
V.B.9 Hydrocarbon Membrane

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Objectives

- Improve the fuel cell operating performance at low relative humidity (RH), elevated temperature, and -30°C by designing a hydrocarbon proton exchange membrane (PEM) that can operate more efficiently at these diverse conditions.
- Improve the efficiency of hydrocarbon-based PEM materials by utilizing alternative electrolytes within catalyst structures.
- Improve overall PEM fuel cell operating efficiency.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Electrode Performance
- (D) Thermal, Air, and Water Management
- (F) Fuel Cell Power System Integration

Technical Targets

This research task addresses several technical challenges and barriers as outlined in the Hydrogen Fuel Cell and Infrastructure Technologies (HFCIT) Multi-Year Research, Development and Demonstration Plan (MYRDDP). The technical tasks addressed by this research project include fundamental research needs in the areas of: high temperature membranes for distributed power applications, advanced membrane R&D, membrane electrode assembly (MEA) materials, components, and processes, advanced MEA meeting 2010 targets, direct methanol fuel cells, and fuel cell cold start.

Accomplishments

- Demonstrated good fuel cell performance of a hydrocarbon-based PEM versus Nafion® and Sandia's hydrocarbon ionomer within the electrode structure.
- Demonstrated initial results that O₂ transport within the cathode becomes mass transport limited with sulfonated Diels-Alder polyphenylene ether (SDAPPe).
- Completed initial investigation of pilot-scale hydrocarbon ionomer scale-up.
- Completed synthesis of rationally designed highly fluorinated monomers.

Introduction

The objective of this research task is the development of a hydrocarbon-based PEM that has high material durability, manufacturability, low cost, and has fuel cell performance characteristics that meets the DOE's HFCIT 2010 goals. The ideal physical properties of this hydrocarbon-based PEM will be a low-humidity function that can also operate at low to elevated temperatures. In addition to these material challenges, the hydrocarbon PEM must maintain the physical integrity to survive material stresses during cycling (-30°C to 120°C and shutdown to startup).

The development of a PEM material that requires little to no water for proton conduction is the primary goal of this work. A simplification in water management within a fuel cell stack would lead to a reduction in stack weight, improve heat management, and reduce the cost of the stack. This research project will develop a structure-property-performance relationship in order to develop the fundamentals necessary for the design and development of hydrocarbon PEMs and MEAs.

Approach

This research project addresses several fundamental material research needs in the area of hydrocarbon PEMs. We are working towards the development of new hydrocarbon PEMs and the challenges of hydrocarbon ionomer electrode structures based upon random and structured polyphenylene-based ionomers. An electrode ionomer task is being developed in order to improve and enhance fuel cell performance through the improvement in electrode adhesion and the lowering of interfacial resistance between the hydrocarbon PEM and catalyst layer. Our research approach is directed at understanding the role of the PEM and the interrelationships between ionomer content, ionomer type, electrode structure, water and gas transport, proton conductivity, and fuel cell performance in order to tailor transport and fuel cell function.

Results

Initial Pilot Scale Production

Although our work has shown that Diels-Alder Poly(phenylene)s are attractive candidates for fuel cell usage, this family of polymer is not currently commercially available, unlike poly(styrene), poly(ether sulfone), or polyether ether ether ketone. Therefore, we sought to assess the viability of large-scale production through collaboration with Hydrosize[®] Technologies, Inc., who specializes in the development and manufacture of state-of-the-art sizings (film formers), binders, and resins for the composites industry.

In our initial pilot-scale, our primary goal was to attempt to synthesize +300 g of polymer, with the highest concern to obtain high enough monomer purity for synthesizing high molecular weight polymer. +500 g of the monomers were prepared with a 73% overall yield. The resultant large scale polymer is tough and fibrous, with a molecular weight of 113,000 (Mn), with a polymerization yield of 97%. In Figure 1, 11 and 12 show the progression of the polymerization reaction, 13 is a portion of precipitated fibrous polymer, and 14 and 15 are both solution and film of sulfonated polymer from large-scale reaction. The second goal of this portion of the project focused on identifying the chemical steps that are not amenable to a pilot-scale setting and we are evaluating solvent alternatives and their impact on material quality.

