

Advances in Materials for Proton Exchange Membrane Based Fuel Cells

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Introduction

Less than a decade ago, most alternate membrane materials for fuel cells relied upon a post-sulfonation process to generate ionic groups capable of transporting protons from the anode to the cathode. These random post sulfonations showed some promise, but in general they produced materials that were not sufficiently stable, ductile, or protonically conductive at ion exchange capacities where aqueous swelling could be restricted. In order to change the situation, our group began to synthesize disulfonated monomers that could be used to incorporate into random copolymer proton exchange membranes.¹ One expected limitation was that the aromatic polymers might not be stable enough to withstand fuel cell conditions. However, this was mostly based upon an accelerated test known as the Fenton's Reagent, which did not seem to this author as being a reliable predictor of performance. A much better approach has been to evaluate the open circuit voltage (OCV) for alternate membranes in cooperation with colleagues at UTC, as well as the benchmark perfluorosulfonic acid systems. When this is done, the aromatic ionomers, primarily based upon disulfonated polyarylene ether sulfones, show up quite well. Moreover, real-time 3000 hours DMFC results have also been generated in cooperation with the Los Alamos National Labs (LANL), wherein several of the new systems can outperform Nafion largely due to lower permeabilities. Obtaining conductive materials at low humidities is another major issue where alternate membranes have not up to now been particularly successful. In order to address this problem, multiblock copolymers with relatively high water diffusion coefficients have been designed, which show promise for conductivity at lower humidity. Several preprints/lectures at the San Francisco Fall ACS meeting will be presented by our group in the PMSE, POLY, and Fuel Chemistry programs. An overview of these systems will be discussed in this lecture.

Discussion

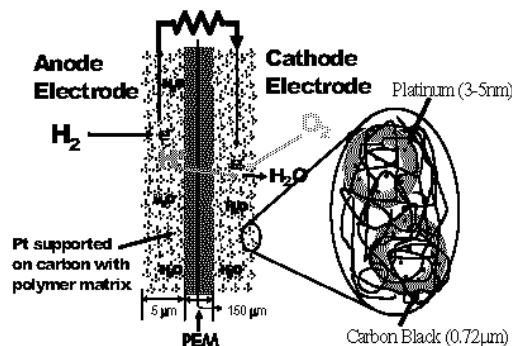
The requirements for proton exchange membranes have been summarized in Figure 1 and also in Reference 1. Clearly, high protonic conductivity is of critical interest and this needs to be achieved not only aqueous or high humidity conditions, but also at low, preferably ambient relative humidity. The membrane must show low permeabilities to hydrogen, methanol and oxygen to prevent catastrophic mixing.

Fundamental transport properties, such as diffusion and electro-osmotic drag, relate to water transport. The membranes must be both thermally, oxidatively, and hydrolytically stable under the fuel cell acidic conditions for thousands of hours. The current guidelines are about 5000 hours for transportation, 40,000 hours for stationary power, and for greater than 2000 hours in portable power.

In addition to the electrochemical behavior, the mechanical properties both under ambient essentially dry and/or wet conditions must be sufficient for long periods of time. And last but certainly not least, the membranes and membrane electrode assemblies must be easily fabricated into robust MEAs. This essentially laminated composite-like material consists in the simplest case of anode membrane and cathode.

Of course, in the more pragmatic cases one must add also a diffusion layer and bipolar plates for the single cell. And then integration of the single cells into stacks is well known to be another important engineering aspect. The work in our group has largely focused on the nature of the membrane, and to some extent the performance of the electrodes and bonding methodologies to produce good MEAs.

Membrane Electrode Assembly (MEA)



The benchmark is Nafion™
for the membrane and electrodes

Membrane (PEM) Requirements

Critical PEM Properties

- High protonic conductivity, even at low RH
- Low electronic Conductivity
- Low permeability to fuel and oxidants
- Low water transport – diffusion and electro-osmotic drag
- Oxidative and hydrolytic stability under acidic conditions, for thousands of hours!
- Good dry and wet mechanical properties at ambient and higher temperatures.
- Cost effective and able to be fabricated into robust membrane electrode assemblies.

Our approach has been to generate thermally, hydrolytically, and oxidatively stable aromatic ion-containing copolymers (or ionomers) with high glass transition temperatures, ductile stress strain behavior and a controlled level of hydrophilicity. Most of our work has involved generating linear statistical copolymers that contain both hydrophobic and hydrophilic units. However, we recognize that for some purposes crosslink systems may be desirable and we are pursuing that area as well.

Currently, the H₂/Air field is limited to modest temperatures and high relative humidities for the higher power density stationary and transportation arenas. Great interest is obvious to increase the temperature to 100-120°C or higher, particularly at ambient and low relative humidities. It is well known that these reasons include minimizing the contamination of the fuel by carbon monoxide, improving the cathode-reaction kinetics, and allowing one to accommodate the heat generated during the process to control dimensions of the transportation system.

