V.A.10 Development of Novel Proton Conducting Membrane Materials and CFD Multi-Phase Porous Flow Models for PEM Fuel Cells

K. J. Berry (Primary Contact), Susanta K. Das, P. Kolavennu, Ali R. Zand, J. Hedrick, and L. Beholz

Center for Fuel Cell Systems and Powertrain Integrations, Kettering University
1700 West Third Avenue
Flint, MI 48504
Phone: (810) 762-7833; Fax: (810) 762-7860
E-mail: jberry@kettering.edu

DOE Technology Development Manager: Kathi Epping
Phone: (202) 586-7425; Fax: (202) 586-9811
E-mail: Kathi.Epping@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

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Objectives

- Develop new and novel proton conducting membrane materials capable of conducting protons at low relative humidity (RH), withstanding temperatures in excessive of 110°C and providing electrical insulation.
- Quantify extent of membrane performance enhancement compared to peer materials available in the market place.
- Reduce materials cost and develop simple manufacturing processes.
- Improve durability, dimensional stability, and thermal stability.
- Develop computational fluid dynamics (CFD) multiphase porous flow models to understand thermal and water-transport phenomena in proton exchange membrane (PEM) fuel cells as well as PEM fuel cell stacks.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance

(E) Thermal and Water Management

Technical Targets

This project is conducting fundamental studies to develop a new class of PEM materials capable of conducting protons at low RH. Insights gained from these studies will be applied toward the design and manufacturing of advanced membrane materials that meet the following DOE 2010 membrane materials targets:

- Cost: $20/m^2
- Conductivity at operating temperature (≤120°C): 0.1 S/cm
- Humidity range ≤50%
- Area specific resistance: 0.02 Ohm/cm^2
- Durability with cycling: at operating temperature (≤80°C) – 5,000 hours

Accomplishments

- Reduced Induction Time: Induction time (time required to start proton transfer) is 70% lower than Nafion[®] 212.
- Increased Proton Conductivity: 80% increase in proton conductivity compared to peer materials (Nafion[®] 212).
- Reduced Resistance: 71% lower resistance per unit area than peer (Nafion[®] 212) materials.
- Achieved steady proton transfer capacity at higher rate than Nafion[®] 212 for extended period of time.
- Developed inexpensive membrane materials and design simple manufacturing process capable of producing proton conducting membrane materials at a cost 60% below the DOE targets for 2010.
- Developed mathematical multiphase porous flow models for CFD analysis of a single PEM fuel cell as well as PEM fuel cell stacks.

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Introduction

Higher ionic conductivity, better mechanical strength, lower cost, and durability of proton conducting materials are all important issues to accelerate the commercialization of fuel cell technology. For near-

ambient temperature cells, polymer electrolytes (i.e. Nafion®) must be hydrated appropriately to support proton transport. Without complex high pressure systems, hydration is significantly reduced above 80°C though fuel cells ideally should operate at temperatures >110°C for heat dissipation reasons. Additionally, polymer membranes are easily degraded under high power and during on/off cycling. As such, polymer membranes need considerable improvement. Another concern is to thoroughly understand the water production and proton conduction mechanisms to minimize cathode electrode flooding and to ensure proper membrane hydration. During fuel cell operation, water within membranes is driven from the anode to the cathode by electro-osmosis, and at the same time is driven from the cathode to the anode by diffusion. If the cathode water generation is more than the water transport from the cathode to the anode, then cathode flooding results along with performance degradation. In this project, a novel approach to the design and fabrication of PEMs has been developed whereby a non-structural polymer fabricated for proton exchange capacity is bound to an inert polymer matrix. This fabrication technique separates the proton exchange and structural requirements of the PEM allowing greater flexibility in proton exchange membrane design. To benchmark the performance of the membranes we developed a theoretical model to quantify several physical quantities such as proton exchange capacity, resistance, conductivity, and induction time. The results suggest that there is now a new route for fabricating cost-effective PEMs for fuel cells applications wherein one may focus more on the proton exchange capacity of the membrane allowing the structural properties of the membrane to be considered separately.

