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## Copoly(arylene ether nitrile)s—High-Performance Polymer Electrolytes for Direct Methanol Fuel Cells

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Direct methanol fuel cell (DMFC) performance of sulfonated (arylene ether ether nitrile) (m-SPAEEEN) copolymers is reported. Low water absorption of m-SPAEEEN copolymers enabled increased proton-exchange concentrations in the hydrated polymer matrix, resulting in more desirable membrane properties for DMFC applications. The membrane electrode assemblies (MEAs) using m-SPAEEENs showed improved cell properties which could not be obtained by the MEAs using sulfonated polysulfone or Nafion. The DMFC performance using an optimized m-SPAEEEN membrane exceeded those of the other membrane systems. For example, 265 mA/cm<sup>2</sup> was obtained for an MEA using m-SPAEEEN, compared to 230 and 195 mA/cm<sup>2</sup> for MEAs using sulfonated polysulfone and Nafion membranes, respectively, at 0.5 V, measured under identical conditions. In the comparative evaluations, membrane thickness was selected to give methanol crossover limiting currents that were similar for each of the polymer electrolyte types. Stable cell performance during extended operation (>100 h) suggested that interfacial compatibility between m-SPAEEEN and Nafion-bonded electrodes was good.

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Polymer electrolyte membranes (PEMs) that have high proton conductivity, low reactant permeability, and reduced water uptake are desired for fuel cell applications. The high permeability of methanol results in high methanol crossover rates through currently used perfluorinated sulfonic acid membranes (like Nafion) and the sluggish oxidation kinetics of methanol at the cathode limit direct methanol fuel cell (DMFC) technology. As a result, considerable efforts have been directed to reduce methanol permeability while maintaining high proton conductivity in new PEMs.

Hydrocarbon-based sulfonated copolymers have drawn much attention because of their low methanol permeability and oxidative and hydrolytic stability under fuel cell operating conditions.<sup>1</sup> During the last decade, many hydrocarbon-based sulfonated copolymers have been prepared for DMFC applications and the DMFC performance of a few select membranes has been evaluated.<sup>2–5</sup> Yang and Manthiram reported that the DMFC performance of sulfonated poly(ether ether ketone) (SPEEK) with a degree of sulfonation of around 50% is comparable to or better than that of Nafion 115. However, their operating temperature was limited to 65°C, because the post-sulfonated copolymers they employed exhibited excessive swelling at higher temperatures.<sup>2</sup> Miyatake et al. revealed that the methanol crossover of a sulfonated polyimide copolymer (FSPIH-30) was merely 40% of that of Nafion 112 at open-circuit potential at 90°C. A terminal voltage of 0.38 V at 200 mA/cm<sup>2</sup> using FSPIH-30 was obtained at 90°C with dry oxygen, which was approximately 10% greater than using Nafion 112.<sup>3</sup> They suggested that insufficient membrane/electrode contact limited performance due to increased ohmic resistance. Harrison et al. reported that wholly aromatic sulfonated poly(arylene ether sulfone)s prepared by direct copolymerization with a degree of disulfonation of 35% (BPSH-35) outperformed Nafion 117 at 80°C under DMFC conditions.<sup>4</sup> The current density of the MEA using the BPSH membrane reached 210 mA/cm<sup>2</sup> at 0.5 V, about 15% better performance than that of Nafion 117 under identical conditions (0.5 M methanol). Still, interfacial incompatibility between BPSH and the Nafion-based electrodes limited long-term performance. Fu and Manthiram also reported that sulfonated polysulfone with 50–70% sulfonation exhibited better performance than Nafion 115 in DMFCs at 1 M methanol feed. However, similar interfacial problems occurred after 2 days of operation.<sup>5</sup> The long-term stability of DMFC performance

