Quarterly Progress Report

Project Title: Hydrocarbon Membrane

Project Period: October, 2006 to April, 2007

Research Members

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DOE Managers

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Industrial Partners:

Hydrosize® Technologies, Inc., Raleigh, NC

Project Objective:

This research project 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. The primary objective of our project research is the development and demonstration of an advanced hydrocarbon PEM material that allows low humidity fuel cell operation. Our low relative humidity (RH) proton exchange membrane (PEM) fuel cell research is directed at achieving fuel cell operation over a dynamic temperature range from -30ºC to >80ºC via a hydrocarbon based PEM in order to improve operation. In order to improve the efficiency of hydrocarbon based PEM materials, our research is also engaged in the development of alternative electrolytes to be used within catalyst structures in order to improve durability. 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.

Background:

This research project addresses several fundamental material research needs in the area of hydrocarbon PEMs. We are currently working towards the development of new hydrocarbon PEMs and addressing the challenges of achieving adequate reactant and product transport, proton conductivity, and electrochemical stability of hydrocarbon ionomer electrode structures based upon random and "potentially" 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 hydrocarbon PEMs and their interrelationships between ionomer ion-exchange capacity (IEC), ionomer type, electrode structure, water and gas transport, proton conductivity, and fuel cell performance in order to tailor transport and fuel cell function that meet the HFCIT and MYRDDP goals. This work is being done in order to establish a fundamental understanding of performance and lifetime that will assist in establishing activity-structure-performance relationships to mitigate the effects that cause premature catalyst coated membrane (CCM) and fuel cell performance degradation.

Status:

Summary:

This research program began October 1, 2005, and during the last 14 months, the following research was performed or initiated in order to address the developmental issues associated with a hydrocarbon based PEM. Sandia's research tasks were focused upon two technical research areas for the developmental effort of creating a durable membrane that provides robust fuel cell operation at low relative humidity. The first task is designed to optimize the low relative humidity performance of a first generation hydrocarbon membrane developed by Sandia by beginning a characterization study to evaluate the relationship between IEC and proton conductivity as a function of relative humidity and temperature as it pertains to hydrocarbon PEM structure. This task will provide a basis of an activity-structure relationship for SDAPP (1st Generation termed SDAPP for Sulfonated Diels Alder Polyphenylene) in order to optimize MEA design and fuel cell performance, which may be utilized for "other" hydrocarbon PEM systems. During this work our team demonstrated that we were able to generate improved hydrogen fuel cell performance over Nafion at low relative humidity conditions and that electrolyte inks can be substituted into the anode electrode with no significant loss in fuel cell performance. Our efforts in replacing the cathode electrode with our ionomer have revealed to us that a key performance metric for the cathode ink is adequate oxygen transport as ultimately determined by overall fuel cell performance. The overall research goals for this research project were modified due to limited funding by removing the low temperature testing portion from all tasks. The original tasks for this project are summarized below:

I. *Synthesize and Characterize SDAPP and composite materials via DSC, TGA, DMA, IR, water-uptake, IEC, Tensile Strength, EA and ion conductivity from 10-100%RH and 120°C.*
II. *Demonstrate SDAPP and composite PEM fuel cell performance at 120°C and low relative humidity.*
III. *Continued development of structure-property performance PEM and fuel cell relationships to create improvements in PEM materials.*

Accomplishments and Results of Current Quarterly Progress Report:

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), PEEK. 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 +300g of polymer, with the highest concern of obtaining high enough monomer purity for synthesizing high molecular weight polymer. +500g of the monomers was prepared with a 73% overall yield. The resultant large scale polymer is tough and fibrous, with a number average molecular weight of 113,000 (Mn), with a polymerization yield of 97%. In Figure 1, slide 11 and 12 show the progression of the polymerization reaction, slide 13 is a portion of precipitated fibrous polymer, slide 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 impact on material quality.

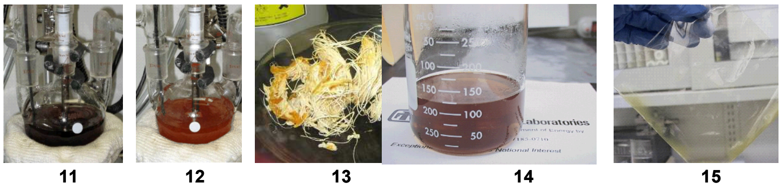

Figure 1 Progression of the DA polymerization reaction and to SDAPP solution and film.

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 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 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 collaborative work, perfluoroated phenyl group decorate the bis-cyclopentadienone monomer unit as shown in Figure 2.

