

V.C.4 Poly(p-Phenylene Sulfonic Acids): PEMs with Frozen-In Free Volume

Morton Litt (Primary Contact), Ryszard Wycisk,
Kun Si, Casey Check and Daxuan Dong

Case Western Reserve University
10900 Euclid Ave.
Cleveland, OH 44106-7202
Phone: (216) 368-4174
E-mail: mhl2@case.edu

DOE Managers

HQ: Donna Ho
Phone: (202) 586-8000
E-mail: Donna.Ho@ee.doe.gov

GO: Gregory Kleen
Phone: (720) 356-1672
E-mail: Greg.Kleen@go.doe.gov

Technical Advisor

John Kopasz
Phone: (630) 252-7531
E-mail: Kopasz@anl.gov

Contract Number: DE-FC36-06GO16039

Project Start Date: March 1, 2006

Project End Date: June 30, 2012

Fiscal Year (FY) 2011 Objectives

The project objectives are to optimize routes to rigid rod poly (phenylene sulfonic acids) (PPDSA), polymers that retain high conductivity at low humidity, develop methods to make water-insoluble polymers and characterize the materials as proton exchange membranes (PEMs). The requirements are:

- Analyze the Ullman polymerization reaction in order to increase polymer molecular weights and decrease reaction time.
- Increase the polymer sulfonic acid density and water absorption: use phenylene disulfonic acid monomer to make homo- and co-polymers.
- Develop reliable methods for making water-insoluble, dimensionally stable PEMs possibly by grafting non-polar groups on the backbone and crosslinking.
- Synthesize comonomers that can be copolymerized to produce water-insoluble copolymers either directly or in a subsequent step.
- Characterize polymers, copolymers and grafts to understand the relationship between molecular structure, supermolecular organization and PEM properties.
- Submit the most successful materials for intensive testing.

Technical Targets

This project involves the synthesis and characterization of homo- and co-polymer rigid-rod aromatic sulfonic acids and developing methods to make them dimensionally stable.

- Our PEMs have passed the 2005 goals for membrane conductivity and probably reach the 2015 goals.
- Earlier tests of MeOH permeability ($<0.04 \text{ mA/cm}^2$ for a 20μ thick film at 100°C with a 2/1 MeOH/H₂O gas input) imply that the very polar membrane environment should reduce oxygen and hydrogen crossover to values much lower than the target values.
- The starting materials are relatively cheap; there are only two steps from commercial starting materials, fuming sulfuric acid and dibromo benzene (or dibromo biphenyl), to the homopolymer sulfonic acids. Copolymers could raise the cost. (Also, it may be possible to replace dibromo benzene with dichloro benzene, lowering the raw materials cost by a factor of 5.)

Remaining Barriers

- Polymers have low elongation (6-9%) and tear easily.
- Polymer molecular weights are too low. Higher molecular weight should give better mechanical properties.
- Grafting and crosslinking succeeded; good PEMs were made. However, better grafting methods need to be developed.
- Procedures for scaling up polymer production without lowering molecular weight have not yet been developed.
- Crosslinked films swell about 15% in the x and y directions and 30 to 40% in the z direction going from 0 to 98% relative humidity (RH). Can swelling be reduced without decreasing conductivity?

Technical Targets

Progress towards meeting the technical targets for PEMS and membrane electrode assemblies (MEAs) is shown in Table 1.

Fiscal Year 2011 Accomplishments

- PPDSA and copolymers containing the biphenyl group (B2P8) were made in molecular weights high enough that cast films could be handled easily.
- One to 16 mole% biphenyl groups were grafted on the polymers to form biphenyl sulfones.
- Films cast from the grafted polymers were completely crosslinked by heating at 210°C for three hours with no loss of acid over that required to crosslink. Crosslinked

TABLE 1. Progress towards Meeting Technical Targets for PEMs and MEAs; Data for Crosslinked B20P80 gBP 12% (D7).

Characteristics	Units	Target 2015	2010 Status
Maximum Operating Temperature	°C	120	120
Area Specific Resistance at:			
Maximum operating temperature and water partial pressures from 40 to 80 kPa	Ohm cm ²	≤0.02	0.093*
80°C and water partial pressures from 25 to 45 kPa	Ohm cm ²	≤0.02	0.040*
30°C and water partial pressures up to 4 kPa	Ohm cm ²	≤0.03	0.06*
-20°C	Ohm cm ²	≤0.2	N/A
Maximum Oxygen Cross-Over	mA/cm ²	2	N/A
Maximum Hydrogen Cross-Over	mA/cm ²	2	1.9
Minimum Electrical Resistance	Ohm cm ²	1,000	31
Cost	\$/m ²	≤20	N/A
Durability:			
Mechanical	Cycles w/<10 sccm crossover	≥20,000	N/A
Chemical	hours	> 500	N/A

*Sample thickness was ~80 micrometers. A 25 micrometer thick film could meet the requirements. A less heavily grafted film (7% instead of 12%) could meet the requirements at 80 micrometers thick.

polymers were stable for at least two hours at 225°C. Some acid was lost after 2 hours at 250°C.