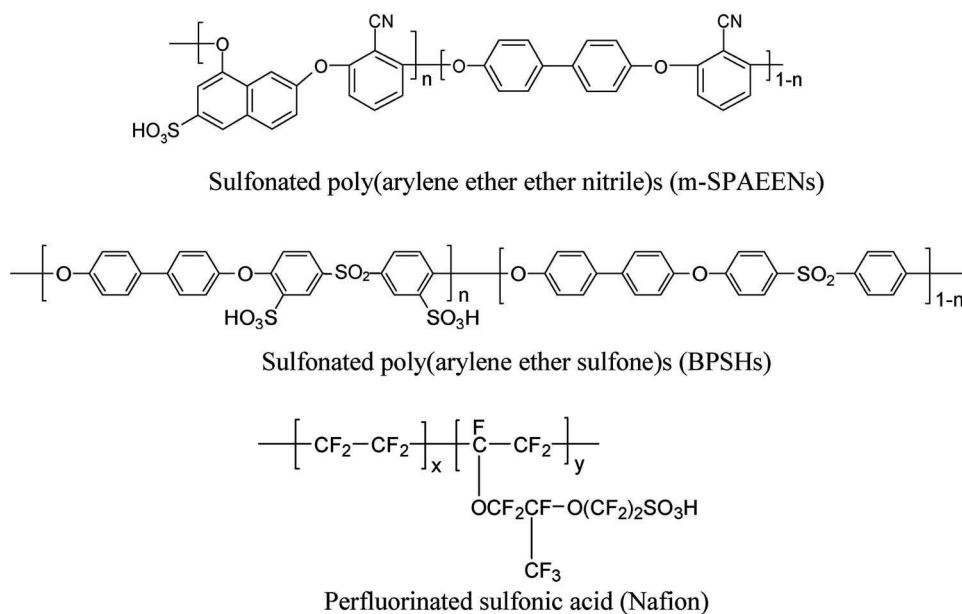
using alternative electrolytes and the inability to match freestanding membrane properties in DMFC testing motivated MEA interfacial studies at Los Alamos National Laboratory. Kim and Pivovar reported that dimensional mismatch (due to differences in water uptakes) between the membrane and Nafion-bonded electrodes resulted in interfacial performance losses and poor long-term stability, likely due to membrane-electrode delamination.<sup>6,7</sup> Reported interfacial losses and long-term stability were improved by tuning water uptake of the PEMs to better match the characteristics of the electrodes.

Previous studies indicated that sulfonated polynitriles had reduced water uptake compared to sulfonated polysulfones or polyketones when compared at similar ion exchange capacity (IEC).<sup>8</sup> Nitrile groups in the sulfonated polymer backbone have been suggested to play an important role in reducing water uptake and dimensional swelling without significantly decreasing conductivity. The DMFC performances of MEA using nitrile copolymers derived from hexafluoroisopropylidene diphenol (6F), 2,6-dichlorobenzonitrile (DCBN), and dichlorodiphenyl sulfone (DCDPS) has been reported as superior to either Nafion or BPSH membrane electrode assemblies (MEAs).<sup>9</sup> Stable long-term performance (up to 700 h) of an MEA using this copolymer has also been reported.<sup>10</sup> However, the increase in proton conductivity and decrease in water uptake of this copolymer could not be wholly attributed to incorporation of benzonitrile groups because this copolymer was also partially fluorinated. Also, the percentage of nitrile groups incorporated into the copolymer was rather small (benzonitrile monomer = 17.5 mol %). Still, these initial results suggest incorporation of nitrile groups might be an avenue to retain conductivity while improving other DMFC relevant properties (water uptake and methanol permeability).