Synthesis of Highly Fluoronated Monomers

Unlike Nafion[®] which has well defined hydrophobic and hydrophilic regions (fluorosulfonic super acid), most hydrocarbon alternative membranes tend to develop “fuzzy” hydrophilic-hydrophobic interfaces, with strongly bound water and slower water and proton

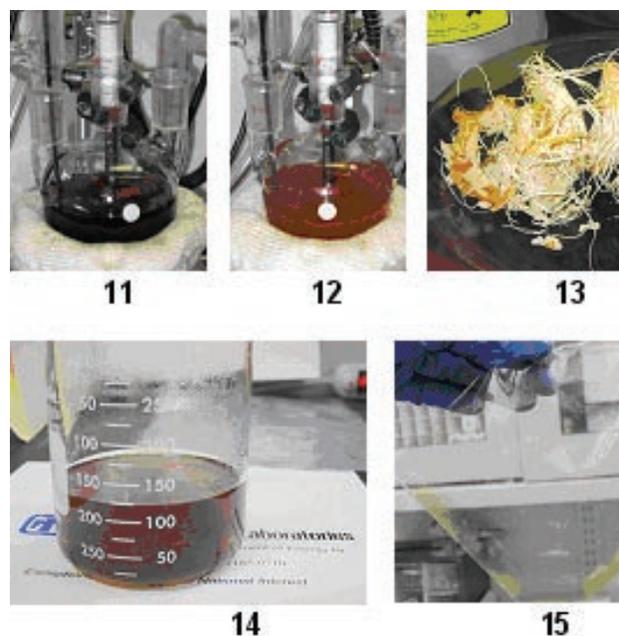


FIGURE 1. Progression of the Diels-Alder polymerization reaction and to SDAPP solution and film.

diffusions. In this work, we chose to increase the differences in polarity of the matrix and conducting phases through generating a series of highly fluorinated monomer units. In a collaborative effort with Paul Deck at Virginia Tech the goal is to synthesize these monomers and incorporate them into the sulfonated Diels-Alder polyphenylene (SDAPP) backbone to improve hydrophilic-hydrophobic phase segregation and proton transport at low water contents. Dr. Deck has devised a unique method of synthesizing bis-cyclopentadienones that enables broad functional group incorporation. In this work, the perfluorinated phenyl group decorate the bis-cyclopentadienone monomer unit as shown in Figure 2.

Monomer 3 has been synthesized in quantities of 25 g batches; initial polymerization of 3 however, has resulted in low molecular weight powder. We are currently evaluating the polymerization chemistry of 3 to further improve polymer properties. Monomer 7 is being synthesized and will be evaluated later in the fiscal year.

Hydrogen Fuel Cell Performance

One of the benefits of SDAPP membranes over Nafion[®] is that of higher temperature and lower RH performance. A series of polarization curves was taken at 60°C, 80°C, 100°C and 120°C at 100%, 75%, 50%, and 25% relative humidity. The performance of N112 membranes with 30 wt% polymer Nafion[®]-based electrodes is shown in Figure 3. This analysis shows that Nafion[®]'s peak power performance is at

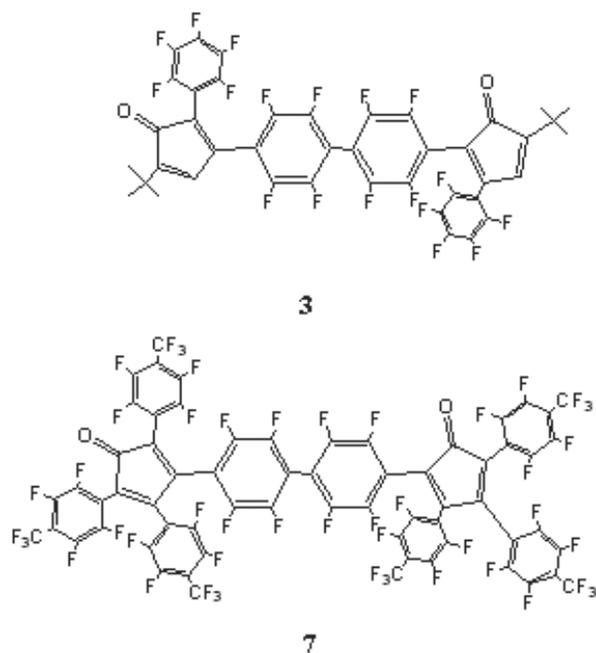


FIGURE 2. Two highly fluorinated bis-cyclopentadienone monomers prepared.

