Final Technical Report

Durable, Low-cost, Improved Fuel Cell Membranes

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Table of Contents

I.	Executive Summary.....	7
II.	Comparison of Accomplishments with Project Objectives	9
III.	Detailed Report.....	10
	Introduction	10
	Sulfonic Acid-Functionalized Membrane (M43 Series).....	13
	Process Optimization of M41	13
	M43 Beginning of Life MEA Testing.....	14
	MEA Hot-Pressing Study	15
	Ionomer/Membrane Interface Study	17
	Test protocol studies.....	19
	Improved Conditioning Protocol for Arkema Membranes.....	19
	MEA Performance Testing : Flow Rate Setting	21
	Durability Testing of M43	22
	OCV Testing.....	22
	RH cycling protocol study: effect of air flow rate.....	23
	Factors impacting M43 membrane mechanical durability in RH cycling...25	
	Post Mortem Analysis of M43 Durability Test Samples	26
	OCV Hold	27
	M43 RH cycling:	27
	Large size MEA testing (HNEI)	28
	Phosphonic Acid Functionalized Membranes (M50 Series)	29
	Synthesis of Vinylbenzyl Phosphonic Acid (VBPA).....	29
	Michaelis-Arbuzov Route	30
	Sodium Diethylphosphite (NaDEP) Substitution Route	30
	VBP-(OH) ₂ Synthesis	31
	VBP-(OH) ₂ Copolymerizations	31
	Alternative Sulfonic Acid Functionalized Membranes (M60 Series)	35
	Disulfonated Styrene Functionalized Membranes (M70 Series).....	38
	M70 Membrane Development.....	39
	Fuel cell performance of Laboratory cast M70 membranes.....	41
	M70 Pilot Production.....	43
	Durability testing	46
	RH cycling	46
	OCV hold test.....	47
	Water Transport Properties.....	48
	Electro-osmotic Drag (EOD) Coefficient.....	48
	Water Permeation	50
	Membrane Blends of M43/M70.....	51
	Modified M70 System – Sulfonated Crosslinking Agent	51
	BPSH-Based Membranes	52
	BPS-60/PVDF Membranes.....	54
	BPSH-100/PVDF Membrane Blends	58
	Ethynyl-functionalized BPSH-100	59
	Amine-functionalized BPSH-100	59
IV.	Summary	61

Acronyms.....	61
References	62

Table of Figures

Figure 1. Schematic of Arkema's process for producing membranes.....	11
Figure 2. 10k magnification SEM images of (a) uncompatibilized and (b) compatibilized membranes (conductivities below images are measured at 70°C, fully hydrated membrane).	12
Figure 3. M41 conductivity as a function of relative humidity at 80°C. The membrane was tested in cooperation with the Florida Solar Energy Center (FSEC) and BekkTech LLC.	12
Figure 4. M41 and M43 conductivity as a function of relative humidity at 80°C. The membranes were tested in cooperation with the Florida Solar Energy Center (FSEC) and BekkTech LLC.....	13
Figure 5. MEA performance of M43 under different RH conditions.....	14
Figure 6. Comparison of BOL performance of M43 at 0.6 vs. 1 mil at 50% RH. The 1mil membrane data shown in Figure 5 and Figure 6 were prepared from different samples (sample variability is $\pm 10\%$).....	15
Figure 7. Image of a M43 membrane showing severe membrane wrinkling at the electrode edges after wet hot-pressing the wet membrane with PFA blanks (simulated hot-pressing conditions).	16
Figure 8. Non-hot-pressed MEA AFTER performance testing with the GDL removed. The electrode layer was completely transferred to the membrane, showing excellent adhesion between the two components.	17
Figure 9. MEA resistance vs. membrane thickness for M43 and Nafion [®] at 80°C 100%RH.	19
Figure 10. Response of a M41 MEA to a conditioning protocol developed for a PFSA material.....	20
Figure 11. Data from the conditioning protocol developed for M41.....	21
Figure 12. M43 MEA performance under different gas flow conditions (higher and lower/normal conditions).	22
Figure 13. OCV hold durability performance of M43 using USFCC and DOE conditions.....	23
Figure 14. MEA resistance responses during RH cycling using 50cm ² at a flow rate of 2 slpm and 25cm ² at a flow rate of 1 slpm.	24
Figure 15. M43 MEA resistances response of 25cm ² and 50cm ² cells with 2 slpm.	25
Figure 16. Effect of hot-pressing temperature on RH cycling durability of M43.	26
Figure 17. Effect of membrane thickness on RH cycling durability of M43.	26
Figure 18. Thickness and sulfur content change of M43 after OCV hold test.	27
Figure 19. Optical images of M43 membrane showing failure points in RH cycling tests. The image on the left shows a fracture near the edge of electrode and the image on the right shows a hole that developed near the gas inlet.	28
Figure 20. Performance comparison of M41 and PFSA membrane from Johnson Matthey in 400cm ² UTC cells (conditions were 80°C, 1.5x H ₂ and 2x air stoich, fully humidified).	29
Figure 21. Synthetic routes to VBP from VBC. Top: Michaelis-Arbuzov rearrangement, Bottom: S _N 2 sodium diethylphosphite substitution.	30

Figure 22. Synthesis of VBP-(OH) ₂	31
Figure 23. SEM image of the cross-section of a membrane containing PVDF and a polyelectrolyte based on VBPA and a crosslinkable monomer.....	32
Figure 24. SEM image of the cross-section of a M51 membrane. Image was taken by Karren More at Oak Ridge National Laboratory.	33
Figure 25. 80°C ex-situ conductivity of M51 membrane. Data was collected from a 4pt probe inserted in a humidity chamber at 80°C.	33
Figure 26. 80°C MEA performance of a phosphonated membrane (M52) vs. M41 at various RH levels.....	34
Figure 27. 120°C MEA performance of a phosphonated membrane (M53) vs. M41 at various RH levels.....	35
Figure 28. TEM image of M61. The image was taken and analyzed by Karren More at ORNL. The image contains a spherical fluorine-rich, sulfur-depleted phase (→) and a matrix that has modulating contents of fluorine and sulfur (→).....	36
Figure 29. 80°C ex-situ conductivity of M61 membrane. Data was collected from a 4pt probe inserted in a humidity chamber at 80°C.	37
Figure 30. 80°C in-cell conductivity of M61 membranes at a) 100%RH and b) 53%RH gas inlets.	37
Figure 31. Performance of M61 membranes at 80°C and 53%RH at gas inlets. The three curves for M61 represent different MEAs constructed to test reproducibility.....	38
Figure 32. Generalized structure of the disulfonated monomer used in the polyelectrolyte for the M70 membrane.....	39
Figure 33. Influence of process parameters on M70 membrane appearance, morphology, and conductivity.	40
Figure 34. Labcast M70 conductivity compared to M43 and Nafion® NR-211. M70 – Initial Method was material made from an unoptimized process early in the project. M70 – Improved Method used an optimized process to fabricate the membrane, which is similar to process “C” in Figure 33. Data was collected from a 4pt probe inserted in a humidity chamber at 80°C.	41
Figure 35. MEA performance of lab-produced M70 samples under high (top) and moderate (bottom) RH conditions. The test conditions are given in each of the graphs.....	42
Figure 36. 80°C conductivity vs RH of M70, M43 and Nafion® NR211 at 80°C.	43
Figure 37. Hydrogen crossover rates of M70, M43 and NR211 membranes.	44
Figure 38. BOL MEA performance of pilot fabricated M70 at high RH.....	45
Figure 39. BOL performance of M70, M43 and NR211 at 30% RH.	46
Figure 40. RH cycling test of M70, M43 and NR211 membranes.	47
Figure 41. Chemical stability of M70, M43, and Nafion® NR211 membrane under an OCV hold test (USFCC conditions).....	48
Figure 42. Electro-osmotic drag coefficients of Arkema and Nafion® membranes.....	49
Figure 43. Water permeability of Nafion® and Arkema membranes.....	50
Figure 44. Conductivity of M43/M70 blend membranes in water at 70°C. The legend indicates the weight ratio of M70/M43 in the membrane. The line	

shows the theoretical response of the blends assuming ideal mixing behavior.	51
Figure 45. 80°C RH conductivity of M70 containing a sulfonated crosslinking agent.....	52
Figure 46. Disulfonated poly(arylene ether sulfone) random copolymers (BPS) via direct copolymerization.....	53
Figure 47. SEM images of three membranes containing 60wt% PVDF and 40 wt% BPSH60 that were produced from processing methods A (left), B (center), and C (right). Membranes from processing methods A and B were opaque, while the membrane from method C is transparent.	54
Figure 48. 90% RH conductivity data of BPSH60/Kynar membranes and M41 at 80°C. Points for the BPSH60 represent individual runs.	56
Figure 49. Water uptake and X,Y swelling of BPS60/Kynar membranes. For reference, M41 has an X,Y swelling = 20% and a water uptake of 65%. Nafion [®] has a water uptake of 40% and an X,Y swelling of 15%.....	56
Figure 50. SEM images of a membrane containing 15 wt% Kynar and 85 wt% 6F50. The image on the left is the membrane before exposure to boiling water (transparent membrane) and the image on the right is the dry membrane after exposure to boiling water for one hour (opaque membrane).	57
Figure 51. TEM image/elemental maps of PVDF/BPS60 membrane containing 60wt% BPS60. The image was taken and analyzed by Karren More at ORNL.....	58
Figure 52. Ethynyl (top) and amine (bottom) functionalized BPSH-100. M_w ranged from 3-5kg/mol for the materials tested.	58
Figure 53. 80°C RH conductivity performance of several amine-functionalized BPSH/PVDF membranes cured with epoxide. The loading of BPSH-100 is indicated in the graph legend.....	60

I. Executive Summary

The development of low cost, durable membranes and membranes electrode assemblies (MEAs) that operate under reduced relative humidity (RH) conditions remain a critical challenge for the successful introduction of fuel cells into mass markets. It was the goal of the team lead by Arkema, Inc. to address these shortages. Thus, this project addresses the following technical barriers from the fuel cells section of the Hydrogen Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

Arkema's approach consisted of using blends of polyvinylidene fluoride (PVDF) and proprietary sulfonated polyelectrolytes. In the traditional approach to polyelectrolytes for proton exchange membranes (PEM), all the required properties are "packaged" in one macromolecule. The properties of interest include proton conductivity, mechanical properties, durability, and water/gas transport. This is the case, for example, for perfluorosulfonic acid-containing (PFSA) membranes. However, the cost of these materials is high, largely due to the complexity and the number of steps involved in their synthesis. In addition, they suffer other shortcomings such as mediocre mechanical properties and insufficient durability for some applications.

