V.C.10 Novel Hydrocarbon Ionomers for Durable Proton Exchange Membranes

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Overall Objectives

- Develop hydrocarbon-based polymer electrolyte membrane (PEM) composites capable of operating at 120°C for automotive applications.
- Optimize chemical and mechanical properties of developed PEM doped composites.
- Demonstrate operation of low cost PEMs in fuel cells with high proton conductivity over a range of temperatures and humidity conditions.

Fiscal Year (FY) 2016 Objectives

- Synthesis a series of non-perfluorinated sulfonic acid materials of polymer electrolytes via known synthetic routes stable to automotive fuel cell conditions.
- Optimize proton conductivity, film-forming properties, and acid-doping levels.
- Demonstrate preliminary operation of acid-doped polymer composites at low humidity levels and high (120°C) temperatures.

Technical Barriers

This project seeks to address the following technical barriers from the Fuel Cell 3.4.1 section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability

(B) Cost

(C) Performance

Develop a 65% peak-efficient, direct hydrogen fuel cell power system for transportation that can achieve 5,000-hour durability and be mass produced at a cost of $40/kW by 2020 (ultimate $30/kW).

More specifically, this research effort shall progress to develop new polymer electrolyte membranes displaying:

- High proton conductivity over a range of temperature and humidity conditions.
- Good film forming properties enabling formation of thin membranes.
- Durable membranes (chemical durability of hours >500[1])

Technical Targets

Progress has been made in achieving the DOE targets listed in the Multi-Year Research, Development, and Demonstration Plan. The table excerpt (see Table 1) are some of DOE technical targets specific to PEMs.

TABLE 1. DOE 2020 Technical Targets for Polymer Electrolyte Membranes Per the Multi-Year Research, Development, and Demonstration Plan

Membranes/Electrolytes

- Develop and identify electrolytes and membranes or matrices (for low and high-temperature proton exchange, alkaline membrane, molten carbonate) with improved conductivity over the entire temperature and humidity range of a fuel cell and increased mechanical, chemical, and thermal stability, with reduced or eliminated fuel cross-over
- Fabricate membranes from ionomers with scalable fabrication processes, increased mechanical, chemical, and thermal stability, and reduced cost
- Perform membrane testing and characterization to improve durability

The goal of this project is to develop durable hydrocarbon-based polymer electrolyte membrane composites. The hydrocarbon composites shall improve upon the current capabilities of expensive perfluorinated sulfonic acid-based membranes. The developed PEM composites will be manufactured by easily scaled, solution casting fabrication techniques on a reasonable scale to ensure appropriate market suitability and cost.

[1] Based on Fuel Cell Technologies Office Fuel Cell RD&D plan, table 3.4.6, http://energy.gov/sites/prod/files/2016/06/f32/fcto_myrdd_fuel_cells_0.pdf

FY 2016 Accomplishments

- Synthesized several high molecular weight polymer structures as a novel backbone for tough, ductile polymeric films.
- Designed and demonstrated a straightforward procedure to reproducibly functionalize polymers as PEM precursors.
- Developed a procedure to successfully prepare up to 8 in x 8 in films via solution casting as stable intermediate prior to composite activation. This procedure will allow for successful scale up and significant cost saving in manufacturing.

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INTRODUCTION

The widespread use of fossil fuels and continuous demand for energy over the past several decades has resulted in environmental concerns and an accelerated need for alternative energy and related technologies. Fuel cells are electrochemical energy conversion devices that convert chemical energy in fuels directly into electrical energy without combustion. The concept and principle of environmentally friendly fuel cells offer a unique collection of advantages in design, system management and flexibility, energy density, and fuel sources over other alternative energy systems. DOE has recognized the need for low cost, alternative PEMs to current state-of-the-art perfluorinated polymer membranes which have limited service range and no applicability at temperatures above 80°C. PEMs capable of operating at 120°C afford more efficient operation, potential for lower catalyst loadings or even non-platinum catalyst usage.

Indeed, all PEM systems require a medium for proton conductivity. Liquid water is the natural selection, however, water is not applicable at 120°C for fuel cell operation. The objective of this DOE Small Business Innovation Research project is to develop acid-doped PEMs with maximum protonic conductivity and good mechanical strengths to provide hundreds of hours of duty cycles. The appropriate acid doping levels will be a function of several factors but is expected to be lower that classic phosphoric acid fuel cells, hence avoiding corrosive side reactions.

APPROACH

The general approach for this project is to synthesis tough, mechanically stable polymeric film with select backbone functionality. Those films showing good mechanical stability will be tested for protonic conductivity and durability. The down-selected membrane candidates will undergo preliminary fuel cell testing (Table 2).