Portable power has largely focused on direct methanol fuel cells (DMFC) and here the temperature range is typically from ambient to perhaps 80°C. Relatively low concentrations of methanol in water have been used, which has been necessary to minimize the permeation of the methanol through the relatively highly microporous perfluorosulfonic acid benchmark membranes. Thus, systems that lower the methanol permeability are attractive.

The poly(arylene ether sulfone)s are commercial engineering thermoplastics well known for their thermal stability and good resistance to acid, bases, and oxidants. They are also ductile film-forming materials and several of the monomers are commercially available.² However, the arylene ether sulfones have no ion-conducting sites. The early efforts largely focused on post sulfonation reactions with the most available material, known commercially as Udel, which based upon bisphenol-A. It is well established that bisphenol-A based materials have somewhat limited acid resistance, particularly at elevated temperatures and strong acid environments, such as a fuel cell. And indeed the bisphenol-A isopropylidene unit can be cleaved. In fact, this is how the monomer itself is made in a reversible type process. We chose to work with only wholly aromatic systems, which do not have this problem. One then has the choice of doing the post-reaction or to disulfonate the monomer.

Our work has almost entirely focused on the monomer sulfonation, followed by direct copolymerization. Relatively inexpensive starting materials can be obtained from commercial units, and the concentration of the ionic units in the chain can be very well defined during the polymer synthesis. Placement of the disulfonated units on the deactivated portion of the repeat unit enhances stability to disulfonation somewhat, and the direct copolymerization also offers the ability to make 40-50,000 or higher number average molecular weight copolymers.³ The resulting materials have developed in the literature under the term BPSH^{1,3-5}.

The water content of the BPSH random copolymer systems increased monotonically up to about 45-50 mole percent of the disulfonated units. Beyond that, the system shows phase inversion and subsequently very high water sorption. Thus the functional area of interest in these random copolymers is from about 30-45 mole percent of the disulfonated units. Performance of the BPSH-35 copolymer has been evaluated in cooperation with both UTC and BekkTech colleagues.

The conductivity response of the BPSH system is quite competitive at higher relative humidities, but is very significantly lower than the benchmark material at lower humidities. This has been observed by a number of investigators, and the possibilities for this behavior have been attributed either to the somewhat lower acidity of the aromatic sulfonic acids, or in our view, the transport mechanisms that are available for the sulfonic acids in the wholly aromatic ionomers.

Durability has been achieved in a number of ways, including resistance to hydrolysis for over 10,000 hours in boiling water, 3,000 hour DMFC performance done in cooperation with LANL scientists, and good resistance to open circuit voltage degradation at 100°C, and 25% humidity in hydrogen/oxygen, performed in cooperation with UTC scientists.

We have also demonstrated by recovering membranes from month-long aging fuel cell tests at 80°C that the molecular weight, ion content, film swelling characteristics, among other things, are not changed during this aging period.

Efforts are continuing with these random copolymers, particularly in conjunction with selected fillers to determine whether there is an enhancement of conductivity at elevated temperatures with lower humidity environments.

Our major current thrust explores the possibility of generating multiblock copolymers with hydrophilic-hydrophobic components. For example, if a co-continuous structure could be generated, our hypothesis is that the transport through the hydrophilic domains would be enhanced. Early results, which will be discussed at this meeting, include why we are interested in block copolymers, which essentially relates to the fact that protonic conductivity as a function of relative humidity can at least match the perfluorosulfonic acid benchmark materials, in contrast to the random behavior. We propose that this is because of enhanced transport of the proton complex through the challenge of the multiblock systems. Early results on DMFC performance of the BPSH-PI block copolymers are also consistent with enhanced performance in the portable power area.

Conclusions

Hydrogen-Air PEMFC based on alternate membranes, such as the disulfonated poly(arylene ether sulfone) random copolymers have good properties and the potential to provide satisfactory fuel cell performance below 100°C. At higher temperatures, the random copolymers per se are not as attractive largely because of the lack of transport with the low relative humidity conditions. However, significant progress has been made in developing several families of long sequential block copolymers, which appear to generate cocontinuous hydrophilic-hydrophobic morphologies that are capable of enhancing the water diffusion coefficient and may be a mechanism for allowing for conductivity at lower humidities. Higher molecular weight of the membranes, which is possible during the direct copolymerizations is proposed to be a critical parameter in defining durability. Already, it is evident that tailored membrane electrode interfaces are important, particularly in DMFC where one

wishes to use the commercially available perfluorosulfonic acid electrodes.

Acknowledgements

The author would like to thank all of his research group members, past and present. He would also like to acknowledge support from a number of other agencies and companies including Los Alamos, DARPA, The Army Research Office, the Department of Energy, The National Science Foundation, NASA Glenn, The Office of Naval Research, and last but not least, the Nissan Motor Company, Ltd. Acknowledgement is also extended to Solvay Advanced Polymers for providing generous quantities of a critical monomer: 4,4'-dichlorodiphenyl sulfone.

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