The strength and originality of Arkema's approach lies in the decoupling of ion conductivity from the other requirements. Kynar[®] PVDF provides an exceptional combination of properties that make it ideally suited for a membrane matrix (Kynar[®] is a registered trademark of Arkema Inc.). It exhibits outstanding chemical resistance in highly oxidative and acidic environments.

In work with a prior grant, a membrane known as M41 was developed by Arkema. M41 had many of the properties needed for a high performance PEM, but had a significant deficiency in conductivity at low RH. In the first phase of this work, the processing parameters of M41 were explored as a means to increase its proton conductivity. Optimizing the processing of M41 was found to increase its proton conductivity by almost an order of magnitude at 50% RH. Characterization of the membrane morphology with Karren More at Oak Ridge National Laboratory showed that the membrane morphology was complex. This technology platform was dubbed M43 and was used as a baseline in the majority of the work on the project. Although its performance was superior to M41, M43 still showed proton conductivity an order of magnitude lower than that of a PFSA membrane at 50% RH. The MEA performance of M43 could be increased by reducing the thickness from 1 to 0.6 mils. However, the performance of the thinner M43 still did not match that of a PFSA membrane.

In the second phase of the grant, attention was focused on the development of novel polyelectrolytes to increase proton conductivity. Four categories of polyelectrolytes were explored:

1. Phosphonic acid-functionalized monomer: M50 series
2. Alternate sulfonated monomer (drop-in replacement): M60 series
3. Multiacid-functional polyelectrolytes (novel syntheses): M70 series
4. Highly sulfonated BPSH polyelectrolytes (collaboration with J. McGrath)

The M50 series of membranes were prepared with PVDF and polyelectrolytes that contained varying proportions of phosphonic and sulfonic acid groups. The phosphonic acid groups were incorporated in an attempt to promote proton conductivity in dry conditions. All of the polyelectrolytes in the M50 family did not blend as well with PVDF as the M41 polyelectrolyte and significant phase separation was observed in the membrane. The proton conductivity and MEA performance of these materials was substantially below M41.

The M60 membrane series was developed around PVDF and a polyelectrolyte that had about 10% more sulfonic acid groups than the M43 polyelectrolyte at a comparable loading. TEM analysis of the membrane showed an intimate blending of the PVDF and polyelectrolyte components. The membrane showed some variability in testing, but proton conductivity and beginning of life (BOL) MEA data showed slightly higher performance data.

As a follow-up to M60, a new monomer was synthesized that contains two sulfonic acid groups. This new monomer allowed the generation of PVDF-containing membranes, named M70, which had very low equivalent weights (EW). The EW of M70 was typically around 475-525g/equiv, while the EW of M43 was approximately 800g/equiv. The M70 membrane showed substantially improved proton conductivity over M43. The proton conductivity of M70 was higher than that of a PFSA membrane at high RH values (>90%) but was roughly half of the PFSA at 50% RH. The conductivity results at low RH can be used to explain the MEA performance, which shows that M70 is still slightly below that of the PFSA under dry conditions.

In collaboration with James McGrath at Virginia Tech, a series of sulfonated aryl ether sulfonated-based polyelectrolytes were blended with PVDF. At sulfonation levels of 60%, the polyelectrolytes did not blend well with the PVDF and tended to generate large scale phase separation that was attributed to the lower acid content of these materials compared to the polyelectrolytes used in the work described above. The morphologies of the systems also were not stable. Immersing some of the samples in hot water generated opacity and the presence of voids in the membrane. The morphology instability was attributed to polyelectrolyte rearrangement or dissolution. Increasing the amount of sulfonated monomer and providing functional endgroups for crosslinking in the polyelectrolyte resulted in materials that blended well with PVDF and showed

substantially better stability in boiling water. The proton conductivity of the best systems was between that of M43 and M70.

II. Comparison of Accomplishments with Project Objectives

This project was constructed to address the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Durability
- B. Cost

Specifically, the project was aimed at developing membranes with a cost of \$20/m² and membrane electrode assemblies with a durability of 5,000 hr with cycling.

Objective #1: *Develop a membrane capable of operating at 80°C at low relative humidity (25-50%).*

Five polyelectrolyte technologies were evaluated for this objective. M70 is the most promising membrane technology developed in the project for low RH operation at 80°C. At high relative humidity (100% RH H₂, 70%RH air, 100kPa abs) M70 performance is approximately 0.85A/cm² at 0.6V, compared to 0.95A/cm² for Nafion® NR211. At low RH (30%RH) M70 gives a performance at about 0.5A/cm² at 0.6V, while NR211 gives 0.62A/cm² at the same conditions.

Objective #2: *Develop a membrane capable of operating at temperatures up to 120°C and ultra-low relative humidity of inlet gases (< 1.5 kPa).*

While M70 is the most promising technology developed in the project for enhanced proton conductivity at low relative humidity, the polyelectrolyte cannot handle sustained operation at 120°C without decomposition. BPSH/PVDF membranes may potentially be suited for 120°C operation but they were not tested due to low conductivity and the limited amount of material available.

Objective #3: Elucidate ionomer and membrane failure and degradation mechanisms via ex-situ and in-situ accelerated testing.

M43 has excellent OCV durability compared to a 1 mil unreinforced PFSA. M43 lasts more than 3600 hours in OCV testing with the DOE protocol, far surpassing the DOE target of 500 hours. Under the same test conditions, the PFSA membrane lasts only 150 hours. The failure mode in OCV testing of M43 is attributed to a gradual loss of sulfur (i.e. sulfonic acid groups) that eventually causes the membrane conductivity to drop to a point where it can no longer operate. The loss of sulfonic acid is attributed to the aggressive oxidative environment of the test. The membrane thickness did not change substantially

during the test (i.e. the membrane thickness at the end of the test was within 10% of the starting thickness).

M43 shows reasonable RH cycling durability, showing an average of 15,000 cycles of operation during testing. However, this falls short of the DOE target of 20,000 cycles. The failure mode for M43 is the formation of cracks or fractures, which typically form near the electrode edge and gas inlet. This location is where membrane is exposed to dry gas the longest time during the cycling and is therefore subjected to the greatest degree of stress during the cycling of wet and dry gases.

M70 showed significantly better OCV durability than a 1 mil PFSA, but it still failed much sooner than M43 (M70 lasted 300 hours compared to > 2400 hours for M43 and 70 hours for a PFSA membrane under USFCC conditions). Post mortem analysis of the M70 membrane samples showed that the failure is due to membrane fracture around the edge of electrodes.

M70 operated for 50 cycles in the RH cycling durability test. 1 mil PFSA and M43 lasted about 4000 and 15000 cycles, respectively. The low durability of M70 is attributed to its higher degree of swelling in a hydrated environment compared to M43 (XY swelling of M70 is 30% compared to 23% for M43). Higher degrees of swelling reduce RH cycling durability through larger stresses generated during the hydration/dehydration cycles in the test. Qualitatively, the material also appears to be more brittle than M43 at lower RH values.

III. Detailed Report

Introduction

Proton exchange membrane (PEM) fuel cells typically rely on perfluorosulfonic acid-containing perfluoropolymers for the construction of the membranes.¹ An example of a PFSA membrane is Nafion[®], which is commercially available (Nafion[®] is a registered trademark of E.I. DuPont de Nemours & Company). The cost of these materials is high, largely due to the complexity and the number of steps involved in their synthesis. In addition, they suffer other shortcomings such as mediocre mechanical properties, poor gas barrier properties, and insufficient conductivity for lower RH operation conditions that are desired for automotive applications.

Arkema's approach comprises the preparation of blends of poly(vinylidene fluoride) (PVDF) and highly sulfonated polyelectrolyte(s), which are very intimately mixed to form a fine scale morphology. An illustration of the process is shown in Figure 1. The strength and originality of Arkema's approach lies in the decoupling of ion conductivity from the other requirements. Kynar[®] PVDF provides an exceptional combination of properties that make it ideally

suited as the non-sulfonated component in the polymer blend membranes. It exhibits outstanding chemical resistance in highly oxidative environments (such as hydrogen peroxide and bromine), as well as in extreme acidic environments (such as HF, HCl and H₂SO₄). As evidence of the exceptional electrochemical stability and mechanical toughness of Kynar[®] PVDF, it is widely used as binder material in lithium ion batteries. Also, this approach provides flexibility inherent to the production process and can offer a potentially lower cost than PFSA-type membranes (at equal production volume) because synthetic requirements and their preparation process is simpler.

Figure 1. Schematic of Arkema's process for producing membranes.