- Crosslinked films were dimensionally stable, retaining the high conductivity at low RH of the starting graft polymers.
- MEAs prepared from crosslinked films were tested in fuel cells. The best were slightly worse than Nafion211®. This is a very good result for first tests on a completely new class of materials.
- High viscosity copolymers of dibromobenzene disulfonic acid and dibromofluorene disulfonic acid were made. These can be grafted and crosslinked to give dimensionally stable polymers with exceptionally high milliequivalents of acid groups per gram of material (IECs) and high conductivity at low RH (higher than the biphenyl grafted polymers).



Introduction

There are many problems associated with the normal aromatic sulfonic acid PEMs. The better conducting materials swell very much in water. Even with these materials, conductivity drops rapidly as humidity is lowered [1]. Block polymers swell less at high humidity,

but conductivity is still poor at low RH [2]. They can be used only at high humidity which limits the fuel cell operating temperature to < 90°C. The materials described in the following were designed to hold water very strongly at low humidity. They could be used effectively at higher temperatures, up to at least 120°C, with little or no added water in the fuel stream since the water generated in the reaction should be sufficient to maintain high conductivity. High temperature operation has the additional advantages that kinetics are faster, lower purity hydrogen can be used and heat can be removed easily.

Approach

Our approach derives from a combination of polymer structure analysis and cost considerations. What type of polymer backbone can have high sulfonic acid content, hold water strongly, and yet have dimensional stability. The analysis suggested that PPDSA, rigid rod liquid crystals that organize with all molecules locally parallel, should be suitable. These structures have small cross-section backbones with projecting sulfonic acid groups. Absorbed water separates the chains. As water is lost at low humidity, the sulfonic acids hit other acid groups or a neighboring polymer backbone. The molecules still have voids that hold water (frozen in free volume): further water loss compresses the molecule, which distorts bond angles and requires high energy. The last few waters are difficult to remove and resorb easily. Water causes the structure to expand perpendicular to the parallel polymer axes. The final structure can be dimensionally stabilized by grafting cross-linking groups on the backbone and subsequently crosslinking them [3] (PPDSA). Grafted groups protrude further from the backbone than the acid groups; this increases the chain (rigid rod) separation and thus can increase the frozen-in free volume [4]). This structural design generates non-collapsible nanopores lined with a high density of sulfonic acid groups that hold water very strongly.

Polymers with grafted non-polar groups, reported last year, lost coherence at high humidity; the film flowed under pressure and disintegrated in water. Crosslinking avoids these problems. Because the molecules are rigid rods, grafted groups react only intermolecularly to cross-link with sulfonic acids on neighboring chains. Thus, a relatively low mole fraction of crosslinkable groups should make such polymers dimensionally stable with little loss of conductivity. This approach has succeeded for these materials.

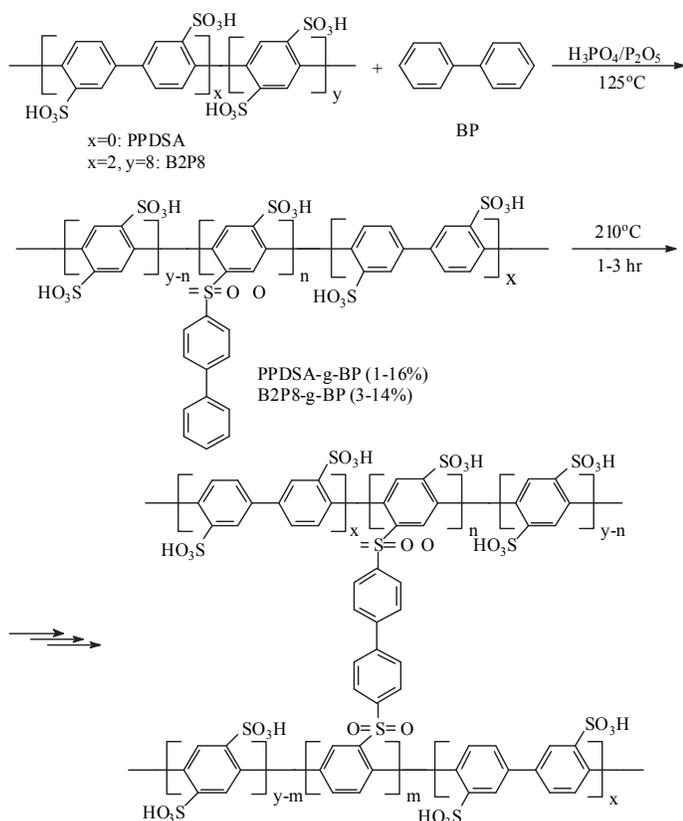
Another approach to generate frozen-in free volume was presented last year. The idea was to make a two-dimensional lattice containing large pores. The molecules should stack to create nano-channels that would contain enough water to give good conductivity along the channels and hold the water even at very low humidity. Cast films with all molecules parallel to the film surface should have very high through conductivity at low RH. The idea was tested and it worked, but as usual, there were complications.

