

Research Paper
**A NOVEL PROCESS TO FABRICATE STABLE BIPOLAR MEMBRANES BY EXPLOITING THE PHYSICAL
PROPERTIES OF THE NAFION™ CATION EXCHANGE MEMBRANES**

By
Nikhita Bontha

Introduction

H₂/O₂ fuel cells represent one of the most important technologies that can transform life in the 21st century [1]. These fuel cells have the ability to dramatically reduce fossil fuel dependence through the use of renewable energy sources. Fuel cells can also significantly reduce global warming related phenomena through a direct reduction of CO₂ and NO_x gases in our atmosphere. Other benefits include highly efficient energy conversion and major reductions in noise pollution.

Despite these amazing benefits and over three decades of focused research, fuel cells have not lived up to their potential. The main reasons for this are the **costs** and **performance challenges** that are driven primarily by the cation exchange membrane that is used to separate the anode and the cathode, as well as, provide ionic conductivity in the cell.

Switching to bipolar membranes (BPM) can allow for the use of inexpensive catalysts and eliminate cathodic flooding, thus dramatically reducing the overall cost and improving performance [2]. A bipolar membrane is a membrane that contains both a cation exchange membrane (CEM) and an anion exchange membrane (AEM) joined together. The junction between the two membranes is called **the bipolar junction**. Bipolar membranes do not let any ions pass through the bipolar junction. Conductivity within bipolar membranes occurs through the water-splitting reaction at the bipolar junction. When used in a fuel cell, the H⁺ and OH⁻ ions generated by the bipolar membrane consume the OH⁻ and H⁺ ions produced at the cathode and anode compartments to produce water and keep the pH at each of the electrodes neutral. These properties make bipolar membranes very attractive for fuel cell applications. Unfortunately, today's bipolar membranes do not meet the electrical, chemical, and mechanical stability requirements of fuel cells.

Research Goal

The research goal of the project was to develop a stable bipolar membrane that will have the electrical, mechanical, and chemical properties of the benchmark Nafion¹ cation exchange membrane that is currently used as the gold standard for fuel cell membranes.

Bipolar Membranes

Bipolar membranes are typically formed by hot-pressing or liquid-casting a CEM over an AEM. In this approach, the bipolarity is limited to the very small interfacial volume at the junction between the two types of membranes. This significantly limits the rate of the water splitting reaction with these membranes. For this reason, bipolar membranes limit the current produced in a fuel cell. Also, at high current densities, gas bubbles begin to form at the interface, causing the membranes to detach.

Recently, researchers at the Georgia Institute of Technology have developed a method to increase the interfacial volume of the bipolar junction by chemically modifying some of the negative fixed charge groups within the pores of the membrane to positively fixed charge groups [3]. In this approach, the bipolar junction is present in each and every pore, as opposed to the traditional interfacial method of synthesis. Their approach increased the water splitting reaction rate by several orders of magnitude.

¹ Nafion™ is a registered trademark of E. I. Dupont de Nemours

Unfortunately, this approach relied on limiting the diffusion of the reactants into the membrane pore and was not easy to scale up. Further, chemical modification made the polymers weak, effecting the membrane as a whole.

Concept and Experimental Approach

The idea introduced here represents a novel approach to exploiting the chemical, mechanical, and thermal stability of Nafion cation exchange membrane for achieving whole pore bipolarity without chemical modification.

The approach relies on two key properties of the Nafion™ membrane [4, 5]:

1. Unique “cluster network” pore structure resulting from the extremely hydrophobic Teflon backbone of the polymer and the high concentration of the sulfonate groups
2. Strong dependence of the pore sizes on the solvent in contact with the membrane

These properties facilitate large cations to be incorporated within the pores and preventing them from leaving. This creates a membrane with bipolarity uniformly distributed within its pores. The approach, shown schematically in Figure 1, consists of first swelling the membrane pores in methanol to incorporate large cations. Then the pores are shrunk to their normal size by transferring the membrane to water. If the size of the cation is larger than the narrow channels (~10 Å) in Nafion, they are trapped within the pores to impart bipolarity to the membrane.

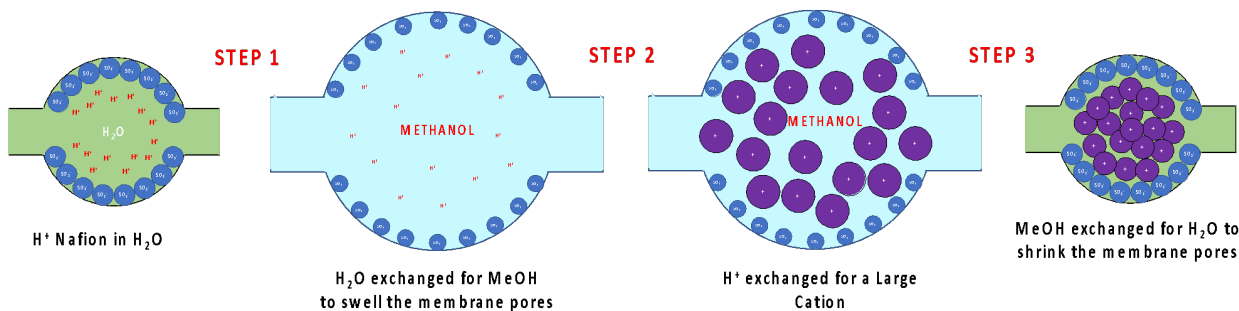


Figure 1. Concept for converting Nafion membrane into a Bipolar Membrane

The concept was tested using two different salts [Dodecyltrimethylammonium Bromide (DTAB) and Cetyltrimethylammonium Bromide (CTAB)] and two polymerizable cations (Aniline and Pyrrole). Variables tested included concentration of the salts, polymerization conditions, and mixed salt/polymerizable ion combinations.