Strict control of the resulting blend morphology is required to obtain the high proton conductivity necessary for fuel cell applications. With the help of previous DOE grant #DE-FC36-04GO14051, Arkema and its partners were able to significantly advance the technology and develop processing conditions needed to blend PVDF and various polyelectrolytes. Blending hydrophilic and hydrophobic polymers typically yields gross phase separation of the two polymers as shown on the SEM micrograph in Figure 2a. However, the Arkema process uses a compatibilizer technology that allows Kynar[®] PVDF and sulfonated polyelectrolytes to produce a much finer morphology and yielding excellent proton conductivities as shown in Figure 2b.

Figure 2. 10k magnification SEM images of (a) uncompatibilized and (b) compatibilized membranes (conductivities below images are measured at 70°C, fully hydrated membrane).

At the end of the previous grant, a membrane technology known as M41 was developed which was used in this grant as a starting point to develop improved membranes capable of operating at low relative humidity. The ex-situ proton conductivity of M41 as a function of relative humidity is shown in Figure 3. Figure 3 shows that the ex-situ conductivity of M41 drops rapidly as the RH is reduced. At 50% RH, the conductivity of M41 is two orders of magnitude below Nafion® 212. As mentioned above, M41 was used as the basis for the start of the grant and improvements to the M41 technology as discussed in the section below.

Figure 3. M41 conductivity as a function of relative humidity at 80°C. The membrane was tested in cooperation with the Florida Solar Energy Center (FSEC) and BakkTech LLC.

Sulfonic Acid-Functionalized Membrane (M43 Series)

Process Optimization of M41

At fixed chemical composition (i.e. fixed levels of polyelectrolyte and PVDF) the process conditions used to prepare the membrane constitute another important set of parameters that can influence its performance at low relative humidity. It has been established that fuel cell membrane properties can vary depending upon how they are processed. The casting conditions and post-treatment (e.g. acidification or annealing) can strongly affect physical properties, including conductivity, mechanical properties, and swelling.^{2,3,4}

After the film formation step in M41, the membrane requires an activation step to prepare it for use in testing and MEA fabrication. By improving the activation process, we were able to demonstrate conductivity of 130-150 mS/cm, slightly lower than the value we observed with 1 mil Nafion® (160 mS/cm).^{*} The conductivity vs. humidity plot recorded at the Florida Solar Energy Center is shown in Figure 4 below. A noticeable improvement is observed relative to the regular M41 produced with the standard process. The conductivity of membranes made with the improved process is an order of magnitude higher than M41 at 50% RH. The membrane prepared by the new process was dubbed M43.

Figure 4. M41 and M43 conductivity as a function of relative humidity at 80°C. The membranes were tested in cooperation with the Florida Solar Energy Center (FSEC) and BakkTech LLC.

^{*} Conductivity was measured on a completely hydrated membrane in deionized water at 70°C.

M43 Beginning of Life MEA Testing

The beginning of life (BOL) performance of M43 as a function of RH is shown in Figure 5. The membrane performance is strongly affected by relative humidity and is essentially inoperable at 30% RH.

Figure 5. MEA performance of M43 under different RH conditions.

In an effort to understand the envelope of adequate performance, we evaluated a thinner version of M41 0.6 mil (vs. 1 mil). The thinner membrane was possible because M43 exhibits good mechanical properties and outstanding gas cross-over characteristics. As can be seen in Figure 6, the thinner M43 exhibits improved performance at 50% due to the lower areal resistance of the membrane. The 0.6mil membrane exhibits about 0.6V at 600mA/cm², a value approaching that of the 1mil membrane run at 100% RH. However, the thinner membrane still does not match the performance of Nafion®.

Figure 6. Comparison of BOL performance of M43 at 0.6 vs. 1 mil at 50% RH. The 1mil membrane data shown in Figure 5 and Figure 6 were prepared from different samples (sample variability is $\pm 10\%$).

Johnson Matthey gas diffusion electrodes (GDEs) were used in all the fuel cell performance testing in this project. The GDE is based on JM catalyst formulation coated carbon paper. The same GDE is used on both the anode and cathode in test cells.

MEA Hot-Pressing Study

Previously, a wet layout hot-pressing process was used at Arkema for laminating MEAs. In this process, each membrane was fully hydrated in deionized water and assembled in the GDE construction for hot pressing. Several problems have been observed with the wet hot-press practice:

- Significant membrane thinning underneath the electrode, up to 33% loss of thickness;
- Severe membrane wrinkling/buckling around the edge of electrodes, due to membrane shrinkage caused by the loss of hydration during hot-pressing. An example of this behavior is shown in Figure 7.

Figure 7. Image of a M43 membrane showing severe membrane wrinkling at the electrode edges after wet hot-pressing the wet membrane with PFA blanks (simulated hot-pressing conditions).

Membrane thinning after hot-pressing has been confirmed by scanning electron microscopy (SEM). SEM images of MEA constructions made from wet layups that showed the thickness was reduced from about 25 μm to 16-19 μm after hot-pressing. Simulated hot-pressing (hot-press the membrane with 2 PFA blanks cut to the same dimension as the electrode) also showed that membrane thickness was reduced from 24-25 μm to 17 μm in the active area.

The thickness change can be explained by the membrane shrinking from a fully hydrated state with the constraint that the membrane in contact with the surface of electrodes is fixed. Because of the constraint at the electrode surface, the membrane can only freely contract in the z direction (i.e. thickness) when it is dried during hot pressing. The loss of thickness stems from the membrane occupying a larger area across the GDE when hydrated, compared to the dry state.

To further confirm that the thinning is not from the hot-pressing conditions (i.e. exposure to higher temperatures and pressure), simulated hot-pressing was tested on dry membranes. M43 samples were tested with various hot-pressing parameters: temperatures up to 165 $^{\circ}\text{C}$, pressures up to 400psi, and duration up to 30min. No membrane thinning was observed under any of the tests. However, the samples started to show substantial discoloration above 140 $^{\circ}\text{C}$, possibly caused by degradation of polyelectrolyte.

Because the problems associated with the wet hot-pressing process, dry (membrane) hot-pressing became our standard MEA lamination procedure. The

best conditions for hot-pressing M43 MEAs are: 135°C, 220psi (1.5MPa), 4min, using a dry layout.

Ionomer/Membrane Interface Study

As mentioned previously the Arkema technology platform is based on membranes comprised of a blend of PVDF with a hydrocarbon based polyelectrolyte. The electrode material was provided by our partner, Johnson Matthey Fuel Cell, and uses a PFSA ionomer as a binder and proton conductor. Questions were raised about the compatibility between PFSA ionomer in the catalyst layer and the hydrocarbon-based membrane. Potential issues include: poor physical bonding between catalyst/ membrane interface and high interfacial resistance. The bonding between JM electrodes and Arkema membranes is good, as evidenced from inspecting the adhesion between the catalyst layer and membrane after peeling off the gas diffusion layer.

As shown in Figure 8, after cell testing, the non-hot-pressed MEA (mechanical compression in fuel cell hardware) showed a very good adhesion of the catalyst layer to the membrane. The catalyst layer almost completely transferred onto the membrane from the JM GDE. This is partially attributed to the fact that both PVDF and PFSA are fluoropolymers.

Figure 8. Non-hot-pressed MEA AFTER performance testing with the GDL removed. The electrode layer was completely transferred to the membrane, showing excellent adhesion between the two components.

To investigate the interfacial resistance between the catalyst layer and Arkema membrane, the methodology proposed by Kim, *et al* was used.⁵ The MEA resistance dependence on membrane thickness was measured and plotted. In this plot the y-intercept gives the non-membrane resistance (interfacial resistance plus other electronic resistance in the cell setup) and the slope is the reciprocal

of membrane conductivity. The results for M43 and Nafion® MEAs are shown in Figure 9.

From Figure 9, the interfacial and electronic resistance is $13.4\text{m}\Omega\cdot\text{cm}^2$ for Nafion MEAs, and $20.8\text{m}\Omega\cdot\text{cm}^2$ for M43 MEAs. The electronic resistance of the cell setup was measured separately with a blank cell, showing a value of approximately $15\pm 1\text{m}\Omega\cdot\text{cm}^2$. Therefore the interfacial resistance for the Nafion MEAs is close to zero, while it is about $7\text{m}\Omega\cdot\text{cm}^2$ for the M43 MEA. Thus interfacial resistance of M43 MEAs is slightly higher than that of Nafion® MEAs, but it is still very low. The difference in interfacial resistance translates to a loss of 7mV at $1\text{A}/\text{cm}^2$ between M43 and Nafion based MEAs. Similar results were also obtained for M70 membranes (this technology will be discussed later in the report).

The in-situ through-plane membrane conductivity can also be calculated from the data. As shown inside Figure 9, the conductivity for M43 and Nafion® is $84\text{mS}/\text{cm}$ and $119\text{mS}/\text{cm}$, respectively, at 80°C under fully humidified conditions. Both conductivity values of M43 and Nafion agree well with ex-situ conductivity measurements on a BekkTech instrument. However, the conductivity value for M43 measured by this method is much lower than that measured by the four-probe method in 70°C water. The conductivity test in 70°C water is a routine test used internally for quickly screening membranes. It usually gives a value of $130\text{--}150\text{mS}/\text{cm}$ for an M43 membrane, which is much higher than those measured in-situ or by BekkTech. One reason for the higher conductivity in the 70°C water test is that the membrane sample is boiled in water first prior to the test, and it has been confirmed by experiment that this pretreatment step induces the membrane into a highly conductivity state (likely due to complete swelling) that can not be reproduced in actual fuel cell operation. Although the absolute value of conductivity obtained by the 70°C water method is not accurate, one can still use it for screening membranes by looking at the relative trend.

In summary, both M43 and M70 show excellent bonding to the PFSA based catalyst layer. As a result, the interfacial resistance is only slightly higher than that of a PFSA electrode/PFSA membrane combination and should not cause any significant performance loss.

