V.C.2 Advanced Hybrid Membranes for Next Generation PEMFC Automotive Applications

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Project Start Date: October 1, 2013
Project End Date: September 30, 2016

Overall Objectives

- Fabricate a low-cost, high-performance proton exchange membrane to operate at the temperature of an automotive fuel cell stack, and requiring no system inlet humidification
- Optimize the membrane to meet durability, cross-over, and electrical resistance targets
- Incorporate the membrane into a 50-cm^2 membrane electrode assembly

Fiscal Year (FY) 2014 Objectives

Show that heteropoly acid (HPA) containing films can be fabricated thin and have a low area-specific resistance (ASR) at the temperature of an automotive fuel cell stack

- Increase HPA loading and organization for maximum proton conduction in two different perfluorinated polymer systems
- Demonstrate that a zirconium phosphonate polymer system is competitive with HPA-based polymer systems

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:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

The technical targets are shown in Table 1

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

	DOE Target 2017 ASR, Ω cm^2	**Result** Ω cm^2	**Thickness** µm	**Conditions**
System I, TFVE-HPA	<=0.02	0.04	16	80ºC 95% RH
System II, Dyneon-HPA	<=0.02	<=0.02	5-27	80ºC 95% RH
System III, ZrP/VPA	<=0.02	0.05	149	60ºC 95% RH

RH – relative humidity; VPA - vinyl phosphoric acid

FY 2014 Accomplishments

- Showed that development of membranes that eliminate the need for the system humidification system will lower system costs to <$40/kW.
- Using highly purified trifluorovinyl ether (TFVE) monomers synthesized next generation HPA-based proton conductors.
- Showed that TFVE-HPA polymers fabricated from material stable to boiling water can be fabricated into thin films with low ASRs.
- Demonstrated HPA attachment to commercial Dyneon™ polymers with desirable mechanical properties.
- Showed that zirconium phophonate polymers can be fabricated into a novel proton conducting film with low ASR under vehicular operating conditions.

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INTRODUCTION

The objective of this project is to fabricate a low-cost high-performance hybrid inorganic/polymer membrane that has a proton ASR <0.02 ohm cm^2 at the operating temperature of an automotive fuel cell stack (95-120°C) at water partial pressures from 40-80 kPa with good mechanical and chemical durability. Additionally the membrane will be optimized for low hydrogen and oxygen crossover with high electrical ASR at all temperatures and adequate proton ASR at lower temperatures. We also seek to gain valuable insights into rapid proton transport at the limit of proton hydration. Additional research will be performed to incorporate the membrane into a 50-cm^2 membrane electrode assembly (MEA). The materials at the start of this project are at a technology readiness level (TRL) of 2, as we have shown that they have proton conductivity under high and dry conditions, but we have not yet consistently shown that they will function in an operational fuel cell. At the project's end the materials will be at a TRL of 4 and will be integrated into an MEA, demonstrating that they can function with electrodes as a single fuel cell. This work will enable hydrogen-powered fuel cells as it will negate the need for costly and bulky external humidification unit operations in the fuel cell system. Additionally excess water will not be an issue for freeze or fuel cell reactant supply. The project is addressing the 2017 DOE technical targets for membranes for transportation applications.

APPROACH

In past funding from the Department of Energy/National Science Foundation we have developed completely new ionomer systems based on incorporation of inorganic super acids into polymer systems, which have high proton conductivity under conditions of low humidity, higher temperature operation, high oxidative stability, and little swelling when wet. This project will perform the work to optimize the proton conductivity and mechanical properties in these materials to produce a robust thin film for proton exchange membrane (PEM) fuel cells in automotive applications. The technical concept is to use functionalized inorganic super acids that utilize little water for high proton conductivity, as the protogenic group covalently attached to a polymer backbone optimized for all other functions of the membrane.

Many composite inorganic/polymer films have been fabricated, but unless the particles have dimensions on the nano-scale there is no advantage as the improvement to film properties occurs at the particle polymer interface. The limit of this approach is to use molecules with high acidity as the highly activating functionalities, but to do this we must immobilize them, control the morphology of the proton conducting channel, and fabricate an amorphous material. The two moieties that have received the most attention and appear to greatly enhance proton transport are HPAs and zirconyl phosphonates. In previous work, we demonstrated both composite membranes and true inorganic/polymer hybrid materials with very high proton conductivity, but the inorganic super acid in the membrane was not immobilized and the inorganic/polymer hybrid material transformed into undesirable crystalline phases at low RH. These materials are not yet fuel cell ready. In this project, we will overcome all of these disadvantages with an innovative approach to amorphous materials to produce high proton conductivity and all other properties desired of a PEM.

RESULTS

Work was performed on three polymer systems that have all shown promising proton conductivities under automotive fuel cell operating conditions. Progress towards making fuel cell ready membranes for each is described below.