Results

PPDSA and B2P8 Copolymers

Copolymerization: The polymers used for most of this research were PPDSA and a 20/80 copolymer of 1, 4-dibromo phenylene 2, 5-disulfonic acid (DBPDSA) and 4, 4'-dibromobiphenyl 3, 3'-disulfonic acid (DBBPDSA), B2P8. As reported last year, both were made with reasonably high molecular weights. As expected from the discussion above, λ at low RH rose rapidly and stabilized at 2 to 3 waters higher than Nafion117[®] at higher RHs. This resulted in high conductivity down to very low RHs but with high swelling and poor mechanical properties.

Grafting and Crosslinking: Grafting of alkyl benzene groups on the polymer was abandoned since the resulting grafts had very poor mechanical properties. We have shifted to grafting cross-linkable groups. Biphenyl, the first of many possible cross-linkable structures, was grafted on the polymer backbone to generate dangling biphenyl sulfone groups, Scheme 1. Once one benzene ring reacts, the second benzene ring is deactivated; soluble polymer is isolated. Cast films could be almost completely crosslinked by heating under vacuum at 210°C for at least 1 hour. Studies of heating times and temperatures showed that the polymer was stable for at



SCHEME 1. Grafting and Crosslinking of PPDSA Polymers and Copolymers

least two hours at 225°C, but showed some acid loss after 2 hours at 250°C. The 10 and 12 mole% grafts were extensively characterized, though conductivity and water absorption data were obtained for most grafts.

1, 4-Dibromobenzene 2, 5-disulfonic acid was successfully copolymerized with 2, 7-dibromofluorene 3, 5-disulfonic acid in 10/1 and 20/1 mole ratios to give high viscosity copolymers. However, we still have not been able to graft benzyl groups effectively on the fluorene moieties. Each should add two benzyl groups, but as yet we have only reached about 0.5 groups. Films crosslink when heated but they swell too much to be useful.

Properties: Grafted polymer films showed almost the same conductivity and mechanical properties before and after crosslinking. Swelling at a given graft percent was identical up to 50% RH, independent of crosslinking. Crosslinked PEMs (7 to 16 mole% biphenyl graft) swelled 90 to 60% when the RH rose from 0 to 98%. The x and y dimensions increased only 10 to 15% for all crosslinked films. At 98% RH, λ before crosslinking was about 2.5 to 3 higher than after crosslinking, with a corresponding dimensional increase.

Stress/strain measurements were made on many films before and after crosslinking. Elongation at break (22 to 30% RH) varied randomly between 6 and 9%; crosslinked films broke at much higher stress (35 to 45 MPa) than the uncrosslinked films (20 to 25 MPa). Stress concentrators, bubbles or particles in the film or edge defects, probably initiated failure. Lower humidity raised the modulus and break stress but lowered break elongation. Higher humidity drastically lowered the modulus of the uncrosslinked films; they tended to creep at constant force above 3% elongation.

Water absorption from 0 to 98% RH was measured for grafted films before and after crosslinking. Uncrosslinked films had final λ s of 12.5 to 14.5; when crosslinked, λ decreased to 8.5 to 12. Differential scanning calorimetry measurements showed that about 9 molecules of water per acid group were strongly bound, much higher than that found for Nafion 117[®], and others.