Figure 9. MEA resistance vs. membrane thickness for M43 and Nafion® at 80°C 100%RH.

Test protocol studies

Improved Conditioning Protocol for Arkema Membranes

M43 MEAs condition very slowly under the traditional break-in protocols, which were developed for PFSA membranes. One example of an MEA conditioning protocol applied to M41 is shown in Figure 10 (M41 and M43 behave the same under conditioning protocols). The figure shows that it takes 72-100 hours to condition the M41 MEA.

Figure 10. Response of a M41 MEA to a conditioning protocol developed for a PFSA material.

A new conditioning protocol was developed to reduce the time needed to break in MEAs constructed with Arkema membranes. The new protocol features a much quicker voltage cycling, and a larger range of voltages. Figure 11 depicts the change of performance over time during the new conditioning process. The cell reached its optimal performance (as indicated by the current and resistance) in just 3-4 hours. This is a significant improvement over the old protocol.

Figure 11. Data from the conditioning protocol developed for M41.

MEA Performance Testing : Flow Rate Setting

In the early part of this grant period, the BOL MEA performance was tested using very high gas flow rates (1 slpm for H₂ and 5 slpm for air/O₂ for 25cm² cell, about 11 stoich air @ 1.0A/cm²) and over-saturation (150%RH). The rationale was to minimize mass transfer limitations and any dehydration effects in the electrode. It was designed to characterize the membrane in its fully hydrated state. However, most other labs use much lower flow rates, and the flow rate is stoichiometry based (1.5 stoich for hydrogen, 2.0 stoich for air). The low stoichiometry flow rate settings are the most relevant for automotive applications.

An M43 MEA was tested under the high and normal flow conditions to understand the performance difference created by the two conditions. The results of the testing are shown in Figure 12. Compared to the old high flow/RH conditions, the performance under the lower flow conditions is about 30% lower at 0.6V. The higher than normal performance is mainly caused by the high backpressure (high pressure drop due to the high air flow rate), thereby creating a higher oxygen concentration. Higher gas flow rates also facilitate better water removal, and improve fuel cell performance.

Because the lower flow condition is more relevant for most applications, most of the performance testing in the project was done using the low stoich based flow

conditions. This also enables a straightforward comparison with test results from other labs. A few data sets generated with the higher flow rate that are shown later in this report are specifically identified as such.

Figure 12. M43 MEA performance under different gas flow conditions (higher and lower/normal conditions).

Durability Testing of M43

OCV Testing

The OCV hold test was designed to test membrane chemical stability. Two slightly different protocols exist: DOE and USFCC. The major difference between the two protocols is that the DOE protocol uses air as the oxidant, while the USFCC calls for pure oxygen. Our own tests compared the two protocols using M43 and the results are shown in Figure 13. It is clear that USFCC protocol is more aggressive, which is due to the use of pure oxygen instead of air.

Regardless of the protocol used, M43 performs much better than Nafion[®] NR-211 in the test. M43 comfortably passes the DOE requirement of 500 hours of testing. For most of our testing, the USFCC protocol was chosen because it

shortens the testing time. The failure mode for M43 in this test is discussed below.

Figure 13. OCV hold durability performance of M43 using USFCC and DOE conditions.

RH cycling protocol study: effect of air flow rate

The DOE standard protocol for RH cycling test is a 50cm² cell with a flow rate of 2 slpm and a 2 min cycle of 150%/0% RH gas. However, 25cm² cell hardware is more widely used in development and lab testing for cost and efficiency reasons. For a 25cm² cell, it is logical to scale down the air flow rate from 2 to 1 slpm because the active area of the cell is half that of the 50cm². 25cm² cell hardware was used initially in our testing and M43 lasted over 40,000 cycles under 1 slpm flow conditions in this configuration. Subsequently, M43 was tested with 50cm² cell hardware and it failed much quicker (< 3,000 cycles).

The effect of air flow rate on the RH cycling test was investigated by monitoring the change of high frequency resistance (HFR) of the MEA over time. The HFR results are dominated by membrane resistance at low RH. Therefore it can be used as a measurement of hydration status of the membrane during cycling. From the MEA resistance and ex-situ RH-conductivity data, one can derive the average membrane hydration level. The M43 MEA resistance responses from RH cycling using 50cm² at 2 slpm and 25cm² at 1 slpm are shown in Figure 14.

Figure 14. MEA resistance responses during RH cycling using 50cm² at a flow rate of 2 slpm and 25cm² at a flow rate of 1 slpm.

A significant difference exists in hydrations levels between 50cm²/2slpm and 25cm²/1 slpm. The lowest RH at the end of a drying cycle in the 50cm²/2slpm case is 20-30%, but in the 25cm²/1slpm case it is 50-60%. Therefore the 50cm² cell with 2 slpm is a much more stressful test since the membrane reaches a much lower degree of hydration and will contract more at this stage. In conclusion, data collected at 1 slpm on 25cm² hardware does not correlate well with the data collected at 2 slpm on 50cm² hardware and should not be used to benchmark against the DOE target of 20,000 cycles.

2 slpm flow rate was also tested for 25cm² cell. The M43 MEA resistance responses using 25cm² and 50cm² cells with 2 slpm are shown in Figure 15. With these conditions, the 25cm² cell test response looks very similar to that of the 50cm² cell. The use of the 25cm² hardware with 2 slpm is actually a little bit harsher than the standard DOE protocol. All of the RH cycling test data shown in this report after this section uses 25cm² hardware with a 2 slpm air flow rate.

Figure 15. M43 MEA resistances response of 25cm² and 50cm² cells with 2 slpm.

Factors impacting M43 membrane mechanical durability in RH cycling

The hot-pressing (HP) temperature was found to have a drastic impact on RH cycling durability of M43 membranes. The effect of HP temperature of 125 vs. 135°C on RH cycling durability of 1 mil M43 membrane is illustrated in Figure 16. It is clear from Figure 16 that a 135°C HP temperature increases the RH cycling durability of 1 mil M43 by a factor of 4-5. The improvement is partially attributed to a change in the distribution of the PVDF crystal size during the hot-pressing process. The same test was conducted on Nafion[®] NR211 membrane and no effect on the durability of the membrane was observed.

Figure 16. Effect of hot-pressing temperature on RH cycling durability of M43.

Membrane thickness also has a significant impact on M43 RH cycling durability, as shown in Figure 17. The RH cycling durability of 1 mil M43 (135°C HP temperature) is more than double than that of a 2.2 mil membrane. A similar effect was also seen on M43 membranes hot-pressed at 125°C

Figure 17. Effect of membrane thickness on RH cycling durability of M43.

Post Mortem Analysis of M43 Durability Test Samples

OCV Hold

In the section on durability above, the results of OCV testing with M43 was discussed. In this test M43 can last up to 2500-3600 hours, depending upon the testing protocol used. There are no significant changes in the average membrane thickness after the long OCV tests (>2,500 hrs), but a significant amount of sulfur is lost, as shown in Figure 18. Close to 50% of sulfur is lost in the sample tested for 2,500 hr using the USFCC protocol (pure O₂ as the oxidant). 42% sulfur loss was observed in the membrane that was run for 3,660hr with the DOE protocol (air as the oxidant). Even after more than 2,000 hrs in the OCV hold test, M43 showed no sign of high H₂ crossover or electrical shorting, the typical failure modes in PFSA membranes. The failure in M43 is triggered by the low OCV due to extremely high membrane resistance under low RH (30% RH, 90°C). Under this low RH condition, combined with significant amount of loss in conducting phase (as indicated by sulfur loss), the membrane became essentially an insulator, and OCV become lower than 0.8V. The OCV recovers immediately after the membrane is exposed to high RH. It is worth pointing out that the extreme degree of sulfur loss occurs after 1000s of hours of testing and that the membrane is able to meet the DOE requirements for this test.

Figure 18. Thickness and sulfur content change of M43 after OCV hold test.

M43 RH cycling:

No membrane thinning was observed with M43 or Nafion® NR211 samples in this test. Both membrane chemistries failed due to fractures or fissures formed over the course of the test. The failure points in M43 were usually located near electrode edges and the gas inlet, where the membrane is exposed to dry gas

the longest time during the cycling. Micrographs of typical membrane fracture points in M43 are depicted in Figure 19. The failure points are distributed more randomly through the Nafion[®] samples.

Figure 19. Optical images of M43 membrane showing failure points in RH cycling tests. The image on the left shows a fracture near the edge of electrode and the image on the right shows a hole that developed near the gas inlet.

Large size MEA testing (HNEI)

Large-sized MEAs (400cm²) made with M41 were tested at the HNEI facility using UTC S300 cell hardware with porous water transport plate technology. M41 and JM reinforced PFSA membrane performances were compared at 80°C and 60°C. The results at 80°C are shown in Figure 20. The 60°C results show a similar trend and thus are not shown here.

As shown in Figure 20, the M41 membrane gave inferior performance relative to the PFSA membrane in both oxygen and air operations. The performance difference is consistent with results using small-scale cell hardware (50cm² and 25cm²). Nevertheless, the test results demonstrated that M41 can be successfully scaled up and operated in a large-sized MEA.

Figure 20. Performance comparison of M41 and PFSA membrane from Johnson Matthey in 400cm² UTC cells (conditions were 80°C, 1.5x H₂ and 2x air stoich, fully humidified).

Phosphonic Acid Functionalized Membranes (M50 Series)

One major drawback of current fuel cell membrane technology is poor H⁺ conduction performance at reduced RH. A membrane that efficiently retains water and conducts protons mainly through a ‘Grotthuss’ type mechanism is one potential pathway to address this problem. One approach to this end is to use a polyelectrolyte in a blended membrane that contains phosphonate groups covalently bound to the polymer backbone. Phosphonate groups (and phosphoric acid) have been shown in the literature to more efficiently retain water, thus increasing H⁺ conduction at reduced RH. Such structures were targeted to improve performance at low RH. Here, routes to styrenic copolyelectrolytes are explored as model systems to determine their performance relative to the M43 membranes.

