V.M.15 Design and Development of High Performance Polymer Fuel Cell Membranes

Ryo Tamaki (Primary Contact), Steven T. Rice, Joseph A. Suriano

GE Global Research
One Research Circle
Niskayuna, NY 12309
Phone: (518) 387-4572; Fax: (518) 387-5336
E-mail: tamaki@research.ge.com

DOE Technology Development Manager:
Ingrid M. Milton

Phone: (202) 586-1507; Fax: (202) 586-9811
E-mail: Ingrid.Milton@ee.doe.gov

DOE Project Officer: David Peterson

Phone: (202) 586-9583; Fax: (202) 586-9811
E-mail: David.Peterson@go.doe.gov

Technical Advisor: John Kopasz

Phone: (630) 252-7531; Fax: (630) 972-4405
E-mail: kopasz@cmt.anl.gov

Contract Number: DE-FG36-06GO16034

Project Start Date: April 1, 2006
Project End Date: March 31, 2011

Objectives

- Design and synthesize cross-linked polyelectrolyte in porous supports with high acid concentration
- Demonstrate proton conductivity (0.1 S/cm at 120°C, 25% relative humidity), economic feasibility ($20/m^2), and durability with temperature and humidity cycling (2,000 h at >80°C) of best membranes

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

Technical Targets

The goal of this project is to design, synthesize, and characterize new polymer electrolyte membrane (PEM) materials to improve performance at high temperature and low relative humidity (RH). These materials will be designed to meet the DOE 2010 targets (see Table 1) for fuel cell membranes for transportation applications, particularly:

- Proton conductivity: 0.1 S/cm at 120°C, 25% RH
- Cost: $20/m^2
- Durability: 2,000 h at temperatures >80°C

TABLE 1. Progress Towards Meeting Technical Targets for Membranes for Transportation Applications

Characteristics	Units	2010/2015 Targets	FY 07 GE Status
Conductivity	(S/cm)	0.1/0.1	0.11
Temperature	(°C)	≤120	80
Inlet Water Vapor Pressure	kPa	1.5	
RH	(%)	25	75

Accomplishments

- Designed and prepared cross-linked electrolytes in porous supports with high acid concentrations
- Demonstrated high proton conductivities at 80°C: 0.22 S/cm (100% RH), 0.11 S/cm (75% RH), 0.02 S/cm (50% RH)

✧   ✧   ✧   ✧   ✧

Introduction

The performance of existing perfluorosulfonic acid (PFSA)-based and hydrocarbon-based membrane materials over a wide range of temperatures and relative humidity strongly indicates that entirely new polymer materials must be developed to achieve commercially viable high temperature PEM fuel cells. Currently, no membrane materials meet DOE's targets of high conductivity (>0.1 S/cm) at high temperature (120°C) and low relative humidity (25-50%). Many promising materials exhibit high proton conductivities at 100% RH, but water uptake and swelling data indicate that large weight increases and dimensional changes also occur. Dimensional stability is absolutely crucial to the

development of viable PEM materials. Therefore, all new polymer materials must also show a good balance of water uptake and proton conductivity.

GE has developed first- and second-generation PEM materials based on engineering thermoplastic polymers. This work has clearly shown that proton conductivity, water uptake, and mechanical properties can be improved by controlling the polymer architecture, which strongly influences the resulting membrane morphology. Third-generation membrane materials based on thermally stable aromatic hydrocarbon polymer architectures were designed to promote the formation of membrane morphologies that demonstrated good balance of proton conductivity and lower water uptake by enhancing hydrophilic/hydrophobic phase separation. Hydrophilic/hygroscopic organic additives were also designed to help retain water in combination with third-generation polymers. However, significant improvements in conductivities were not observed with these additives. The results of having concentrated proton conducting functionalities in the membrane are promising, as demonstrated with the block functionalized polymers. However, it is believed that the maximum proton conductivity in these thermoplastic PEM materials may be limited by the water solubility. Since none of these materials has conductivity greater than 0.07 S/cm, further work will focus on increasing proton conductivity with more concentrated proton conducting functionalities utilizing new methodology.

Approach

We shifted our main focus from the thermoplastic polymer approach to new methodology in order to have more concentrated proton conducting functionalities. With higher acid concentration, thermoplastic polymers become more soluble in water and suffer possible leaching during fuel cell operation. Another problem is that with higher acid concentration, the polymers tend to have higher water uptake and swelling, thus compromising the dimensional stability and the operation lifetime. Our approach for the achievement of the high acid concentration as well as prevention of the leaching and the suppression of swelling is to introduce cross-links to polyelectrolyte.

Generally, however, these cross-linked materials tend to be brittle, especially when they have high cross-link density. We employed porous supports to prevent mechanical failure. The cross-linked electrolytes are imbedded inside the porous supports which render the mechanical strength. Thus, even with high cross-linking density, membranes with high mechanical stability were obtained.