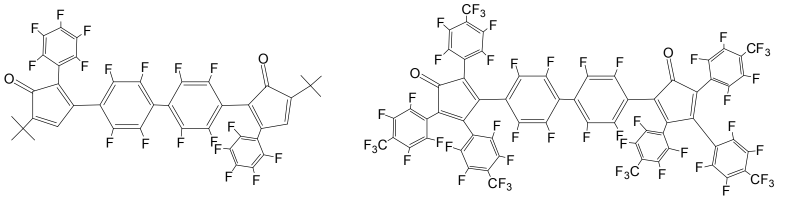

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Figure 2 Two highly fluorinated bis-cyclopentadienone monomers prepared.

Monomer **3** has been synthesized in the requested 25 g batch per the contract goals set between Sandia and VT. An initial polymerization of monomer 3 resulted in low molecular weight polymer. The intent of utilizing monomer **3** was the enhancement of polymer phase separation in order to improve fuel cell performance by concentrating the sulfonic acid domains for enhanced proton conduction. While monomer 3 and monomer **7** were unable to be synthesized in to a high molecular weight polymer, we are still confident that the "concept" of concentrating proton conductive domains by controlled phase separation is the correct approach for achieving improved proton conduction at low relative humidity.

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 80°C, 100°C and 120°C at 100%, 75%, 50%, and 25% RH. The performances of Nafion (N112) versus SDAPP4 with 30 wt% polymer Nafion-based electrodes are shown in Figure 3. The comparison of current density at 0.6V and peak power reveals the dependence of temperature and relative humidity versus fuel cell performance. Overall, SDAPP4 with Nafion electrodes has a higher temperature and better lower RH performance than N112 demonstrating its potential as a low humidity membrane.

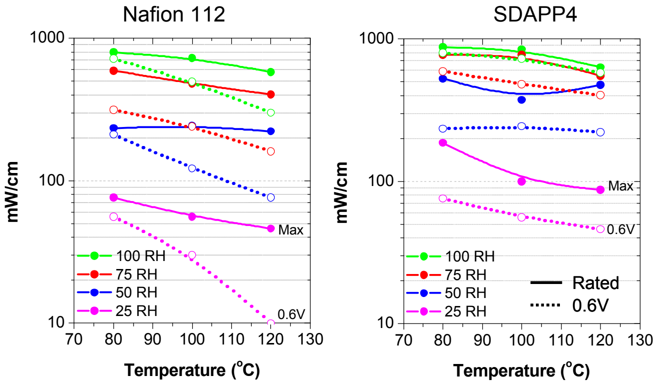
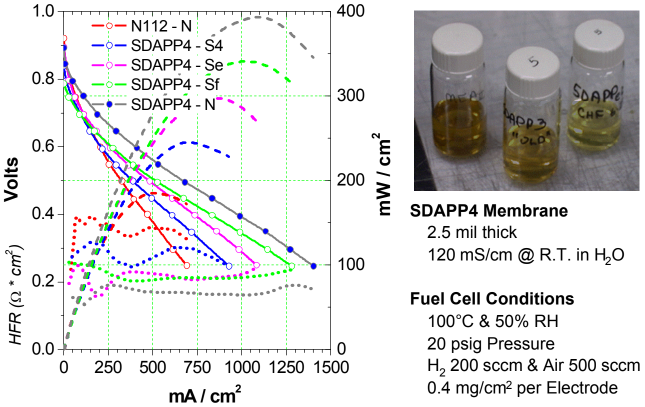


Figure 3 Hydrogen fuel cell performance of N112 versus SDAPP4 at a cell potential of 0.6V and peak power as a function of relative humidity. Catalyst loading was 0.4 mg/cm^2 per electrode and 30wt% Nafion and membrane thickness of N112 and SDAPP4 are equivalent.

A completely hydrocarbon MEA was constructed with a SDAPP4 membrane and a series of SDAPP-based electrodes (a non-Nafion MEA). The performance at 50% RH and 100oC is shown in Figure 4. The performance at this condition reveals the improved SDAPP performance over Nafion and that the non-Nafion electrode inks have performances that increase in performance S4, Se, and Sf. While using Nafion within the electrode structure still has better performance than these non-Nafion inks, it does show the potential of using them in order to create an entirely hydrocarbon based MEA.



SDAPP4 Membrane
2.5 mil thick
120 mS/cm @ R.T. in H_2O

Fuel Cell Conditions
100°C & 50% RH
20 psig Pressure
H_2 200 sccm & Air 500 sccm
0.4 mg/cm² per Electrode

Figure 4 Hydrogen fuel cell performance of N112 versus SDAPP4 at a cell potential of 0.6V and peak power as a function of relative humidity. Catalyst loading was 0.4 mg/cm^2 per electrode and 30wt% Nafion. SDAPP4 has improved performance over Nafion. SDAPPf ink has best hydrocarbon ink performance and approaches Nafion.