Synthesis of Vinylbenzyl Phosphonic Acid (VBPA)

Vinylbenzyl phosphonate (VBP) is a phosphonic acid-functionalized monomer and can be synthesized by two routes using vinylbenzyl chloride (VBC). The two

routes are shown in Figure 21 and both produce VBP in the (organic-soluble) diethyl ester form, which may be copolymerized under a number of conditions (e.g. bulk, organic solution, and aqueous emulsion).

Figure 21. Synthetic routes to VBP from VBC. Top: Michaelis-Arbuzov rearrangement, Bottom: S_N2 sodium diethylphosphite substitution.

It is understood that this monomer may not provide the durability needed for long-term operation, especially at higher temperatures. This monomer was pursued as a model compound as a straightforward way to test the idea of using this functional group.

Michaelis-Arbuzov Route

This route involves the heating of an alkyl halide (VBC) with triethylphosphite (TEP). A substitution/rearrangement ensues, forming an alkyl phosphonate (VBP in this case) and alkyl chloride. An excess of triethylphosphite to starting alkyl halide is used to ensure high conversion. The product is purified by vacuum distillation of the triethylphosphite and remaining starting alkyl halide (VBC) away from the product (VBP). An example reaction with the post-purification results is shown in Table 1.

Table 1. Reaction charges and post-purification results for Michaelis-Arbuzov VBP synthesis.

Initial Charge			Post-Purification		
	VBC (initial)	TEP (initial)	Residual VBC %	Residual TEP %	Conversion (NMR) %
(g) [mol]	50 [0.33]	164 [0.98]	7.6%	<5%	92.4%
Equiv.	1	3			

Sodium Diethylphosphite (NaDEP) Substitution Route

For this preparation, diethylphosphite is reacted with metallic sodium in an initial step to form sodium diethylphosphite (NaDEP). The NaDEP is then added to VBC with the concomitant precipitation of NaCl. After aqueous workup, residual

DEP is removed via rotary evaporation. Results from several reaction procedures are shown in Table 2. Optimization revealed that 99% conversion could be attained using 2eq. of NaDEP to VBC. While removal of residual DEP was not quantitative, residual DEP can be lowered to less than 4%. This synthesis was scaled to produce 200g of VBP monomer with similar results to smaller scale reactions.

Table 2. Reaction parameters for VBP synthesis using NaDEP.

DEP (eq.)	Na (eq.)	VBC (eq.)	% Conversion	Residual DEP
1	1.2	1	74	10.6% to VBP
1.2	2.2	1	87	<4.0% to VBP
2	2.2	1	99	8.6% to VBP

VBP-(OH)₂ Synthesis

VBP-(OEt)₂ is deprotected using a two-step, one-pot synthesis via the trimethylsilyl intermediate as outlined in Figure 22. Hydrolysis of the bis(trimethylsilyl) intermediate affords VBP-(OH)₂ as a white solid. The product is purified by recrystallization from H₂O/acetonitrile mixed solvent.

Figure 22. Synthesis of VBP-(OH)₂.

VBP-(OH)₂ Copolymerizations

VBP-(OH)₂ was used as the monomer to introduce phosphonic acid groups into polyelectrolytes containing a crosslinkable monomer. These polyelectrolytes were prepared and formulated for incorporation into membranes with PVDF membranes. Processing of these copolymers proved challenging, as our compatibilizer was not as effective as it was with other polyelectrolytes that contain sulfonic acid groups and significant phase separation was seen in the membranes (Figure 23). These membranes also showed low ex-situ conductivity (7mS/cm in deionized water).

Figure 23. SEM image of the cross-section of a membrane containing PVDF and a polyelectrolyte based on VBPA and a crosslinkable monomer.

Terpolymers of VBPA, sulfonated monomer, and crosslinkable monomer were prepared to increase the effectiveness of the compatibilizer. The terpolymerizations were made with various ratios of the three monomers (Table 3) and were optimized for high conversion and molecular weight and then scaled up to provide 100g (solids) samples to be blended with PVDF. The nomenclature for the various polyelectrolytes incorporated into membranes (e.g. M51, M52, M53) is also shown in Table 3.

Table 3. Terpolymer compositions prepared in the phosphonic acid-functionalized series of membranes.

Membrane	Mol% VBPA in Polyelectrolyte	Mol% Sulfonated Monomer in Polyelectrolyte	Mol% Crosslinkable Monomer in Polyelectrolyte	Conductivity (mS/cm) [†]
M50	80	---	20	7
M51	60	20	20	37
M52	40	40	20	17
M53	20	60	20	No measurement

The use of the sulfonated monomer in the membranes did improve the effectiveness of the compatibilizer, as shown from the image in Figure 24. Some degree of phase separation is still observed, but it is not as severe as that seen with VBPA copolymer (Figure 23).

[†] Conductivity was measured on fully hydrated membranes conditioned for 1 hour in boiling water. The measurement was done at 70°C in deionized water with a 4pt probe.

Figure 24. SEM image of the cross-section of a M51 membrane. Image was taken by Karren More at Oak Ridge National Laboratory.

The membranes were tested for conductivity and MEA performance. The conductivity in water decreased as more VBPA was put in the polyelectrolyte (Table 3). All the membranes had a conductivity substantially below that of M43 (M43 is typically 130-150 mS/cm). The RH conductivity was also much lower for these materials. An example with M51 is shown in Figure 25.

Figure 25. 80°C ex-situ conductivity of M51 membrane. Data was collected from a 4pt probe inserted in a humidity chamber at 80°C.

In agreement with the trend in the conductivity data, the MEA performance of the M50 series of membranes was inferior to that of M41 and M43. An example of the MEA performance with M41 and M52 is shown below. We also attempted to evaluate these phosphonated membranes at elevated temperature (120°C). As an example, Figure 8 shows the polarization curve for M53 vs. M41. Unfortunately, the performance declined rather than improved at lower RH. The development of phosphonated or partially phosphonated polyelectrolytes has thus been abandoned.

Figure 26. 80°C MEA performance of a phosphonated membrane (M52) vs. M41 at various RH levels.

Figure 27. 120°C MEA performance of a phosphonated membrane (M53) vs. M41 at various RH levels.

Alternative Sulfonic Acid Functionalized Membranes (M60 Series)

Another idea explored in the project was the use of polyelectrolytes that contained more acid groups to promote conductivity at lower RH values. The first polyelectrolyte used to explore this concept was M60. The polyelectrolyte developed for the M60 membrane generation contained approximately 10% more acid groups than M43 at a comparable loading. A refinement of the polyelectrolyte that further increased the acid content is discussed in the M70 section.

Compared to M43 technology, the polyelectrolyte prepared for the M60 membrane had similar blending properties with PVDF, but it did appear to be slightly more susceptible to producing phase separation. This issue was addressed by adjusting the compatibilizing agent formulation used in the process. Two different membranes were developed in this membrane generation. M60 was our first membrane that was run through a complete series of tests. As M60 was tested, the membrane fabrication process was optimized to produce a material with better conductivity. The material with the optimized process was named M61. The development of M60 and M61 is very similar to the advancements from M41 to M43.

TEM analysis of the membranes was performed in collaboration with Karren More at ORNL. A TEM image of M61 is shown in Figure 28. The image shows a fine-scale distribution of intimately mixed phases. Elemental mapping shows a

spherical fluorine-rich, sulfur depleted dispersed phase. The matrix appears to be phase-separated (phase boundaries are not distinct) with modulating contents of fluorine and sulfur.

Figure 28. TEM image of M61. The image was taken and analyzed by Karren More at ORNL. The image contains a spherical fluorine-rich, sulfur-depleted phase (→) and a matrix that has modulating contents of fluorine and sulfur (→).

The ex-situ RH conductivity of M61 at 80°C is shown in Figure 29. M61 has a slightly higher conductivity than M43 and matches Nafion[®] NR211 at 90% RH. However, the performance of M61 falls below that of Nafion[®] NR211 when the humidity falls below 90%.

Figure 29. 80°C ex-situ conductivity of M61 membrane. Data was collected from a 4pt probe inserted in a humidity chamber at 80°C.

In-cell membrane conductivity was also measured to verify the ex-situ conductivity data. It was calculated based on MEA resistance (subtracting electronic resistance of a blank cell with no membrane, about $20\text{m}\Omega\cdot\text{cm}^2$) and membrane dry thickness. The in-cell conductivity results of M61 and reference membranes are shown in Figure 30.

Figure 30. 80°C in-cell conductivity of M61 membranes at a) 100%RH and b) 53%RH gas inlets.

From the data in Figure 30, M61 membranes showed 50-100% increase in conductivity over M43 membranes at 100% and 53%RH conditions, respectively. Compared to Nafion[®] NR211, M61 showed equivalent or higher conductivity at 100%RH, but lower conductivity at 53%RH conditions. Although M61 membranes showed significant improvement in membrane conductivity over M43, the H₂/Air fuel cell performance is about the same as that of M43 at 100%RH conditions. M61 membranes gave slightly better performance than M43 at 53%RH inlet conditions, but still much lower than that of Nafion[®] NR211, as shown in Figure 31. Additionally, M61 membranes had a higher crossover rate and were prone to electrical shorting in fuel cells.

Figure 31. Performance of M61 membranes at 80°C and 53%RH at g as inlets. The three curves for M61 represent different MEAs constructed to test reproducibility.