Approach

- Use an inert, robust, mechanically and dimensionally stable polymer mesh that may be chemically modified on the surface to render it adhesive or chemically reactive.
- Use patented technology to prepare a proton exchange polymer media that has been designed primarily to have high proton exchange capability.
- Cast the proton exchange polymer media onto the robust polymer support to prepare the hybrid proton exchange membrane.
- Use mathematical model with an efficient and simple experimental method of testing the proton exchange characteristics of the new PEMs.
- Alter the composition of the proton exchange polymer media to optimize proton transport.
- Compare the performance of new proton exchange membrane materials with the peer materials such as Nafion® 212.

- Use finite element based computer software (COMSOL) for CFD analysis of thermal and water management of a unit fuel cell as well as fuel cell stacks.

Results

The patented technology [1] used in this study allows the attachment of the SAS (**s**tyrene-**a**crylonitrile-vinyl**s**ulfate) matrices to the ETFE (ethylene-tetrafluoroethylene) mesh. It's an inexpensive, benign water-borne process that results in the selective addition of chemical species to the polyethylene regions of the ETFE mesh allowing greater flexibility in design by separating the proton exchange and structural requirements of the PEM. A significant amount of effort was centered on formulation of a mathematical model to measure membrane properties at the manufacturing stage. The mathematical model developed and validated experimentally is documented in literature sources [2,3]. Properties of new membranes were compared with that of Nafion® 212. Figure 1 shows a plot of pH changes in the water cell for different membranes tested here following the method discussed in [2], as a function of time. The rate of change of pH was plotted against time to obtain a curve consisting of three segments: an initial slightly negative slope, a greater negative slope and then a final slightly negative slope. The initial and final slopes were generally very similar and were likely indicative of pH electrode drift. The curve was then separated into
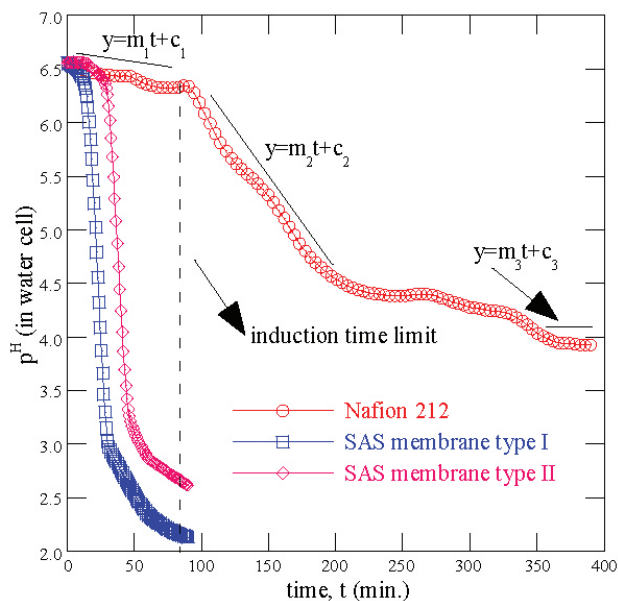

FIGURE 1. Experimental results for the change of pH in water cell as a function of time with different membranes [2]. Linear regression is fitted for each of the three distinct phases: induction phase, transfer phase and equilibrium phase. Slope of the curves denotes the pH change rate in each phase.

three separate curves, one for each region of different slope, and a linear regression line fitted to each curve segment with corresponding linear equations. The slope of each curve was obtained. The slope of the middle, strongly negative curve, represents the maximum rate of proton transfer per minute provided as the "change in negative log of the hydrogen ion (proton) concentration per minute" or $-\log[H^+]/min$. The two intersections of the three curves were then obtained to provide the onset of protons crossing the membrane and the attainment of pseudo-equilibrium. The slope was then converted to moles of protons to obtain the "change in concentration of protons/minute" and also multiplied by 6.02×10^{23} to obtain the actual number of protons per minute. From Figure 1 we can see clearly that the induction time varies for different membranes. Induction time has great impact on power supply from fuel cell during start-up [4]. We calculated the rate of change (slope) of pH for each of the tested membrane, using linear regression shown at the inset of Figure 1. Figure 2 represents the profile of proton flow as a function of time in water cell for various membranes obtained experimentally and the corresponding results obtained using the theoretical model [2]. For theoretical calculation, we used values of C_0 and C_f obtained experimentally through the rate of change of pH given in Figure 1. In Figure 2, experimental results and the theoretical results are indicated in parentheses. As we can see from Figure 2, there is excellent agreement between the experimental and theoretical profiles in all three phases. The peak of the protons' flow profiles represent the maximum rate of proton transfer. Among the profiles of proton flow for different membranes, SAS Type 1 PEM has the highest peak and Nafion® 212 has the lowest peak. It means that the SAS Type 1 PEM has a greater proton transfer capability than the Nafion® 212 membrane. Hence, we see that both the SAS type PEMs can transfer a higher number of protons per unit time than the commercial membrane Nafion® 212.