System I: TFVE-HPA

For the TFVE system to work well we needed very pure monomers as any material without a perfluorinated ether is not polymerizable. In the first quarter of the year we demonstrated that we could make these small molecules extremely pure. The HPA functionalized monomer is shown in Figure 1. This monomer is easily polymerized via a thermal process in which the perfluoro vinyl ethers combine to make perfluorocyclobutane linkages, as shown in Figure 1. The system is very versatile in that there are a large number of additional monomers that can be used to form co-polymerized materials which can be tailored to have desirable properties for incorporation into MEAs. We also have the option of forming the polymers in the presence of binders such as PVDF-HFP or perfluorinated sulfonic acid (PFSAs) such as the 3M ionomer. As our objective here is fuel cell ready materials all polymers made are first boiled in water to ensure that they will be stable to liquid water during operation. The resultant materials are then recast into thin films for further testing.

Some of our preliminary data is shown in Figure 2. These films are inherently brittle and so an easy way to form them into films is to blend them with other polymers with good film forming properties. Surprisingly the film using PVDF-HFP out performs the film fabricated with 733 equivalent weight 3M ionomer. The reasons for this are not clear, but may indicate that as the HPA mediates proton conduction differently than a PFSA that the PFSA may be slowing down proton transport in these films. Recently we have successfully made free standing films of the TFVE-HPA polymer by using a hot press. Thin films, <20 µm, have shown ASRs of 0.04 Ω cm^2.

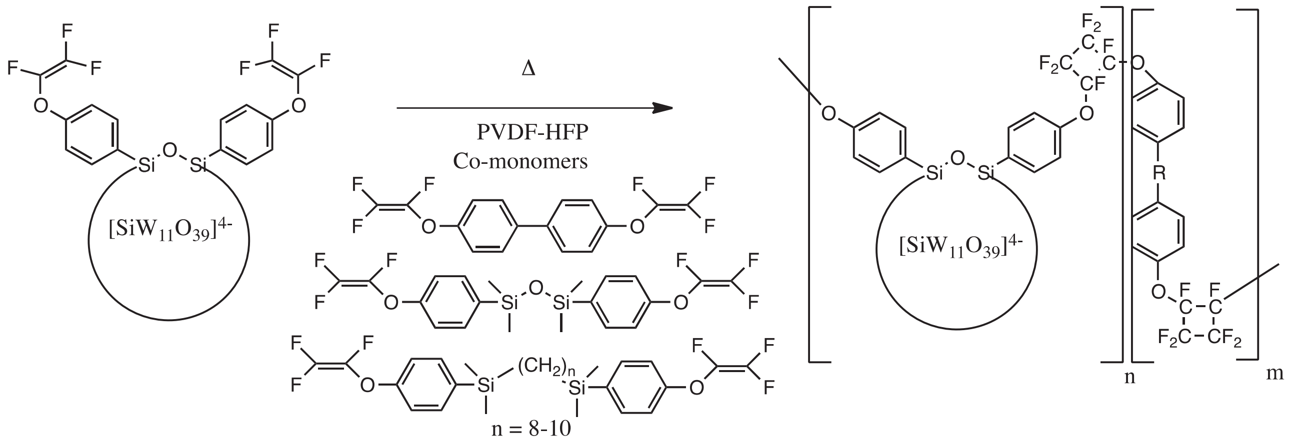

FIGURE 1. Monomers and the synthesis of the trifluorovinylether HPA functionalized polymer.

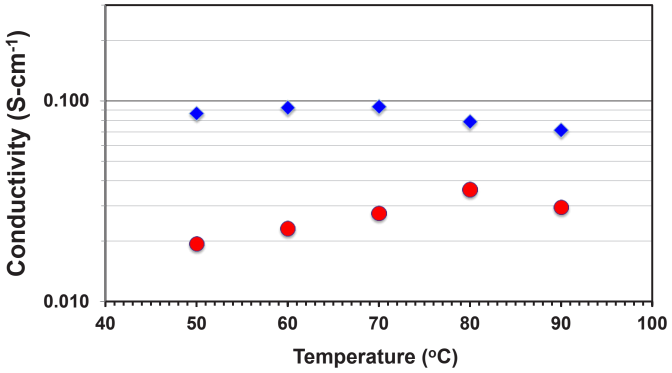

FIGURE 2. Proton conductivity data at 95% RH for 73% $H_8SiW_{11}O_{39}[(TFVE)_2O]$, 19% TFVE-C10 dimer, 8% PVDF-HFP, diamonds, 71% $H_8SiW_{11}O_{39}[(TFVE)_2O]$, 23% TFVE-C10 dimer, 6% 3M PFSA 733 equivalent weight, circles, both films >100 µm.