In summary, although M61 showed improved conductivity over M43, the performance and conductivity at low RH are still lower than those of Nafion[®] membrane.

Disulfonated Styrene Functionalized Membranes (M70 Series)

As discussed in the previous section on M60, one approach to reach higher conductivities is to reduce the equivalent weight (i.e. increase the concentration of protogenic sulfonic acid groups in the polyelectrolyte). With M43 the EW can be lowered by increased the amount of polyelectrolyte in the film. However, increasing the polyelectrolyte past 50 wt% produces only a modest increase in conductivity but leads to excessive swelling and poor mechanical properties.

M60 had a slightly higher content of acid than M43 at comparable loadings, which provided a marginal improvement in conductivity but no improvement in MEA performance.

It is theorized that low or very low EW polyelectrolytes/membranes should exhibit improved conductivity at low relative humidity without having to resort to using higher polyelectrolyte loadings. One way to achieve this is to use monomers with multiple acid groups, as depicted in Figure 32.

Figure 32. Generalized structure of the disulfonated monomer used in the polyelectrolyte for the M70 membrane.

The synthesis of targeted monomers with this general formula is not described in the literature. A synthetic route was devised to produce the monomer in Figure 32. Its isolation is challenging due to its extremely hygroscopic nature. Nonetheless, with proper handling, this can be overcome. Optimized conditions were defined and multiple batches in the range of 50 to 100g have been prepared. The reaction is reproducible and scaleable and the monomer has been made in kg quantities.

The monomer was used with a crosslinkable comonomer to produce polyelectrolytes for incorporation into membranes. Hydrolytic stability tests of the membrane were conducted at 80°C to check for polyelectrolyte leaching and/or sulfur loss. Based on gel permeation chromatography (GPC) and ion chromatography (IC) data, it appears that some polyelectrolyte was leaching out of the membrane in the materials produced early in the project. However the lack of significant sulfur loss by IC suggests that the polyelectrolyte is hydrolytically stable under the test conditions.

The leaching of the polyelectrolyte is related to the fact that one of the monomers used is not homogeneously distributed in the copolymer. A kinetic study revealed that this monomer is consumed at approximately twice the rate of that of the other species. This problem was addressed by systematically optimizing the feed of the monomers during polymerization. Different strategies for continuous or sequential monomer additions were also probed.

M70 Membrane Development

While the polymerization conditions were optimized, the blending and activation processes were explored for the M70 membrane. Figure 33 illustrates 3 process variants and their impact on membrane transparency, morphology and conductivity in water. As the morphology becomes finer, the membrane shows

increased transparency and higher conductivity. The conductivity in water of the membrane fabricated with process “C” is higher than both PFSA and M43 materials.

Figure 33. Influence of process parameters on M70 membrane appearance, morphology, and conductivity.

As expected from the conductivity measurements in water, the process parameters also have a significant influence on the conductivity at various RH (Figure 34). After optimizing the processing method, M70 exhibits almost an order of magnitude improvement in conductivity at 50% RH compared to M43. The new M70 membrane shows very impressive conductivity at 90% RH (>200 mS/cm), but has roughly half of the conductivity of Nafion® NR-211 at 50% RH. Due to the lower EW, M70 displayed elevated degrees of swelling compared to M43. XY swelling of M70 is 30% compared to 23% for M43.

Figure 34. Labcast M70 conductivity compared to M43 and Nafion® NR-211. M70 – Initial Method was material made from an unoptimized process early in the project. M70 – Improved Method used an optimized process to fabricate the membrane, which is similar to process “C” in Figure 33. Data was collected from a 4pt probe inserted in a humidity chamber at 80°C.

Fuel cell performance of Laboratory cast M70 membranes

In parallel with the optimization of the fabrication method and the conductivity testing, the BOL MEA performance was tested. The lab produced M70 membrane fabricated by an optimized process shows a polarization curve comparable to that of a PFSA-based MEA (NR-211) at high (100/70%) and moderate (50/50%) RH, as illustrated in Figure 35. The RH cycling durability results were very low on the laboratory cast samples, approximately 50 cycles. However at the time it wasn't clear how much of the poor performance was attributed to the higher XY swelling, as opposed to the fact they were laboratory prepared samples. Laboratory prepared samples typically show mediocre RH cycling results, regardless of composition, from the presence of defects that form during the fabrication process in the laboratory. For example lab-cast M43 has a durability of about 2000 cycles, while pilot produced material has a durability of 15,000 cycles.

Figure 35. MEA performance of lab-produced M70 samples under high (top) and moderate (bottom) RH conditions. The test conditions are given in each of the graphs.

Based on the promising BOL MEA results, we produced M70 membrane on a pilot scale to perform more-detailed studies of its properties, including beginning of life, OCV durability, and RH cycling. Our previous experience has shown that the conductivity typically increased when materials were scaled to the pilot level. The RH cycling testing was also of particular interest due to the poor performance of the laboratory prepared samples, as the pilot material has a much lower amount of defects originating from the fabrication process.

M70 Pilot Production

M70 was produced on a pilot scale in the second quarter of 2010. Approximately 200 linear feet of high quality, defect free 1 mil membrane was produced in the campaign. M70 pilot membrane was tested for its conductivity, hydrogen permeability and beginning of life fuel cell performances. Membrane conductivity under various levels of relative humidity (RH) at 80°C was tested using a 4-probe Bekktech setup, and the results of M70 compared to NR211 and M43 are shown in Figure 36. It is worth pointing out that the experimental setup to collect the conductivity data in Figure 34 and Figure 36 are different. The two setups produce conductivity profiles with different values, but the trends are essentially the same.

Figure 36. 80°C conductivity vs RH of M70, M43 and Nafion® NR211 at 80°C.

M70 showed higher conductivity than Nafion above 90%RH. Compared to M43, M70 showed much improved conductivity over the whole RH range. At 50%RH, the M70 conductivity is about 10 times higher than M43 but is about a half an order of magnitude lower than Nafion®. Overall, the data trends look the same as what was observed in the labcast materials (i.e. scaling to the material to a pilot level did not increase its performance). The exact reason is not understood as to why the typical increase in conductivity performance that was observed in past did not occur in M70.

The hydrogen crossover rate for pilot fabricated M70 was measured electrochemically in MEAs. The results are shown in Figure 37. Both M70 and M43 showed much lower hydrogen crossover rate than Nafion® (about 1/3 to 1/4 of Nafion® NR211).

Figure 37. Hydrogen crossover rates of M70, M43 and NR211 membranes.

Beginning of life fuel cell performance tests were also performed at 80°C, 100kPa absolute pressure, under high RH (100%/70%RH anode/cathode) and low RH (30%RH anode/cathode). The results are shown in Figure 38 and Figure 39.

Figure 38. BOL MEA performance of pilot fabricated M70 at high RH.

Under high RH conditions, the performance of M70 is between M43 and Nafion® NR211. M43 showed higher MEA resistance due to lower proton conductivity. M70 showed the same MEA resistance as NR211, but the performance is still slightly lower. In agreement with the conductivity data, the relative performance between Nafion®, M70, and M43 did not appear to change appreciably by scaling the material to the pilot level.

The performance difference between Nafion® and M70 cannot be explained by difference in MEA resistance (membrane conductivity) at high RH. The performance loss is attributed to cathode flooding caused by slower water back-diffusion of M70, is discussed in more detail below. It has also been noted that the GDEs display lower ORR (oxygen reduction reaction) activity when used with Arkema membranes, which is a second source for the lower performance of M70. The lower ORR activity is not discussed in this report.

Figure 39. BOL performance of M70, M43 and NR211 at 30% RH.

Under 30%RH, M43 showed extremely low performance due to very high MEA resistance (not shown in figure due to limit of plotting scale). M70 showed drastic improvement over M43, but is 20% lower than Nafion® NR211.

Durability testing

Two standard DOE/USFCC protocols, RH cycling and OCV hold, were used for testing M70 mechanical and chemical durability under operation in a MEA.

RH cycling

RH cycling durability test results are shown in Figure 40. Both M43 and M70 samples shown were produced on a pilot scale. While M43 lasted more than 3 times longer than Nafion® NR211, M70 membranes failed within 50 cycles. As with the conductivity, the RH cycling performance was not increased by fabricating M70 on a pilot scale. Therefore, the low durability of M70 is probably due its higher degree of swelling in a hydrated environment compared to M43 (XY swelling of M70 is 30% compared to 23% for M43). Higher degrees of swelling reduce RH cycling durability through larger stresses generated through the hydration/dehydration steps in the test.⁶ Another factor likely contributing to the low durability is that M70 appears to be more brittle than M43 at lower RH values. This was a qualitative observation that was never measured in an analytical test.

Figure 40. RH cycling test of M70, M43 and NR211 membranes.

OCV hold test

OCV hold test results of M70, M43 and NR211 using USFCC protocol are shown in Figure 41. M43 lasted more than 30 times longer than Nafion® NR211 in OCV hold test, showing vastly superior chemical stability than Nafion® membrane. M70 showed significantly better OCV durability than NR211, but did not reach DOE target of 500 hr.

Post mortem analysis of the failed M70 membrane samples showed that the failure is due to membrane fracture around the edge of electrodes. This failure is attributed to the poor mechanical property of M70 under low RH (OCV hold test is conducted at 30%RH, 90°C), as discussed in RH cycling durability section.

Figure 41. Chemical stability of M70, M43, and Nafion® NR211 membrane under an OCV hold test (USFCC conditions).

Water Transport Properties

Previously our efforts focused on measuring conductivity and low RH MEA performance. However, the performance difference between Arkema and Nafion® membranes is only partially explained by differences in conductivity, especially under higher RH operating conditions in an MEA.