The bipolarity of the membrane was determined by measuring cation uptake by the membrane, i.e., an unconverted membrane would take up cations equal to the total negative charges on the Nafion™ membrane while a fully converted membrane will take up no cations.

Results and Discussion

Figure 2 shows the bipolar conversion for the different cations used in the current study. It can be seen from the data in Figure 2 that the bipolarity varied between 45% to 97% with the best bipolarity obtained with the CTAB surfactant. It is believed that the CTAB and DTAB surfactants performed best because, at the concentration used in testing, they form micelles [1] whose size (~20Å) is sufficiently small for them to enter the methanol swollen Nafion™ membrane pore but larger than the pores in water to keep them trapped.

To test this hypothesis, pyrrole and aniline were added to the micellar solutions before incorporating into the membrane. The resultant membrane bipolarity increased dramatically from ~50% to 90%.

In addition to salt uptake measurements, the modified membranes were also characterized using Helium ion microscopy (HIM) and X-ray Photoelectron spectroscopy (XPS) to demonstrate cation and aniline/pyrrole polymer incorporation in the membrane.

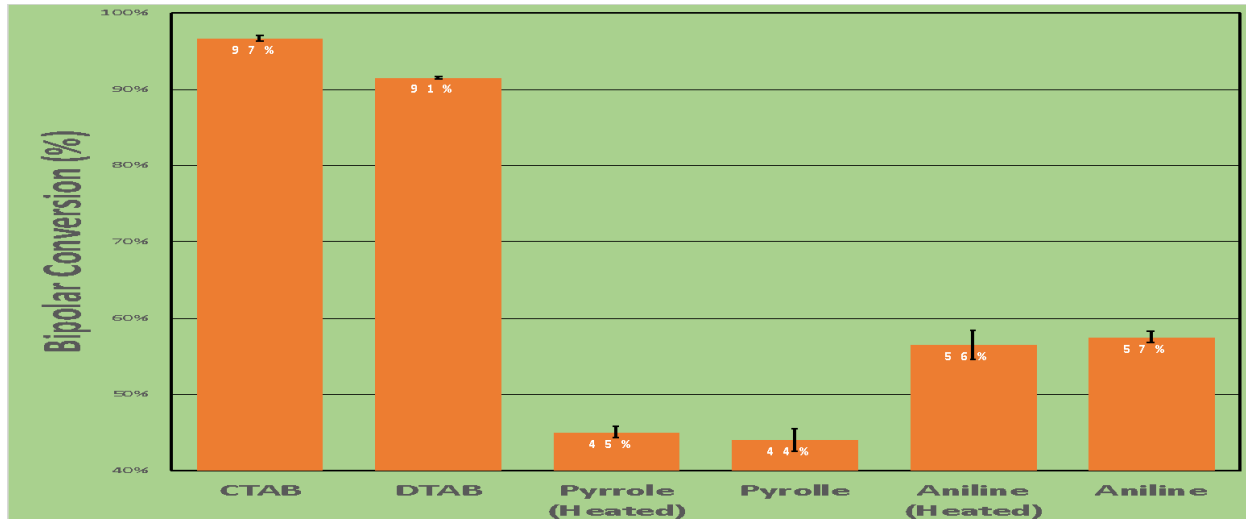


Figure 2. Bipolarity of the Nafion™ Membrane with different incorporated cations.

Conclusions

- A new approach for synthesizing bipolar membranes from Nafion™ was developed and tested
- The approach involved incorporating large cations into the membrane by swelling the Nafion™ membrane pores and keeping them from leaving the pores through self-assembly or polymerization and solvent swap
- Unlike traditional bipolar membranes, the bipolarity is distributed throughout the entire pore/membrane
- The bipolar membranes synthesized this way have the chemical, mechanical, and thermal stability of the parent Nafion™ membrane

References

1. Bahattin, T. et al. Overview of the next quarter century vision of hydrogen fuel-cell vehicles, *Journal of Membrane Science*, 2019, 44, 10120-10128
2. Sikan Peng, X, et al. A self-humidifying acid-alkaline bipolar membrane fuel cell, *Journal of Power Sources*, 2015, 299, 273-279.
3. Ahlfield, J.M., L.S. Liu, and P.A. Kohl, PEM/AEM Junction Design for Bipolar Membrane Fuel Cells. *Journal of the Electrochemical Society*, 2017. 164(12): p. F1165-F1171.
4. HeitnerWirguin, C., Recent advances in perfluorinated ionomer membranes: Structure, properties and applications. *Journal of Membrane Science*, 1996. 120(1): p. 1-33.
5. Pintauro, P.N., et al., Equilibrium Partitioning of Monovalent Divalent Cation-Salt Mixtures in Nafion Cation-Exchange Membranes. *Journal of Physical Chemistry*, 1995. 99(34): p. 12915-12924.
6. Bales, B.L. and R. Zana, Characterization of micelles of quaternary ammonium surfactants, as reaction media I: Dodecyltrimethylammonium bromide and chloride. *Journal of Physical Chemistry B*, 2002. 106(8): p. 1926-1939.