Results

Cross-Link Chemistry A

First, acid unit-A was polymerized by itself and imbedded in a porous support without a cross-link unit to evaluate its conductivity performance. Proton conductivity was determined by standard 4-point AC impedance measurements at 80°C over 25-100% RH. The electrolyte membrane demonstrated reasonably high proton conductivity through a wide range of RH. Above 50% RH, the numbers even exceed Nafion[®] 112, reaching 0.26 S/cm at 100% RH. At 80% RH, the conductivity is 0.11 S/cm. However, due to the insufficient cross-links, the polymerized acid-unit A was partially soluble in water and 70 wt% was lost upon water extraction test (100ºC for 2h).

Following the above observation, the effect of cross-links on the weight loss and the conductivity was studied. The weight losses by extraction test at various temperatures were suppressed by increasing the amount of the cross-link unit. Weight loss was determined by immersing the sample at 30°C, 60°C, 85°C, and 100°C in series comparing the wet weight at each temperature to the original weight before the extraction test. Total weight loss was also calculated by drying the film after 100ºC extraction. The total weight loss indicates how much of the material leached from the membrane after extraction tests at 30, 60, 85 and 100°C. The total weight loss was reduced from 70% without the cross-link unit to 18% with the cross-link unit (at [cross-linker]/[acid unit] ratio 12). However, the conductivities decreased to 0.013 S/cm at the same time with the increase in the cross-link concentration, due to the dilution of the acid groups in the membrane (Figure 1).

We tried different curing conditions such as temperatures or catalysts. However, significant reduction of the weight losses could not be achieved
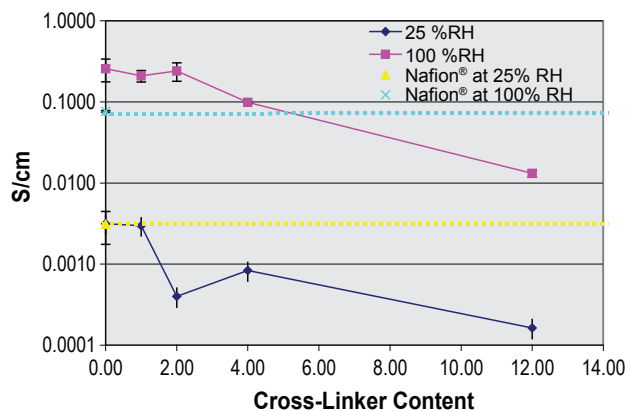

FIGURE 1. Conductivities at 25% RH and 50% RH vs. [cross-linker]/[acid unit A] Ratio

regardless of the reaction conditions. We concluded that the problem is intrinsic to the cross-link chemistry A and decided to try another cross-link chemistry for the formation of polyelectrolyte.

Cross-Link Chemistry B (Gen 4B) – toward higher stability against water extraction

The cross-link chemistry B was applied to the formation of polyelectrolyte. The electrolyte was imbedded inside a porous support as done with cross-link chemistry A. As shown in Figure 2, the conductivity of the new polyelectrolyte (R423-15-1) was found to be comparable to Nafion®. More importantly, the weight loss after 100ºC/2h was found to be negligible, which promises the higher potential of this approach for the formation of more stable polyelectrolyte films.

With assurance of this preliminary result, the optimization in the coating condition to a porous support was carried out. Porous supports with different pore size and porosity were studied. Solvent used for the coating was also optimized to obtain more uniform coating on the porous supports. The results of these experiments were shown in Figure 2. As demonstrated, the optimization in these factors increased the conductivity. 0.22 S/cm and 0.11 S/cm were observed
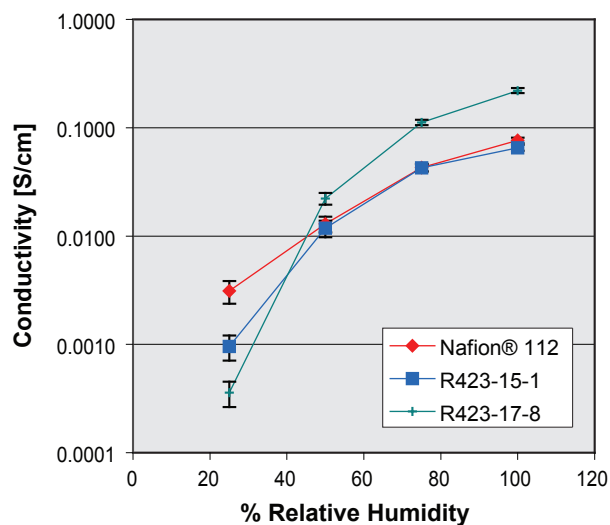
at 100% RH and 75% RH, respectively (Figure 2, R423-17-8). These numbers meet Y2 DOE targets.

It was notable that the polyelectrolyte obtained from this cross-link chemistry B demonstrated high thermal stability. The electrolyte demonstrated the onset of decomposition temperature at 563ºC with the alkaline salt form. The temperature changed to 285ºC and 550ºC after acidification due to the stability of the acid. The study, however, demonstrated the high stability of the polyelectrolyte matrix (Figure 3).

