

V.C.9 Low-Cost Proton Conducting Membranes for PEM Fuel Cells

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- (A) Durability: Membrane and membrane electrode assembly durability
- (B) Cost: PEM that is much cheaper than Nafion membranes
- (C) Performance: High membrane electrode assembly performance at low relative humidity and high temperatures

Technical Targets

Table 1 lists DOE's technical targets with regard to fuel cell membranes for transportation applications.

TABLE 1. DOE Technical Targets: Fuel Cell Membranes for Transportation Applications

Characteristics	Units	2020 Target
Maximum operating temperature	°C	120
Area specific proton resistance at:		
Maximum operating temperature and water partial pressures from 40 kPa to 80 kPa	Ohm cm ²	≤0.02
80°C and water partial pressure from 25–45 kPa	Ohm cm ²	≤0.02
30°C and water partial pressure up to 4 kPa	Ohm cm ²	≤0.03
-20°C	Ohm cm ²	≤0.2
Maximum oxygen cross-over	mA/cm ²	2
Maximum hydrogen cross-over	mA/cm ²	2
Minimum electrical resistance	Ohm cm ²	1,000
Cost	\$/m ²	≤20
Durability:		
Mechanical	Cycles with <2 mA/cm ² crossover	≤20,000
Chemical	Hours	≥500

Overall Objectives

- Develop a low-cost, high-performance proton conducting membrane for polymer electrolyte membrane (PEM) fuel cells. Determine the best material system for the new PEM.
- Establish a suitable process for fabrication of the new PEM.
- Characterize the new PEM in terms of physical and chemical properties.
- Test the new PEM under fuel cell conditions.
- Evaluate economical significance of the new PEM.

Fiscal Year (FY) 2016 Objectives

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Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

This project is developing a new type of proton conducting membrane to meet the DOE targets in all facets. It will present not only high proton conductivity and fuel cell performance over a wide range of temperature and humidity conditions, along with high chemical stability and mechanical durability, but also low cost to meet the targets in the membrane cost (≤\$20/m²). As the new membrane will be very thin, the DOE targets of low area specific proton resistance, as shown in Table 1, can also be easily met.

FY 2016 Accomplishments

New PEM samples of 15–20 μm have been prepared. The new PEM shows high mechanical durability and chemical

stability, high proton conductivity, and low area specific proton resistance, promising to meet the DOE targets.



INTRODUCTION

Polymer electrolyte membrane fuel cells represent a promising power source for a variety of applications. They are a leading candidate to power zero emission vehicles, with several major automakers already in the early stages of commercializing fuel cell powered vehicles. Fuel cells are also of interest for stationary power applications, including primary power, backup power, and combined heat and power. While many breakthroughs have been made over the last few years in the development of fuel cells, technical and economic barriers for their wide spread commercialization still exist. Key areas where improvements are still needed are in expanding the temperature range and lowering the humidification requirements of the stack. For transportation applications, requirements of system size, efficiency, performance, start-up and cooling mean that fuel cells must be able to run robustly and exhibit adequate durability under a wide variety of operating temperatures, including temperatures up to 120°C. They must also be able to do this with little or no external gas humidification (i.e., “dry”), and during start-up, shut-down, or periods of lower stack temperatures, they must run in the presence of, and be stable to, some liquid water in the gas channels. The polymer electrolyte membrane, typically being PEM, is the key component in PEM fuel cells that critically determines the system performance and its economic viability. Presently, the state-of-the-art PEMs, such as Nafion® membranes, are based on perfluorosulfonic acid (PFSA) ionomers. But these ionomer materials are expensive, particularly at the low volumes that will be needed for initial commercialization. Besides, they are not suitable for fuel cells operated beyond 100°C, because of the limitations connected to the humidification requirement of such membrane materials, limiting the maximum operating temperature to about 90°C. Non-PFSA polymer electrolyte membranes, including those based on hydrocarbon membranes, represent a lower-cost alternative, but relatively low performance and durability has limited applications of these alternative membranes to date. Therefore, DOE is seeking new approaches in the development of novel non-PFSA ionomers and PEMs for fuel cells.

Amsen Technologies LLC chooses to address the DOE call with a novel reinforced PEM approach based on new, non-PFSA proton conducting ionomers developed from our previous DOE Small Business Innovation Research projects. The reinforcement scheme will make the membrane highly durable yet very thin (15–20 μm). As such, the new proton conducting membrane to be developed is expected to meet the DOE targets in all facets.