   To determine the relative resistance among membranes we calculated the proton transfer capacity and time required for each individual membrane to allow a specific amount of protons to pass through it. Table 1 represents both experimental and theoretical

results of maximum and average proton transfer capacity as well as minimum and average time required for each of the membranes examined here. Maximum proton transfer capacity is determine using the highest peak slope shown in Figure 2. On the other hand, average proton transfer capacity is calculated using the average slope in the entire transfer phase of the proton concentration profiles displayed in Figure 2. We can see from Table 1 that the experimental results agree well with the corresponding theoretical predictions. Comparing results among different membranes it can be seen that the SAS-type membranes have 81% higher proton transfer capacity than Nafion® 212 membrane. The relative resistance and induction times are shown in Table 2. SAS-type membranes have a shorter induction time. Comparing calculated results in Table 2 we can see that the SAS Type I membrane took the lowest time and Nafion® 212 membrane required highest time for
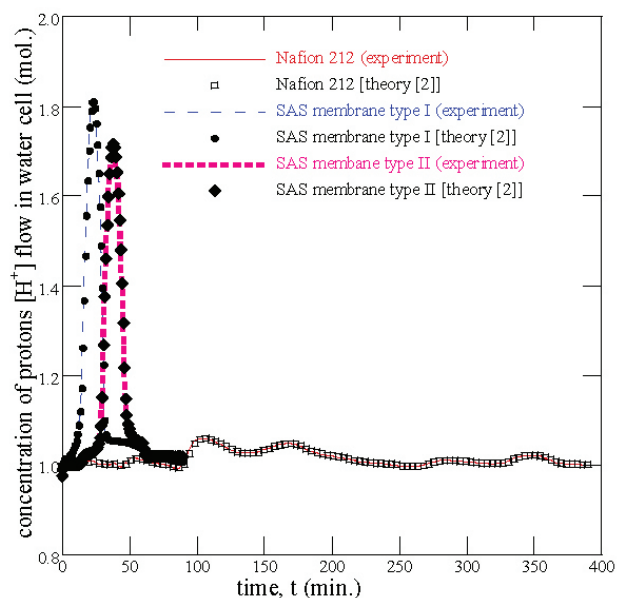

FIGURE 2. Concentration profiles of proton flow in water cell as a function of time with different membranes. Symbols represent theoretical model predictions [2]. Solid-, dashed- and dotted-lines represent experimental results for different membranes.

TABLE 1. Comparison of Proton Transfer Capacity among Different Membranes

Membrane Type	Maximum Proton Transfer Capacity (moles/min)		Average Proton Transfer Capacity (moles/min)		Minimum Time Required for Protons to Cross the Membrane (min/mole)		Average Time Required for Protons to Cross the Membrane (min/mole)	
	Experiment	Theory [Eq. (21) – (2)]	Experiment	Theory [Eq. (21) – (2)]	Experiment	Theory [Eq. (21) – (2)]	Experiment	Theory [Eq. (21) – (2)]
Nafion®	1.0593	1.0590	1.0321	1.0321	0.9440	0.9443	0.9689	0.9689
SAS Type I	1.8140	1.8121	1.7632	1.7631	0.5513	0.5518	0.5671	0.5672
SAS Type II	1.7174	1.7166	1.6707	1.6707	0.5823	0.5825	0.5985	0.5986

TABLE 2. Comparison of Induction Time and Relative Resistance among Different Membranes

