEK and stir for 5-7 days. After the reaction is complete, the solution is quenched in DI water by pouring a continuous thin stream to ensure that the polymer stays connected and is uniform thickness. Then, as often as possible, the acidic water must be poured out of the beaker and new distilled water must be added so that acid exchange can occur. Once the polymer has been neutralized it will be placed in an oven to dry for 3-5 days to remove water from the product (Figure 3). After drying, a small amount of product is dissolved and cast into a film for testing (Figure 4).

Figure 4: First film casted

Figure 3: Polymer before (left) and after (right) drying in the oven

Characterization: Water uptake and percent sulfonation are carried out following the current methodology.[6] Impedance testing is run by first trimming the cast film into a rectangle and recording the dimensions. Then, it is placed in the conductivity cell and tightly secured before attaching the electrodes to the cell (Figure 6). The cell is then placed in DI water and the instrument is ran from 1-1,000,000 Hz and a Nyquist Plot is obtained (Figure 1). That plot can then be used to find the resistivity of the PEM using the quadratic equation to solve for the x intercept (Figure 2).



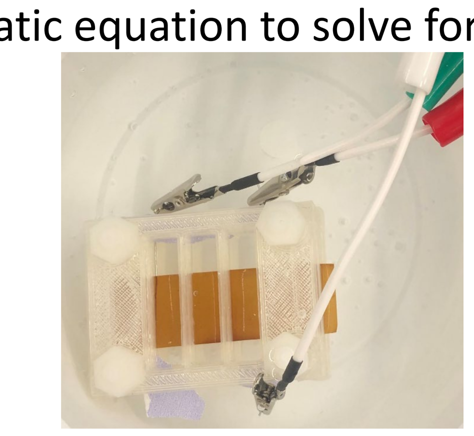


Figure 5: Exploded-view of a conductivity cell[7]
Figure 6 (far right): Constructed conductivity cell

## Conclusion

The primary goal of this research was to improve the current Proton Exchange Membrane Synthesis and Characterization laboratory exercise for CHEM 411. Commercial membranes, such as Nafion, have multiple issues: high cost, high methanol permeability, poor function at elevated temperatures and at low humidity being some of them. Using PEEK to synthesize PEMs can be used as a reduced cost alternative to Nafion as well as reduce methanol permeability. Improvements to this lab were made by creating a conductivity cell and a procedure for measuring the conductivity of the PEM with electrochemical impedance spectroscopy. In addition to using electrochemical impedance spectroscopy, water uptake and percent sulfonation will be used to compare PEEK PEMs to Nafion PEMs.

## Acknowledgments

I would first like to thank Dr. Kopitzke for giving me the opportunity to research and for putting up with my crazy schedules over the years, without him this wouldn't be possible. We would also like to thank Dr. Klankowski for teaching us how to use impedance spectroscopy to characterize our PEMs. Additionally we would like to thank Luke Zwiefelhofer for helping us to construct the circuit that we used in our impedance testing. Lastly, we would like to thank WSU for providing us with funding for our research.