Parallel conductivity was measured at 80°C as a function of RH for many films, both here and at the Florida Solar Energy Center (FSEC). Results agreed within experimental error. Conductivity decreased with higher grafting; however on a log conductivity vs. RH graph, all plots were parallel. Crosslinking did not change conductivity even though it decreased the IEC. Even at the highest grafting levels, low RH conductivity was still very high. Through plane conductivity for a 12 mole% biphenyl grafted and crosslinked B2P8 copolymer, uncorrected for electrode/film resistance, is shown in Figure 1 (measured by Dr. Kevin Cooper, Scribner Associates). The through plane conductivity at 80°C is about that of the parallel conductivity (measured at Case and at Bekktech). Its conductivity at 120°C and 30% RH is 100 mS/cm, close to the DOE 2015 goals. We expect that materials with a lower percentage of grafting will have higher conductivity.

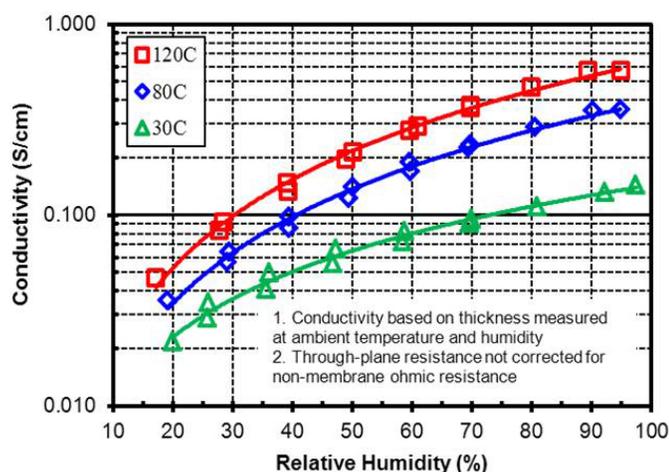


FIGURE 1. Through-Plane Proton Conductivity for B20P80-g-BP12%-210C-3hr (D7) as a function of RH at 30, 80 and 120°C

Fuel Cell Testing: Several grafted materials (both as uncrosslinked (D9) and as a final crosslinked film (D7) were sent to the FSEC for testing in MEAs. They tested the film crosslinked at Case Western University (D7) and a second film (D9) cast and crosslinked at FSEC. Both showed high hydrogen leakage, probably from small tears generated in the brittle films during electrode application. Figure 2 shows some results for D7, the best film, a B2P8 copolymer grafted with 12 mole% biphenyl. The hydrogen leakage lowers the voltage at low current densities. Above 100 mA/cm², the curves follow each other closely, with the power output for the D7 cell about 95% that of the reference Nafion211® cell over the useful current range. Considering that this was the first fuel cell test on a new material with very different chemical and mechanical properties from the normal PEMs, such good performance is remarkable. We expect that a film

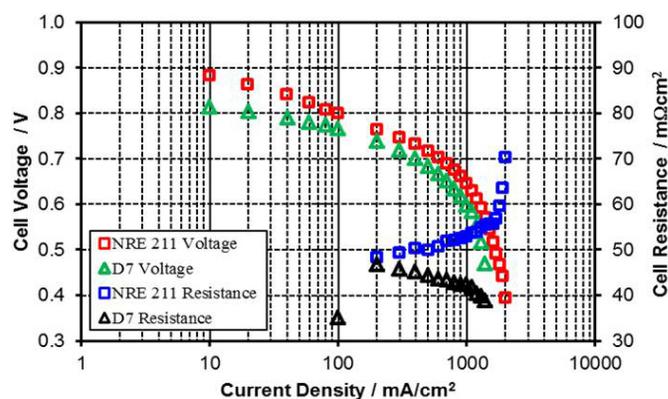


FIGURE 2. Single-Cell Performance of an MEA using B2P8-g-BP12%-210C-3hr (D7, 80 μ thick) compared to that of Nafion® (NRE211) at 80°C, 100% RH, H₂/air, Ambient Pressure (Work done at FSEC.)

without defects should have very low hydrogen and oxygen permeability; the highly polar aqueous phase is a very poor solvent for the non-polar gasses while the organic phase consists of rigid aromatic rings that cannot dissolve the gasses.

A summary of the results for films D7 and D9 compared with that of NRE211, is shown in Table 2. D6, the first entry, is an octyl benzene graft; this could not be crosslinked and disintegrated during testing. The major problem was gas leakage through the membrane that varied widely from one day to the next (probably due to micro tears that opened and closed with changing humidity and history). When gas leakage was accounted for, the membrane performance was about that of DRE211. Since the films had lower resistance, this was unexpected; MEA preparation needs to be improved. However, these are excellent results for a first study.