Membrane Type	Induction Time (min) – (time required to start transfer proton) [Fig. 1]	Minimum Relative Membrane Resistance		Average Relative Membrane Resistance		Rank of Membrane Based on Low to High Relative Resistance
		Experiment	Theory [Eq. (22) – (2)]	Experiment	Theory [Eq. (22) – (2)]	SAS Type I
Nafion® 212	87.6045	1.71	1.71	1.76	1.76	SAS Type II
SAS Type I	15.0915	1	1	1.03	1.03	
SAS Type II	29.9235	1.06	1.06	1.09	1.09	Nafion® 212

starting proton transfer. The SAS Type I membrane started proton transfer within as little as 16 minutes whereas Nafion® 212 did not begin to transfer protons even after 87 minutes. For the case of relative resistance, we can see that Nafion® 212 membrane has 71% higher resistance compared to the SAS Type I membrane. Once again, for determining relative resistance among membranes, the experimental results are in excellent agreement with the results obtained from theoretical model as can be seen from Table 2. Based on the resistance we can rank the membranes. As per our results of tested membranes, SAS Type I has rank 1 and Nafion® 212 has rank 3. Thus using the developed two-cell model [2] and simple experimental set-up [2] we can measure relative resistance of membranes at least at the time of manufacturing.

Conclusions and Future Directions

From FY 2006 up to date has resulted in a great expansion in knowledge with manufacturing processes of PEM materials and testing their properties. We now understand the manufacturing process of new materials and the performance validation process in quantitative terms. We have a good understanding on the polymer chemistry, thermodynamics and kinetics. This information is critical to develop new membrane materials for fuel cell applications where chemical treatment, polymer casting, and performance evaluations are going to be of utmost importance. In this year we intend to continue evaluation of membrane properties and begin to study some compounds for cross-linking agent which will increase the stability of new membrane materials.

Although the DOE deliverables have been achieved, the following membrane attributes are necessary to further evaluate the membrane performance:

- Refining manufacturing process to reduce the cost and use of low-cost raw materials.
- Test the conductivity over the entire temperature and humidity range (e.g., operation up to 120ºC).

- Test the thermal stability of the membrane over the entire temperature and humidity range.
- Implement CFD two-phase porous flow model in single fuel cell as well as fuel cell stacks for designing improved water management strategies.

FY 2007 Publications/Presentations

1. *Two-cell theory to measure membrane resistance based on proton flow: Theory development and experimental validation*, Susanta K. Das and K. Joel Berry, Journal of Power Sources, 2007 (submitted).

2. *Polymer Mesh Supported Proton Exchange Membrane: Manufacturing Process and Performance Validation*, Susanta K. Das, Beholz, L., Hendrick, J., Ali R. Zand and K. Joel Berry, Journal of Advanced Functional Materials, 2007 (submitted).

3. *Improved Performance of Proton Exchange Membrane Materials for Fuel Cell Applications*, Susanta K. Das, Panini Kolavennu, J. Hedrick, Beholz, L., Ali R. Zand, K. J. Berry and Etim U. Ubong, Journal of Fuel Cell Science and Technology, 2007 (submitted).

4. *Improved Performance of Proton Exchange Membrane Materials for Fuel Cell Applications*, Susanta K. Das, Panini Kolavennu, J. Hedrick, K. J. Berry and Etim U. Ubong, ASME Fuel Cell Conference, held on June 18–20, New York, 2007.

5. *Advanced Proton Exchange Membrane for Fuel Cell Applications*, Susanta K. Das, Beholz, L., Hendrick, J., Ali R. Zand and K. Joel Berry, Fuel Cell Seminar, to be held on October 15–19, San Antonio, Texas, 2007.

6. *Control Oriented Model with Improved Membrane Hydration of PEM Fuel Cell Stacks*, Panini Kolavennu, Susanta K. Das, and K. J. Berry, The Second European Fuel Cell Technology and Applications Conference, to be held on December 11–14, Rome, Italy, 2007.

7. *Proper Flow Channel Design for Uniform Distribution of Gas in PEM Fuel Cell Stacks*, Susanta K. Das, and K. J. Berry, The Second European Fuel Cell Technology and Applications Conference 2007, to be held on December 11–14, Rome, Italy.

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2. Susanta K. Das and K. Joel Berry, *Two-cell theory to measure membrane resistance based on proton flow: Theory development and experimental validation*, Journal of Power Sources, 2007 (submitted).

3. Susanta K. Das, Beholz, L., Hendrick, J., Ali R. Zand and K. Joel Berry, *Polymer Mesh Supported Proton Exchange Membrane: Manufacturing Process and Performance Validation*, Journal of Advanced Functional Materials, 2007 (submitted).

4. Larminie J. and Dicks A., *Fuel cell systems explained*, John Willey & Sons, New York, 2000.