80°C and high relative humidity, which are standard conditions for many reports in the literature. At higher temperature and at lower relative humidity the performance of Nafion® declines. The performance of SDAPP4 membranes with Nafion® 30 wt% electrodes was tested under the same conditions as shown in Figure 3. SDAPP4 with Nafion® electrodes has a higher temperature and better lower RH performance than N112. In addition, the peak performance for SDAPP4 is at 110°C and 75% RH, which is an improvement over standard Nafion®. Furthermore, the performance at both 75% and 50% RH is greater than that at 100% RH, which demonstrated the potential of SDAPP4 as a low humidity membrane.

A completely hydrocarbon MEA was constructed with a SDAPP4 membrane and a fluorinated SDAPP-based electrode (a non-Nafion® MEA). The performance at 0.5 V cell potential for this construction is shown in Figure 3 and is on par with that of the completely Nafion® MEA. The performance at 100°C and 100% RH is virtually identical for the two systems. The Nafion® MEA does perform better at lower temperatures and 100% RH. The full SDAPP system does suffer at low RH as opposed to the SDAPP membrane with Nafion® electrodes. However, these performance studies clearly demonstrate that high performance MEAs can be fabricated from a hydrocarbon membrane and hydrocarbon electrodes with performance at low humidity remaining a big challenge for all systems.

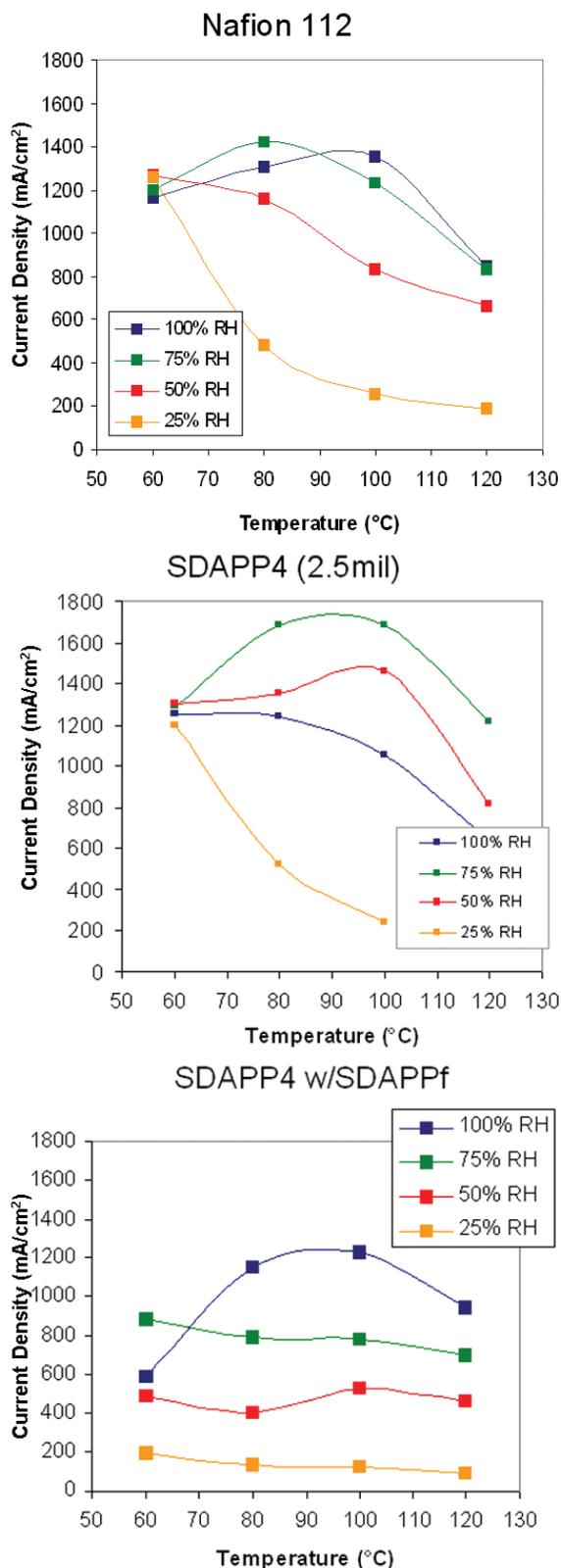


FIGURE 3. Hydrogen fuel cell performance of N112 versus SDAPP4 at a cell potential of 0.5 V. Catalyst loading was 0.4 mg/cm² per electrode and 30 wt% Nafion®. Performance of SDAPP4 at a cell potential of 0.5 V with 15 wt% polymer fluorinated SDAPP-based electrodes.