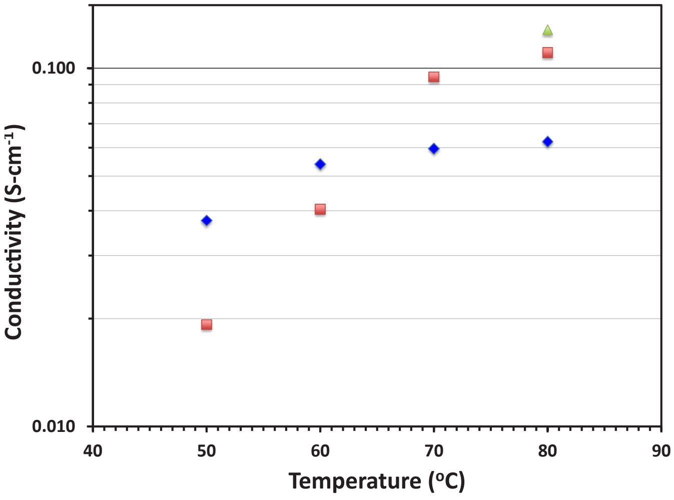

FIGURE 3. Proton conductivity data for a Hybrid HPA-3M Dyneon™ Ionomer, at 95% RH, progress in April (diamonds), August (squares) and membranes that passed the Year 1 Go/No-Go decision point (triangles).

System II: Dyneon-HPA

In the second system that we have been working on, we chemically modify the 3M material Dyneon™ so that we can attach HPAs to it. This is a multi-step process with manipulations to the polymer. We found this to be somewhat cumbersome so we are now initiating a procedure where a small molecule is built up first for attachment to the polymer in a final step. Nevertheless we were able to make HPA containing ionomer films using this approach. The biggest issue has been obtaining enough attachment points to have sufficient HPA in the material such that high proton conductivity can be obtained. As we are still concentrating on the chemistry in this system, we have not begun much film forming work and so the films are still generally thick, <100 µm. Data for one of the Dyneon™-HPA membranes is shown in Figure 3. The data shows high proton conductivity, but it is still not sufficiently high with our current methodology for polymer synthesis. Recent advances in polymer casting procedures have allowed us to fabricate films as thin as 10 microns.

System III: ZrP-VPA

We have shown that vinylzirconium phosphate can be polymerized with vinyl phosphonic acid to make nano-structured films in which the proton conductivity can be extraordinarily high [1]. Unfortunately, the stability of films to boiling water formed from this system is very variable. One possibility is to increase the amount of zirconium-based monomer in the film, but the issue is still that dispersing more than 20 wt% of this monomer is very hard to achieve. We show the typical high proton conductivity achieved for these films in Figure 4. These films are again thick and would have no problem reaching the DOE ASR targets at moderate film thicknesses of <50 µm. Because this system showed a

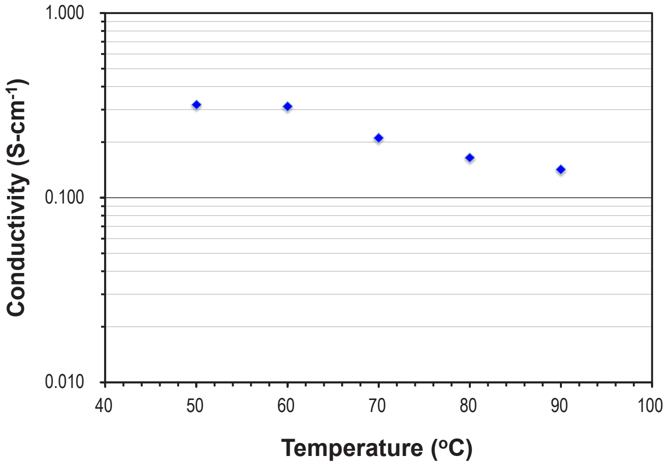

FIGURE 4. Proton conductivity data at 95% RH for a 20% vinyl zirconium phosphate –*co*- 80% vinylphosphonic acid film.

noticeable drop in performance at higher temperatures and could not be stabilized to boiling water, work on this material was terminated under this contract.

CONCLUSIONS AND FUTURE DIRECTIONS

- Demonstrated that TFVE-HPA films could be prepared that were stable to boiling and that low ASRs for these films will be achievable
- Demonstrated that the Dyneon™-HPA system can produce films with high proton conductivity
- Showed that the zirconium phophonate polymers have superior proton conductivity, but their stability to boiling water still provides issues
- Plan to fabricate thin TFVE-HPA polymers or Dyneon™-HPA materials and incorporate into MEAs

REFERENCES

1. "A Hybrid Organic/Inorganic Ionomer from the Copolymerization of Vinyl Phosphonic Acid and Zirconium Vinyl Phosphonate." G.J. Schlichting, J.L. Horan, J. Jessop, S. Nelson, S. Seifert, Y. Yang, and A.M. Herring,* *Macromol.*, **2012**, *45*, 3874.