Water uptake and dimensional changes were studied with Gen 4B membrane. Due to the high acid concentration, the membrane exhibited high water uptake reaching 280% at 30ºC, which is much higher

FIGURE 2. Conductivity at 80ºC - Optimization of Coating Condition and Various Supports with Gen 4B
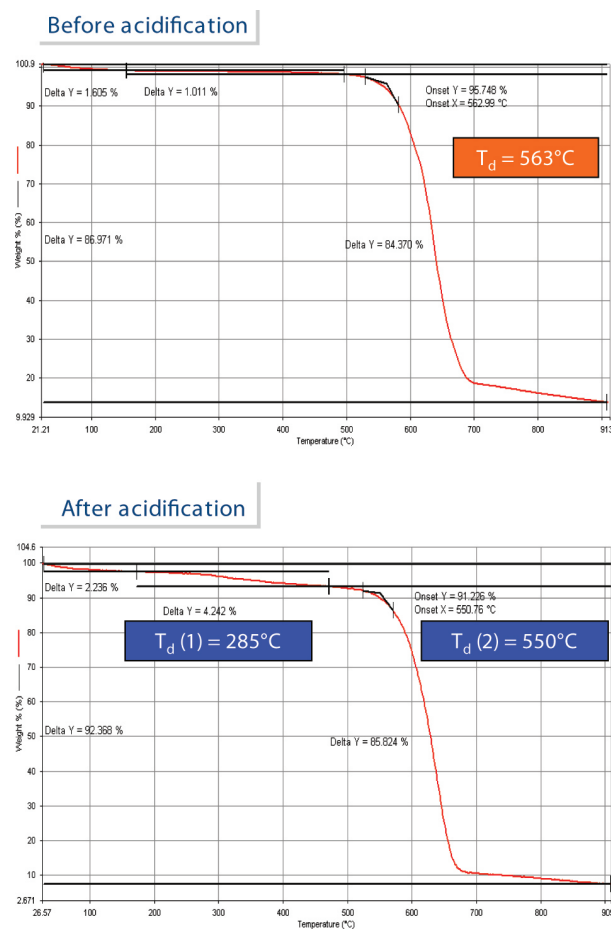

FIGURE 3. Thermal Gravimetric Analysis of Gen 4B Before and After Acidification

compared to 55% of Gen 2 (engineering thermoplastic polymers). However, dimensional changes, especially thickness change, are comparable or smaller compared to Gen 2 (Figure 4).

Conclusions and Future Directions

Alternative cross-link chemistry B was found to be more promising than cross-link chemistry A in terms of stability against water extraction, indicating much higher potential for the long-term operation. However, the water uptake is higher than previous generations and dimensional changes still need to be improved. Furthermore, although high conductivity was observed above 50% RH, the conductivity is yet to be improved to meet the Y3 goal (0.1 S/cm at 50% RH/120ºC). The ultimate conductivity goal is 0.1 S/cm at 25% RH. In the future, these issues will be studied more thoroughly. To further increase conductivity, we will:

- Evaluate the effect of acid/cross-link ratios on the conductivity
- Study the effect of inorganic additives on the conductivity
- Evaluate the effect of pore size, porosity and thickness of porous supports on conductivity

FY 2007 Publications/Presentations

1. Presentation at 2007 DOE Hydrogen Program Review – May, 2007, Arlington, VA.
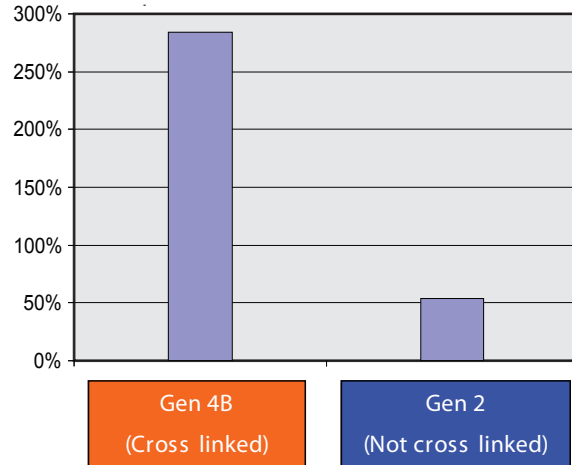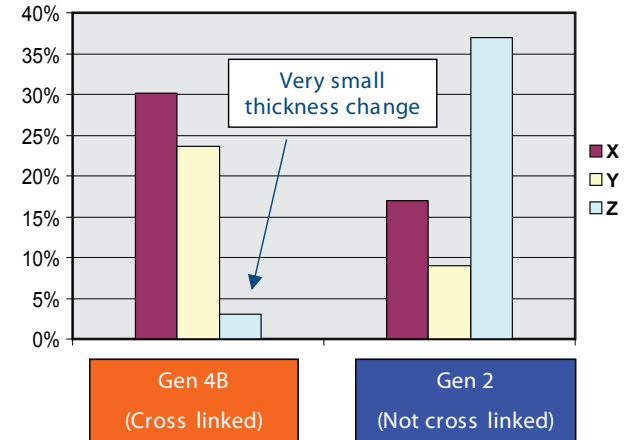

FIGURE 4. Comparison of Water Uptake and Dimensional Changes between Gen 4B and Gen2