APPROACH

Amsen Technologies LLC will develop a novel reinforced PEM based on new, non-PFSA proton conducting ionomers developed from our previous DOE Small Business Innovation Research projects. Specifically, Amsen has developed a low-cost, non-PFSA proton exchange membrane from cheap commodity polymers for redox flow battery applications. Several new proton conducting ionomers have been synthesized for the first time based on copolymers of a ternary system with a poly(vinylidene fluoride) (PVDF) backbone. Unlike some widely-reported hydrocarbon-based ionomers, such as sulfonated poly(ether ether ketone) and sulfonated polysulfone, which are single polymers and have a serious stability problem, our new ionomers are all copolymer in nature, and are highly stable even in the highly acidic and oxidizing vanadium redox flow battery electrolyte. These new ionomers showed higher ion-exchange capacity (IEC) and proton conductivity than Nafion. PEMs made from these ionomers have shown significant potential of not only lower cost than the Nafion membranes, but also superior properties to the Nafion membranes in some aspects, including higher proton conductivity (0.0786 S/cm at room temperature (20°C) and full hydration state, in contrast with 0.0611 S/cm for Nafion 117, measured under the same conditions, showing an increase of 28%), and better performance in vanadium redox flow batteries.

Our effort in development of the new PEM has been distinctly differentiated from many other researchers who have been working in the development of PVDF-based PEMs, in that our new PEM was formed as a whole from ionomer resins that were independently developed and synthesized in our company, while many other researchers produced the PVDF-based PEM by merely surface modification of existing PVDF films. For instance, a PVDF-based PEM was reportedly made by grafting the surface of a commercial available PVDF film with styrene and dimethylaminoethyl methacrylate using γ -irradiation techniques, followed by sulfonation and protonation processes [1]. Most of the reported efforts on PVDF-based PEMS use similar approaches as the referenced one. Apparently, such surface-modification approach has limited potential of producing fundamentally new PEM, because it does not produce new ionomer resins. In contrast, our products are new ionomer resins, from which new PEMs are formed.

However, there are still two major challenges in using our new ionomers to fabricate the new fuel cell PEM meeting the DOE targets: increased durability and significantly reduced thickness. According to the DOE targets, the fuel cell membrane should mechanically withstand $\leq 20,000$ humidity cycles with < 2 mA/cm² crossover of gases, and chemically withstand > 500 h in the fuel cell environment. In the meantime, in order to meet the DOE targets for the low area specific resistance (≤ 0.02 ohm-cm²) and the low cost (≤ 20 \$/m²), the membrane should be very thin (preferably

10–20 μm). Therefore, our current thrust in the present effort is to make the new PEM highly durable yet very thin (≤ 20 μm). Our approach is to reinforce the membrane with ultra-thin microporous polyolefin meshes. This would result in ultra-thin membranes with significantly enhanced durability, which would likely meet all of the technical and cost targets set by DOE.

The prepared PEM membranes will be systematically characterized in terms of relevant physical and chemical properties to demonstrate feasibility of meeting the DOE targets.

RESULTS

In the present project, the new ionomer developed by Amsen has been further optimized. Sample membranes of the new PEM have been successfully prepared by immobilizing the ionomer matrix on the microporous polyolefin reinforcement support. Figure 1 shows a typical sample membrane of the new PEM prepared at Amsen. The critical variables in fabricating the new PEM include the pre-treatment of the microporous polyolefin mesh support, the solvent used to dissolve the ionomer resin into a solution, and the heat-treatment schedule to cure the membrane. With appropriate selections of these variables, the process for integration of the ionomer matrix with the reinforcement support is simply pulling the microporous polyolefin mesh support through the ionomer solution, by which the microporous mesh support is impregnated with the ionomer solution. Then the formed PEM membrane is laid on glass plate and cured at elevated temperatures up to 160°C by a designated heat-treatment schedule.

The pre-treatment of the polyolefin meshes is a significant step of the processing, bringing in two merits to the reinforcement support: First, the originally hydrophobic meshes are modified to be hydrophilic, so as to facilitate the



FIGURE 1. A sample membrane of the new PEM prepared at Amsen

impregnation of the ionomer solution. Second, the originally inert polyolefin surfaces are activated with reactive moieties so as to ensure chemical bonding between the reinforcement support and the ionomer matrix immobilized on it. Therefore, the microporous polyolefin mesh support not only provides mechanical reinforcement to the membrane, but also leads to significant enhancement in chemical stability of the membrane.

The heat-treatment in curing the formed membrane is another significant step of the processing, in that optimized heat-treatment schedule needs to be determined to attain high crosslinking within the ionomer matrix as well as maximum chemical bonding between the reinforcement support and the ionomer matrix.

The resultant membranes are very thin and highly flexible, with thicknesses typically ranging from 15–20 μm . Yet they are quite tough and strong, with tensile strengths measured at about 1,500 kgf/cm^2 , increased by more than one order of magnitude relative to the non-reinforced membranes made from the same ionomer.