Tafel slopes for various electrode formulations were measured to get an idea of the intrinsic catalytic activity of the Nafion[®] and SDAPPe-based electrodes (chemically similar to the fluorinated SDAPP). As can be seen in Table 1, the Tafel slopes in air and oxygen at 100% RH are between -60 and -70 mV/dec, except for Nafion[®] 30 wt% in air, -51 mV, and SDAPPe 15 wt% in air, -79 mV/dec, which are outliers. This result indicates that the intrinsic catalytic activity of electrodes with SDAPPe binder is sufficient. At 50% RH, the Nafion[®] and SDAPPe 30 wt% electrodes show approximately equivalent Tafel slopes, but there is some increase observed in the Tafel slope when the amount of SDAPPe polymer in the electrode was decreased to 15 wt%.

Hydrogen adsorption/desorption cyclic voltammetry was performed on the electrodes to determine the electrochemically active platinum surface area (ECA). Table 1 shows the ECAs for each electrode formulation. With 30 wt% polymer binder in the electrodes, there is a decrease in ECA from 24 m² Pt/mg of Pt for Nafion to 16 m² Pt/mg Pt for ether SDAPP. The amount of polymer binder was decreased in order to expose more of the Pt catalyst surface area for ether SDAPP-based electrodes. When the polymer binder was decreased to 15 wt% SDAPPe binder, the ECA increased to 22 m² Pt/mg Pt which is nearly the same as the Nafion[®]-based electrode.

Bruner, Emmett and Teller (BET) surface areas were measured for each electrode formulation in order to ensure that the SDAPPe electrode had sufficient pore space for gas phase transport to the three-phase reaction interface. Table 1 illustrates that the properties of SDAPPe electrodes can be tailored by changing the amount of hydrocarbon ionomer within the electrode structure in order to optimize porosity for product and reactant transport. The surface area increased with decreasing polymer wt% in the electrodes.

Table 1. Tafel slope (mV/dec) for Nafion[®] and ether SDAPP-based electrodes, ECA surface area determined by hydrogen adsorption/desorption cyclic voltammetry, and BET surface area electrode formulation evaluation.

Ionomer	Tafel Slope				ECA m ² Pt/ mgPt	BET m ² /g
	O ₂		Air			
	100% RH - (mV/dec)	50% RH - mV/dec	100% RH - (mV/dec)	50% RH - mV/dec		
30 wt% Nafion	-59	-51	-87	-83	24	70
30 wt% SDAPPe	-63	-68	-83	-79	16	85
15 wt% SDAPPe	-65	-79	-105	-115	22	131
7 wt% SDAPPe	-	-	-	-	-	135

This series of data demonstrates that SDAPP4 membrane with Nafion[®] electrodes outperforms the standard N112 with Nafion[®] electrode MEA configuration. Also, a pure SDAPP MEA (SDAPP4 membrane and fluorinated SDAPP-based electrodes) is able to equal the performance of the Nafion[®] system at high temperatures and high relative humidity.

Conclusions and Future Directions

Postsulfonated SDAPP-based PEMs perform better than Nafion[®] at elevated temperatures up to 120°C and 50% RH but at lower RH (25%) both SDAPP and Nafion[®] appear to have similar performance. Hydrocarbon ionomer electrode work was demonstrated to limit the performance of hydrocarbon PEM-based MEAs. Consequently, BET, ECA, and Tafel slope analysis of the electrode structure was done and it was discovered that using these ionomers did not significantly contribute to their degradation in performance. It is thought that the lowering in fuel cell performance is due to the lower O₂ mass transport in the ionomer coating surrounding the catalyst (three-phase interface), which is due to the low O₂ permeability of SDAPP as compared to Nafion[®]. In order to mitigate these losses, a more permeable polymer is desired.

Future strategies during this project are directed at enhancing the conductivity under partially dry conditions by controlling the polymer morphology, improving the electrode structure with our hydrocarbon-based electrodes, and consideration of other organic moieties for proton conduction such as organic-inorganic composites.

FY 2006 Publications/Presentations

- Hickner, Michael A.; Fujimoto, Cy H.; Cornelius, Christopher J. "Transport in sulfonated poly(phenylene)s: Proton conductivity, permeability, and the state of water" Polymer (accepted April 18th, 2006).
- Cornelius, C.J. High Temperature Membranes, Gordon Research Conference, Bryant University, Smithfield, RI July 23-28, 2006 (Invited Talk).

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