Tafel slopes for various electrode formulations were measured to ascertain the intrinsic catalytic activity of the Nafion and SDAPPe (Sulfonated Diels Alder Polyphenylene ether) based electrodes are summarized in Table 1. The Tafel slopes in air and oxygen at 100% RH are between -60 and -70 mV/dec. The Tafel slopes in oxygen are very similar to Nafion, but in air the performance deviates from Nafion. This result indicates that the intrinsic catalytic activity of electrodes with SDAPPe binder is sufficient in an oxygen environment but inhibiting in an air at 100% RH. However, at 50% RH, Nafion and SDAPPe 30 wt% electrodes reveal similar Tafel slopes but at a lower SDAPPe loading (15wt%) an increase in the Tafel slope is observed, which indicates an increase in resistance to carrying that will impact fuel cell operation.

Table 1 Tafel slope (mV/dec) for Nafion and ether SDAPP-based electrodes, integrated electrochemically active (ECA) surface area determined by hydrogen adsorpotion/desoprtion cyclic voltammetry, and BET surface area electrode formulation evaluation.

Ionomer	Tafel Slope				ECA	BET	σ
	O_2	Air	O_2	Air	$m^2Pt/mgPt$	m^2/g	*mS/cm*
	100% RH – (mV/dec)		50% RH - mV/dec				
30 wt% Nafion	-59	-51	-87	-83	24	70	85
30 wt% SDAPPe	-63	-68	-83	-79	16	85	125
15 wt% SDAPPe	-65	-79	-105	-115	22	131	125
7 wt% SDAPPe	-	-	-	-	-	135	125
SDAPP4 15wt%	-65	-57	85	76			>100
SDAPPf 15wt%	-68	-70					>100

Hydrogen adsoption/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 m^2 Pt/mg of Pt for Nafion to 16 m^2 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 m^2 Pt/mg Pt which is nearly the same as the Nafion-based electrode.

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 optimization porosity of the catalyst and ionomer structure for product and reactant transport.

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. Initial hydrocarbon ionomer electrode work has revealed that it causes a limitation in fuel cell performance of the hydrocarbon PEM based MEAs and further work is warranted to improve its oxygen and hydrogen gas transport properties. In order to deconvolute the impact of the hydrocarbon ionomer within the electrode, BET, ECA, and Tafel slope analysis was completed and the findings suggest that no appreciable degradation in fuel cell performance is attributable to the ionomer. Therefore, it is our conclusion that the lowering in fuel cell performance is due to the lower O_2 mass transport in the ionomer coating surrounding the catalyst (three-phase interface). This is due to the low O_2 permeability of SDAPP as compared to Nafion. In order to mitigate these losses, a more permeable polymer is desired and being developed for advanced hydrocarbon ionomers. Future strategies during this program 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.

Research Plans and Key Issues for Fiscal Year 2007:

- NONE – New AOP has been submitted for continuation during FY 2008 -

Patents:

1 Patent has been issued, and six technical advances related to this project have been submitted for potential patent application.

Publications / Presentations:

- Fujimoto, C.H., Hickner, M.A., Cornelius, C.J., Loy, D.A. *Macromolecules* **2005**, *38(12)*, 5010.
- Hickner, M.A., Fujimoto, C.H., Cornelius, C.J. *Polymer* **2006**, *47(11)*, 4238.
- 2 publications in progress related to Novel Monomer synthesis with Paul Deck (VT).
- 2 publications in progress related to structural analysis via Neutron Scattering with Dvora Perhia (Clemson).
- Invited Talk: 2006 Gordon Research Conference on Fuel Cells (July 26, 2006)
- Invited Seminar: United Technologies Research Center (August 2, 2006)
- Invited Seminar: 3M (August 21, 2006)
- Invited Seminar: Illinois Institute of Technology (September 20, 2006)
- Invited Talk: American Chemical Society Rocky Mountain Regional Meeting, Tucson, AZ (October 14-18)
- Invited Talk & Technical Professional Award: 28th Annual American Indian Science and Engineering Society (November 3, 2007)
- Invited Talk: Boeing – Everett, WA (January 28, 2007)
- Invited Seminar: Colorado School of Mines (March 2, 2007)

Research Summary – FY2006 to 1st QTR of 2007

Task Schedule

Subtask 1.1 - Low Humidity Fuel Cell PEM						
		Target	Revised	Actual	% Complete	Progress
1.0	Funding Approval	10/1/05		10/1/05	100	Complete
I	*Synthesis and Characterization of SDAPP materials*	04/06		5/06	100	Complete – 2nd Phase to be done in FY2008.
II	*Subtask II – SDAPP Fuel Cell Performance*	07/06		8/06	100	Complete – 2nd Phase to be done in FY2008.
III	*Structure-property Binder Interface*	09/06		7/06	100	Complete – 2nd Phase to be done in FY2008.