Proton conductivity measured from the new PEM is as high as 0.1–0.12 s/cm at room temperature and full hydration state, which is nearly twice of that for Nafion membranes. However, to be conservative we have used the lowest values measured to plot the Arrhenius plots of proton conductivity of the new membrane at 100% relative humidity, as shown in Figure 2. Even with the lowest values as shown, proton conductivity of the new membrane exceeds that of Nafion membranes by over 25%. With the high proton conductivity and the low membrane thickness, it is expected that the DOE

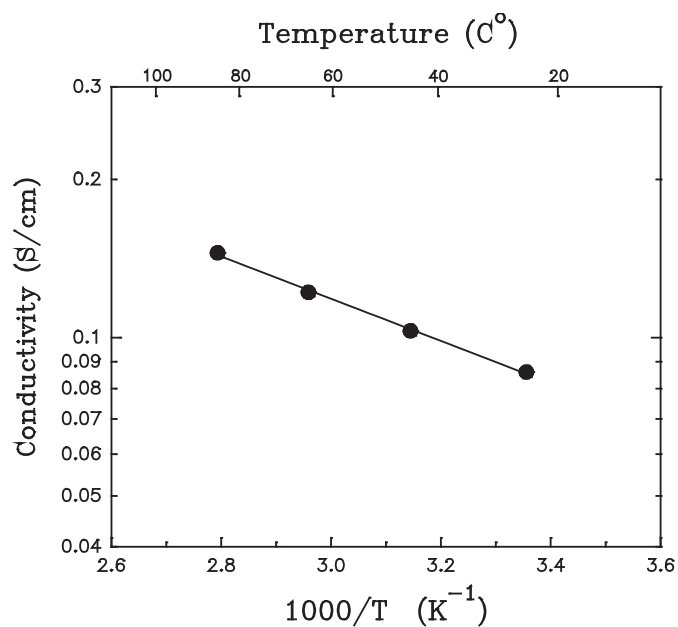


FIGURE 2. Arrhenius plots of proton conductivity of the new membrane at 100% relative humidity

targets of low area specific proton resistance, as shown in Table 1, can be easily met.

Tests conducted so far revealed that these membranes are quite chemically stable and mechanically durable. First, we have exposed the membranes to different environments (1 M hydrogen peroxide at 75°C for overnight; 1 M H₂SO₄ at 90°C for overnight; and water at 90°C for overnight), and have not observed any conductivity loss after such exposures. Furthermore, we have used hydration-dehydration cycling as one of the stability tests. No conductivity loss was observed after more than 10 times of such cycling. Still another method we have used in evaluating stability of the membrane is keeping the membrane sample in water, and periodically measuring its conductivity over a period of time. The results of this test also suggest high stability of the membrane, as no change in conductivity was observed over three weeks.

As the ionomer matrix is strongly confined by the reinforcement support, the new PEM attains high dimensional stability. The dimension change along x-y plane upon hydration is minimum (less 3%, almost no expansion along x-y plane at full hydration), while the expansion along z-axis is 20–25% at full hydration.

Some samples of the new PEM have been sent to Los Alamos National Laboratory for independent testing, while we keep working on further development and evaluation of the new membrane for the remaining three months of the present project.

CONCLUSIONS AND FUTURE DIRECTIONS

New PEM samples of 15–20 μm have been prepared. The new PEM shows high mechanical durability and chemical stability, high proton conductivity, and low area specific proton resistance, promising to meet the DOE targets. In the remaining three months, we will keep working on the project to complete the Phase I work as planned, including:

- Determine the best material system for the new PEM.
- Establish a suitable process for fabrication of the new PEM.
- Characterize the new PEM in terms of structural and microstructural features.
- Characterize the new PEM in terms of physical and chemical properties including maximum operating temperature, proton conductivity and area specific proton resistance in a range of temperature and humidity conditions, oxygen crossover, hydrogen crossover, resistance to electronic conduction, and mechanical and chemical durabilities.
- Test the new PEM under fuel cell conditions.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. H. Hu, “Low-Cost Proton Conducting Membranes for PEM Fuel Cells,” Poster presentation at 2016 Hydrogen and Fuel Cells Program Annual Merit Review meeting, Washington D.C., June 2016.

REFERENCES

1. Qiu J, Zhang J, Chen J, et al. “Amphoteric ion exchange membrane synthesized by radiation-induced graft copolymerization of styrene and dimethylaminoethyl methacrylate into PVDF film for vanadium redox flow battery applications,” *Journal of Membrane Science*, 334, 9-15 (2009).