The water transport coefficient is another important property of PEM fuel cell membranes. It affects overall fuel cell performance, especially at high current densities, creating complications such as electrode flooding. Membrane water transport properties are characterized by measuring the electro-osmotic drag (EOD) coefficient and water permeation coefficient. Both measurements are discussed below.

Electro-osmotic Drag (EOD) Coefficient

Measuring the EOD coefficient in-situ (i.e. MEA) is technically challenging. Two methods were explored: the hydrogen pump and methanol cell. After much effort, the results for Nafion® appeared low using the hydrogen pump method (<1 was obtained while literature results reports values >2). As a result, a methanol/H₂ half-cell method was developed based on an LANL DMFC method⁷. The advantage of a DMFC half-cell over the full-cell is no water is generated from crossover methanol and oxygen reduction reactions. This simplifies the data processing and reduces background noise.

The results of Nafion and Arkema membranes are shown in Figure 42. Using this method, the EOD coefficient for Nafion® 117 is very similar to results reported by LANL under similar conditions (2.9 at 60°C by full cell method⁷).

Figure 42. Electro-osmotic drag coefficients of Arkema and Nafion® membranes.

Both M43 and M70 membranes have EOD coefficients in the range of 1.3-1.6, about half of N117. It is known in the literature that hydrocarbon electrolytes generally have lower EOD coefficient than Nafion® membrane, partially attributed to “relatively large, regular, water-filled domains” of the conductive phase in Nafion®.⁸

Nafion® NR212 showed similar EOD results to N117. The effects of PDVF/polyelectrolyte ratio on EOD were also measured for M70 membranes. No change of EOD coefficients was found for M70 with PVDF content varying from 60 to 80 wt%. In summary, the membrane PVDF/PE weight ratio has little effect on the EOD coefficient.

During the EOD experiments, it was found that the treatment of gas diffusion media (GDM) at the anode has a strong effect on results. GDM with either MPL or wetproofing (PTFE coating) significantly reduces the “apparent” EOD coefficient, as list in Table 4. It appears that the hydrophobic media increases water transport resistance. This phenomenon has not been reported in literature.

Table 4. EOD coefficients of Nafion® MEAs with various treatment in anode GDM at 60°C.

Membrane	Wet Proof in GDL	MPL	EOD Coefficient
N117	No	No	3
NR-211	Yes	Yes	0.6
	No	Yes	1.5
NR-212	No	No	3.5
	Yes	No	1.3
	No	No	3

Water Permeation

Membrane water permeation was measured by applying hydraulic pressure to an MEA device. Specifically, the cathode side was pressurized with water and the water flow rate at the anode was measured. Results from the work are shown in Figure 43. Both M70 and M43 show substantially lower water permeability than Nafion, and M70 has slightly higher water permeability than M43.

Figure 43. Water permeability of Nafion® and Arkema membranes.

To summarize the work on water transport, M70 and M43 membranes have lower EOD coefficients and water permeability than Nafion®. Lower EOD coefficients lead to less water transported from anode to cathode and impose a lesser degree of cathode flooding, which is desirable for both hydrogen and methanol fuel cell applications. On the other hand, lower water permeability will reduce water back-diffusion rate from cathode to anode. This could exacerbate cathode flooding if water cannot be efficiently removed from cathode by some other means. The lower water permeability of M70 is probably a major cause of

its lower performance compared to Nafion® under high RH conditions, as discussed in the previous membrane performance test section.

Membrane Blends of M43/M70

While displaying improved conductivity compared to M43, M70 membranes have poor durability in the MEA RH cycling test. As discussed earlier, a contributor to the poor durability is excessive membrane swelling, which may also be reducing conductivity. Decreasing the amount of polyelectrolyte lowers swelling, but also lowers the membrane conductivity very quickly. To decouple the effects of simultaneously altering EW and volume fraction by varying the loading of polyelectrolyte, membranes were fabricated that contained blends of the polyelectrolytes used in M43- and M70-based membranes. This study is to investigate whether increasing the EW while keeping the same volume fraction could lead to reduced swelling and higher performance in a M70-based system.

The two polyelectrolytes blended well together at all ratios of testing and produced transparent membranes. Conductivity and swelling did not show a synergistic increase from blending the two polyelectrolytes together (Figure 44). Instead, the conductivity varies linearly with composition (i.e. ideal mixing behavior). XY swelling showed essentially the same trend.

Figure 44. Conductivity of M43/M70 blend membranes in water at 70°C. The legend indicates the weight ratio of M70/M43 in the membrane. The line shows the theoretical response of the blends assuming ideal mixing behavior.

Modified M70 System – Sulfonated Crosslinking Agent

As a compliment to the previous study examining the effects of increasing the membrane EW, a sulfonated crosslinking agent was incorporated into M70 to lower the EW. The crosslinking agent was incorporated into the membrane formulation at different loadings that all initially produced phase-separated membranes. The phase separation was removed after adjusting the blending/compatibilization procedure. The crosslinking agent had the desired effect on RH conductivity – it shows higher ex-situ conductivity than Nafion down to 40-50% RH (Figure 45). The crosslinking agent increased the degree of swelling in water by 25% over the swelling of M70. Some MEA characterization was performed but results were inconclusive due to pinhole formation in the membrane during the testing. The pinholes are believed to be coming from weaker mechanical properties/greater swelling introduced by the use of the crosslinking agent. Nonetheless, the technology could provide a useful pathway towards lower RH performance in the membrane.

Figure 45. 80°C RH conductivity of M70 containing a sulfonated crosslinking agent.

BPSH-Based Membranes

This portion of the project was a collaborative effort between Professor James McGrath's research group at Virginia Tech and Arkema to develop novel membranes containing PVDF and polyelectrolytes based on aryl ether sulfones.

The approach taken has been to generate end functional telechelic phenoxide or disulfonated homo or random oligomers and copolymers. The key monomer is 3,3' disulfonate, 4,4'-dichlorodiphenyl sulfone. This monomer was prepared in kg quantities at Akron Polymer systems, a small start up company in Ohio, during the project. Thus, the monomer has at least semi-commercial potential, if the demand develops. The monomer has been successfully utilized in several copolymerizations, following the general procedures performed earlier and outlined in Figure 46. Activated 4,4'-difluorobenzophenone has also be effectively utilized to produce ketone containing copolymers.

Figure 46. Disulfonated poly(arylene ether sulfone) random copolymers (BPS) via direct copolymerization.

These materials have been shown to be effective proton exchange membranes under high humidity or liquid water conditions. Their conductivity does decrease below 70 or 80% relative humidity, except for copolymers with higher ion exchange capacity (IEC) systems. The acronym "BPS" (BiPhenyl Sulfone) has evolved to describe these materials. The acronym is adjusted to "BPSH" if the sulfonate groups are in the acid form, while BPS is used if they are salts. Two numbers typically follow the acronym (e.g. BPSH-40), which indicate the molar fraction of disulfonic acid units in the copolymer. The hydrophobic-hydrophilic balance determines water swelling conductivity and mechanical behavior. The latter is controlled by the need for a co-continuous hydrophobic phase.

The molecular structures of the poly(arylene ether)s might be expected to affect the mixing capability with the Kynar host matrix resin. Therefore, our initial efforts focused on both wholly hydrocarbon systems (BPSH-60), as well as partly fluorinated systems. In Figure 46, the so-called 6F bisphenol has been used to introduce partial fluorination.

BPS-60/PVDF Membranes

Samples of BPS-60, 6F50, 6F60, and 6F70 were synthesized at Virginia Tech and sent to Arkema for membrane fabrication and testing. The BPS-60/Kynar membranes were extremely sensitive to the fabrication conditions. There is a very narrow processing window where transparent membranes can be made. Most processing methods produced opaque membranes that have large-scale phase separation. An illustration of the processing window is shown in Figure 47.

This degree of sensitivity has not been observed previously in compatibilizing PVDF and polyelectrolytes. The narrow window of adequate compatibilization is attributed to the higher equivalent weight of this polyelectrolyte.

Figure 47. SEM images of three membranes containing 60wt% PVDF and 40 wt% BPSH60 that were produced from processing methods A (left), B (center), and C (right). Membranes from processing methods A and B were opaque, while the membrane from method C is transparent.

Because the EW of BPSH60 is higher than the M41 polyelectrolyte (~400 g/equiv vs. ~230 g/equiv), lower loadings of PVDF were used in order to obtain membranes that had an equivalent weight lower than 1000 g/equiv, ideally in the range of 800 g/equiv. It is expected that this equivalent weight is needed for proper amount of the acid groups in the membrane to obtain adequate proton conductivity. To obtain EW values in this range, the PVDF loading was varied from 10 to 60 wt%.

All of the membranes formulated with 6F polyelectrolytes contained 15-40 wt% PVDF. Compared to the BPS60, membranes made 6F50, 6F60, and 6F70 and PVDF appeared to be slightly less susceptible to large-scale phase separation. However, these compositions were more prone to form defects during film formation, particularly the 6F70 (defect size was mm to cm scale). The defects

could probably be addressed by adjusting the membrane processing conditions, but this optimization was not pursued in the project.

Property Characterization

Conductivity (as a function of RH and in water), water uptake, and X-Y swelling were performed on the BPS-60/PVDF membranes. All of the membranes had low conductivity in deionized water (≤ 65 mS/cm at 70°C), likely due to excessive swelling. For comparison, the conductivity of M41 is about 125 mS/cm and Nafion[®] NR-211 is about 160 mS/cm in this test.

Table 5. Ex-situ conductivity of BPS-60/PVDF membranes.