TABLE 2. Comparison between Nafion® and the Proposed Ionomer Composites

	Nafion®	Functionalized Hydrocarbon Ionomers
Proton Conductivity	✓	✓
Chemical Stability	✓	✓
Cost	$$$	$
Operating Temperature	↓	↑
Low RH Operation	✗	✓
Tolerance to Impurities	✗	✓
Improved Catalyst Activity	✗	✓
Additional Catalysts Viable	✗	✓
Straightforward Thermal Management	✗	✓
Low Methanol Crossover	✗	✓

RH – Relative humidity

RESULTS

The overall goal of the first phase of this project is the synthesis hydrocarbon-based polymer electrolyte membrane composites for automotive fuel cell applications capable of operating at 120°C. The PEM composites must be durable for a greater service lifetime and lower cost than perfluorinated sulfonic acid-based PEM systems.

To date, 10 different polymers have been synthesized as candidate polymeric backbones. These polymers differ in polarities and also stiffness. Variations in polarities are of interest with regard to the acid-doping step and the stability of the composites. Backbones with different stiffness are important when evaluating toughness and durability. The ideal polymer backbone will have the right balance of polarity and stiffness. Polymers that are too stiff may be brittle, also polymers with very high polarity may swell too great to be an effective barrier to the fuels (i.e., hydrogen gas, methanol, and air). Characterizations, which include chemical, thermal, and mechanical testing and thermomechanical analysis, are ongoing on these polymeric systems. Figure 1 shows the influence of functionalization on the polymer thermos-oxidative stability. The level of functionalization is also confirmed from this type analysis. This representative thermogram displays the exceptional stability of the control, un-functionalized polymer (green) and the polymer backbones modified with two different levels of polar side groups (red, blue).

Characterization of the polymer backbones and their corresponding functionalized membranes will be presented in detail elsewhere. Below is a collection of some of the data for the various systems:

Glass Transition (Tg):	130–220°C
Melting Temperature:	160–250°C
Modulus (GPa):	2.2–3.4
Percent Elongation (%):	5–25

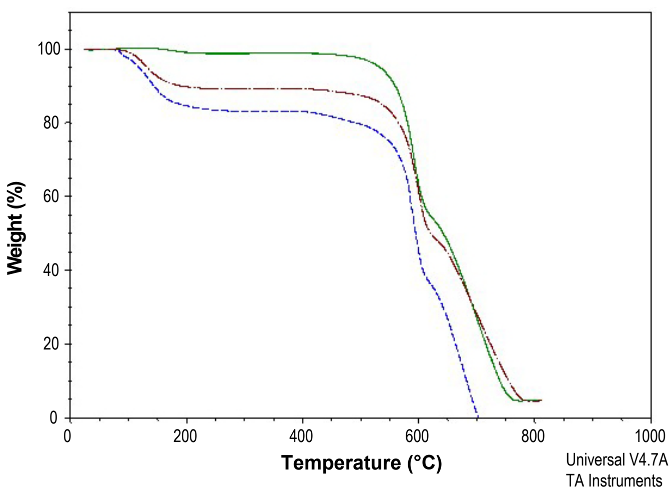

FIGURE 1. Thermogravimetric analysis of one series of functionalized hydrocarbon polymers

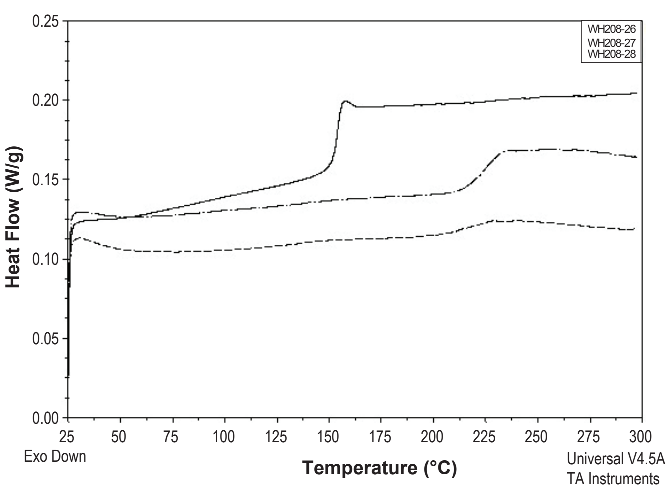

FIGURE 2. Differential scanning calorimetry of select candidate polymer systems displays high glass transition temperatures, greater than the 120°C target use temperature

CONCLUSIONS AND FUTURE DIRECTIONS

Although early in the project, several novel polymer backbones have been synthesized. These materials have undergone preliminary characterization and demonstrate exceptional thermal stability and mechanical strength. Select polymer backbones have successfully been functionalized with polar moieties. The polar moieties are expected to have significant influence the properties of the acid-doped membranes and stability of the composites fuel cell performance. Tough, ductile films have been fabricated via simple solution casting procedure.

Ongoing characterizations will guide further polymer development. Future works include:

- Film preparation and durability evaluations
- Acid composite fabrication
- Composite(s) proton conductivity measurements
- Initial fuel cell performance testing