TABLE 2. First Tests of Case Membranes against NRE211, compared to DOE 2015 Targets

Characteristic	Units	Target 2015	D6 ^d	D7 ^d	D9 ^d	NRE211
Area specific proton resistance ^e at:						
120°C and water partial pressures from 40 to 80 kPa	Ohm-cm ²	≤0.02	N/D	0.093	0.13	0.18
80°C and water partial pressures from 25-45 kPa	Ohm-cm ²	≤0.02	0.076	0.040	0.042	0.05
Maximum hydrogen cross-over ^a	mA/cm ²	2	10.8	1.9	136	0.76
Minimum electrical resistance ^b	Ohm cm ²	1,000	8.4	31	14	2,100
Performance @ 0.8 V (¼ power)	mA/cm ² mW/cm ²	300 250	N/D N/D	34 27	N/D N/D	151 120
Performance @ rated power	mW/cm ²	1000	N/D	108	N/D	480

^a Measured in humidified H₂/N₂ at 25°C.

^b Measured in humidified H₂/N₂ using linear sweep voltammetry curve from 0.4 to 0.6 V at 80°C.

^c Average cell resistance from current interrupt.

^d D6 is B2P8-g-16 mole% n-octylbenzene. D7 is B2P8-g BP 12%, cast and crosslinked for 3 hrs at 210°C at Case Western Reserve University. D9 is the same polymer, cast and crosslinked at FSEC.

N/D - not determined

Conclusions and Future Directions

- We have made PEMs with very high conductivity at low RH and have been able to dimensionally stabilize them through crosslinking.
- Some crosslinked membranes were tested as MEAs in single fuel cells and performed well for a first study.
- The major problem for these materials is their low elongation at break, 6 to 9%, which promoted the formation of micro-tears in the MEAs during their preparation. This is mainly the result of their rigid-rod structure. However, elongation will increase with higher molecular weight.
- There has been no study of possible membrane cost. Some procedures used are fine for laboratory preparations but are wasteful. Work will start on lower cost approaches - possible alternate monomers and grafting methods.
- In the coming year, we will concentrate on making higher molecular weight polymers. We are considering two approaches. First, determine the best polymerization conditions. Second, develop comonomers that increase polymer solubility, allowing it to reach higher molecular weight before it precipitates. With these approaches, we should be able to reach high modulus, high elongation PEMs.
- In addition, grafting procedures need to be improved. Grafting is inhomogeneous and expensive. Inhomogeneity reduces crosslinking effectiveness: poorer mechanical properties for a given percent graft. We will work to develop methods to graft homogeneously using minimal amounts of reagents. This should result in PEMs with higher conductivity and lower swelling.
- As better PEMs are made, they will be submitted to the FSEC for extensive testing as MEAs.

FY 2011 Publications/Presentations

1. 10/12/10 ECS, Las Vegas, NV.
2. 10/28/10 FreedomCar Tech Team Review, Southfield, MI .
3. 12/19/10 Pacificchem 2010, Honolulu HI.
4. 5/11/11 DOE Progress Review.
5. Rigid Rod Poly(p-Phenylene Sulfonic Acid) PEMs: High Conductivity at Low Relative Humidity Due to “Frozen-In-Free Volume”, Morton Litt, Sergio Granados-Focil, Junwon Kang, Kun Si and Ryszard Wycisk, *Polymer Electrolyte Fuel Cells 10* Editor(s): H. Gasteiger, et al, *Volume 33, Issue 1 - October 10 - October 15, 2010, Las Vegas, NV* pp.695-710 (2010).

References

1. F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski and J.E. McGrath, *J. Membr. Sci.* **2002** 197, 231.
2. J. McGrath et al, DOE Program review, 6/08 Washington, D.C.
3. S. Granados-Focil, Ph. D. thesis CWRU, 2006; Sergio Granados-Focil. and Morton H. Litt, *ACS Polymeric Materials Science & Engineering Preprints*, **89**, 438 (2003); Sergio Granados-Focil, Thomas Young and Morton H. Litt, *ACS Fuel Chemistry Division Preprints*, **49(2)** 528-529 (2004).
4. Yue Zhang, Ph. D. Thesis, CWRU, 2001; Morton H. Litt, Sergio Granados-Focil; Yue Zhang and Thomas Young, Molecular design of rigid rod polyelectrolytes: Effect of structure on water retention and conductivity. *ACS Fuel Chemistry Division preprints* **49(2)** 594-595 (2004).