Membrane Composition PVDF/BPS-60 Ratio (w/w)	Conductivity in Water at 70°C (mS/cm)
0/100	*
10/90	38
20/80	51
40/60	48
57/43	65
Nafion [®] NR-211	160
M41	125

*Sample dimensions could not be obtained – sample too fragile

90% RH conductivity results for some of the membranes at the lowest PVDF loadings are higher than M41 but exhibit elevated degrees of swelling (~900 wt% water uptake for the membrane having 20% PVDF and 80% polyelectrolyte). The high water uptake is probably due to the low loading of PVDF in these membranes, which cannot moderate the swelling. BPS/PVDF membranes show a maximum conductivity at 90% RH when the membrane contains 20% polyelectrolyte. This maximum is likely the result of the opposing effects of equivalent weight and swelling.

Figure 48. 90% RH conductivity data of BPSH60/Kynar membranes and M41 at 80°C. Points for the BPSH60 represent individual runs.

Figure 49. Water uptake and X,Y swelling of BPS60/Kynar membranes. For reference, M41 has an X,Y swelling = 20% and a water uptake of 65%. Nafion® has a water uptake of 40% and an X,Y swelling of 15%.

Because of the issues with defect formation, limited testing was done on membranes containing 6F polyelectrolytes. With the compositions that were tested, the conductivity (in water at 70°C) was low : < 10 mS/cm.

One problem encountered with all of the membranes tested was that samples lost 10-20% of their mass during testing and some even turned opaque. This is

attributed to polyelectrolyte leaching from the system after it is exposed to boiling water for sample conditioning.

Morphology

Some aspects of the membrane morphology have been discussed above. We have also noted that the morphology of some of the membranes made with uncrosslinked aryl ether sulfones are not stable in boiling water. For example, a membrane containing 15 wt% Kynar and 85 wt% 6F50 turned opaque after being exposed to the boiling water for one hour and then dried. SEM images of the sample before and after boiling are shown in Figure 50 and show that voids form in the membrane during the immersion in water. As mentioned previously, the voids are believed to be due to removal of the polyelectrolyte. This is an extreme case in the study and not all of the samples showed such a significant change, but highlights the need to use physical or chemical crosslinks to stabilize the membrane compositions.

Figure 50. SEM images of a membrane containing 15 wt% Kynar and 85 wt% 6F50. The image on the left is the membrane before exposure to boiling water (transparent membrane) and the image on the right is the dry membrane after exposure to boiling water for one hour (opaque membrane).

TEM analysis has been completed on a PVDF/BPS60 membranes containing 60 wt% polyelectrolyte and 40wt% PVDF (Figure 13). As expected from the degree of difficulty associated with making transparent membranes, the membrane has a coarser structure than M41/M43 as phase separation is evident on a micron scale. Smaller scale phase separation is expected with polyelectrolytes containing larger amounts of sulfonic acid groups.

Figure 51. TEM image/elemental maps of PVDF/BPS60 membrane containing 60wt% BPS60. The image was taken and analyzed by Karren More at ORNL.

BPSH-100/PVDF Membrane Blends

As discussed in the previous section, the BPSH polyelectrolyte needs to be crosslinked inside of the PVDF matrix to stop leaching of the polyelectrolyte from the membrane and to prevent the morphology from coarsening over time. We have examined two functionalized BPSH-100 materials provided by the McGrath research group that are capable of crosslinking inside of a PVDF matrix. They were terminally functionalized with either ethynyl or amine groups, as shown in Figure 52. All of the samples compatibilized well with PVDF and produced transparent membranes. None of the opacity observed with BPS-60 was observed due to the lower equivalent weight of these polyelectrolytes.

Figure 52. Ethynyl (top) and amine (bottom) functionalized BPSH-100. M_w ranged from 3-5kg/mol for the materials tested.

Ethynyl-functionalized BPSH-100

The ethynyl-functionalized BPSH-100 is thermally cured and does not require a crosslinking agent. Membranes were cast at 20 and 30 minutes at either 225 or 250°C to study the degree of cure and membrane performance. The polyelectrolyte showed a lower, but still acceptable, degree of cure than M43 when cast at 250°C for 30 minutes (Table 6). The membrane had a slightly lower conductivity than M43, probably due to the lower crosslinking efficiency resulting in polyelectrolyte leaching. The 80°C RH conductivity of the membrane was also very similar to M43.

Lowering the casting temperature to 225°C significantly reduced the degree of cure and consequently produced a very low conductivity (80mS/cm). Lowering the casting time from 30 to 20 minutes at 250°C also reduced the degree of cure, but not to the extent of using a casting temperature of 225°C.

Table 6. Properties of ethynyl-functionalized BPSH100/PVDF membranes. All samples were formulated with ~40 wt% BPSH-100 and 60 wt% PVDF.

Casting Temperature (°C)	Casting Time (min)	Conductivity in Water @70°C (mS/cm)	EW (g/eq)	Degree of Polyelectrolyte Leaching (%)
30	250	127	906	22
20	250	129	947	26
20	225	84	1218	52
M43 Membrane Reference		140	800	---

Although the membrane conductivity with ethynyl-functionalized BPSH-100 could be improved by loading more polyelectrolyte into the membrane, the extreme processing temperature required to crosslink the acetylenic groups make it impractical for extended study and scaleup. Therefore efforts were focused on other BPSH-100 crosslinking chemistries, such as amine functionalities.

Amine-functionalized BPSH-100

Amine-terminated BPSH-100 samples were examined with isocyanate and epoxide crosslinking agents. The isocyanate is based primarily on a trimer of hexamethylene diisocyanate, while the epoxide was 4,4'-methylenebis (N,N-diglycidylaniline). The epoxide has a functionality of approximately 3.5. The isocyanate was catalyzed with dibutyltin dilaurate and the epoxide system was catalyzed with 2-ethyl imidazole.

A summary of the casting conditions and results for each sample is shown in Table 7. Casting the membranes 210°C for 7.5 minutes was not adequate to crosslink the system (similar results were observed for the epoxide system, which is not shown in the table). Increasing the casting time to 20 minutes for both crosslinking agents substantially improved the degree of cure.

As with the ethynyl system, the conductivity correlated with the degree of cure (polyelectrolyte content). Interestingly, the membranes with amine groups at a wt ratio of 60/40 PVDF/BPSH-100 showed less polyelectrolyte leaching and lower

EW values than the ethynyl system, but the ethynyl functionalized BPS-100 showed higher conductivity values.

As one would expect, the membrane conductivity does increase as it is formulated with a higher content of BPSH-100. It appears from the leaching, however, the casting conditions are not optimized for higher loadings of BPSH. The membrane materials are also quite friable at the 60% BPSH loading. The epoxide crosslinking agent is clearly superior to the isocyanate at producing higher conductivities, especially as the loading of BPSH-100 is increased.

Table 7. Properties of amine-functionalized BPSH100/PVDF membranes.

Approx Wt Ratio PVDF/BPSH-100	Crosslinker	Casting Temp (°C)	Casting Time (min)	Conductivity - Water@70°C (mS/cm)	EW (g/eq)	Degree of Polyelectrolyte Leaching (%)
60/40	Isocyanate	210	7.5	57	1194	38
60/40	Isocyanate	210	20	90	808	8.0
40/60	Isocyanate	210	20	95	700	28
60/40	Epoxide	210	20	109	791	10
50/50	Epoxide	210	20	126	684	16
40/60	Epoxide	210	20	145	600	20
M43 Membrane Reference				140	800	---
PFSA Membrane Reference				160	~1100	---

The RH conductivity of three amine-terminated BPSH-100/PVDF membranes cured with epoxide is shown in Figure 53. Increasing the loading of BPSH-100 increases conductivity, as observed with the conductivity values in water. The membrane containing 50wt% BPSH is approximately equivalent to M43, while the one containing 60wt% BPSH has performance between M43 and M70. Unfortunately, the composition containing 60wt% BPSH is friable; the compositions at 40 and 50wt% BPSH-100 possess better mechanical properties.

Figure 53. 80°C RH conductivity performance of several amine-functionalized BPSH/PVDF membranes cured with epoxide. The loading of BPSH-100 is indicated in the graph legend.

IV. Summary

The PVDF/polyelectrolyte blending method has produced a robust technology platform that shows complex relationships between polyelectrolyte chemistry, morphology, and processing. The technology platform was used to evaluate technologies based on PVDF and different polyelectrolytes through the course of the project. The polyelectrolytes were functionalized with phosphonic acid groups and sulfonic acids groups. BPSH based materials and polyelectrolytes containing disulfonic acid functionality were also evaluated. Of all of the membrane technologies evaluated, M70 (the technology based on the disulfonated acid polyelectrolyte) is the most promising for low RH conditions. However, M70 does not match the performance of PFSA's at low RH conditions primarily due to the fact that the membrane still has lower conductivity than PFSA's below about 90% RH.

A common theme throughout all of the membranes tested include excellent barrier properties, a feature that has significant advantages in DMFC technology. These materials are currently being evaluated for this application.

Acronyms

BPSH Aryl-ether sulfone-based PEM developed by J. McGrath at Virginia Tech
ECA: Electrochemical Area
EW: Equivalent Weight
JMFC: Johnson-Matthey Fuel Cells Inc.
MEA: Membrane Electrode Assembly
M41: Arkema's Second-Generation Membrane Candidate
M43: Arkema's Third-Generation Membrane Candidate
M51, M52, M53: Arkema's Membrane incorporating phosphonic acid.
OCV: Open-Circuit Voltage
ORNL: Oak Ridge National Laboratory
ORR: Oxygen Reduction Reaction
PEM: Proton Exchange Membrane
PFSA: Perfluorosulfonated Acid
PVDF: Poly(vinylidene fluoride)
RH: Relative Humidity
SEM: Scanning Electron Microscopy
TEM: Transmission Electron Microscopy
USFCC: United States Fuel Cell Council
VT: Virginia Polytechnical Institute

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