Herein, we report the DMFC performance of sulfonated poly(arylene ether ether nitrile) copolymers (m-SPAEEENs) which are nonfluorinated and have nitrile groups in both hydrophilic and hydrophobic repeat units (benzonitrile monomer = 50 mol %).<sup>11–13</sup> The water-absorption properties of m-SPAEEENs are compared with sulfonated poly(arylene ether sulfone)s (BPSHs) and Nafion using volume-based analyses. The properties of MEAs using the membranes are discussed in terms of high-frequency resistance (HFR) and methanol crossover limiting current. Then the DMFC performance of the MEAs are compared at 0.5 and 2 M methanol feed concentration. Finally, extended lifetime stability is evaluated to study interfacial effects. Our goal is to provide important insight on

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**Figure 1.** Chemical structure of m-SPAEENs, BPSHs, and Nafion; the letter n refers to the mole ratio of a sulfonated monomer to a nonsulfonated one.

the benefits of highly conductive and low-water-swelling nitrile copolymers over current state-of-the-art polysulfone and Nafion membranes.

### Experimental

Aromatic poly(arylene ether ether nitrile)s containing naphthalene units with sulfonic acid groups meta to ether linkage (m-SPAEEN) were prepared via direct aromatic nucleophilic substitution polycondensation of 2,6-difluorobenzonitrile (2,6-DFBN), 2,8-dihydroxynaphthalene-6-sulfonate sodium salt (2,8-DHNS-6), and 4,4'-biphenol (4,4'-BP) in dimethylacetamide (DMAc) at 190°C (see Scheme 1 in Ref. 11). The molar ratio of sulfonated 2,8-DHNS-6 to unsulfonated 4,4'-BP for this study was 50:50 (m-SPAEEN-50) and 60:40 (m-SPAEEN-60).<sup>12</sup> BPSH with various degrees of disulfonation (30–45%) have been kindly supplied by Professor James McGrath's research group.<sup>14</sup> Perfluorinated sulfonic acid Nafion membranes with various thicknesses [DuPont, equivalent weight (EW) = 1100] were also used for comparison. The copolymer membranes in their sodium or potassium salt form were converted to the corresponding acid form by a reported procedure.<sup>15</sup> The chemical structure of each copolymer is shown in Fig. 1.

Membrane density was calculated from measurements of membrane dimensions and weight after drying at 75°C for 2 h. Water uptake (WU) was measured after drying the membrane in acid form at 100°C under vacuum overnight. The dried membrane was immersed in water at 30°C and periodically weighed on an analytical balance until a constant weight was obtained and a volume-based WU was calculated. A volume-based dry IEC [IEC<sub>V</sub> (dry)] was obtained by multiplying the dry membrane density by the weight-based (IEC<sub>W</sub>), which was estimated from the copolymer structure. An IEC<sub>V</sub> (wet) was then calculated from IEC<sub>V</sub> (dry), the membrane WU, and the density of water, 1 g/cm<sup>3</sup>.

MEAs were prepared from standard catalyst inks using a previously reported procedure.<sup>9</sup> Unsupported platinum (6 mg/cm<sup>2</sup>) and platinum-ruthenium (10 mg/cm<sup>2</sup>) catalysts (Johnson Matthey) were used for cathode and anode, respectively. The geometric active cell area was 5 cm<sup>2</sup>. Single and double-sided hydrophobic carbon cloths (E-TEK, Inc.) were used as anode and cathode gas-diffusion layers, respectively. All the MEAs tested were prepared by the same procedure. The data presented for Nafion MEAs is representative of reproducible data taken from tens of DMFC experiments in our labs. The data presented for m-SPAEEN was selected from a single membrane sample and showed good reproducibility with a second sample.

Limiting methanol crossover currents through the membrane were measured to estimate the methanol crossover. For the data reported here, 0.5 M methanol solution was fed to one side of the cell, while humidified nitrogen at 500 sccm and ambient pressure were supplied to the other side. The methanol permeation flux was determined from the limiting current density resulting from transport-controlled methanol electro-oxidation at the other side of the cell using a potential-step experiment described in greater detail elsewhere.<sup>16,17</sup> Cell resistance and polarization curves for single cells were performed using a fuel cell test station (Fuel Cell Technology, Inc.) after 12 h break-in under hydrogen/air conditions at a cell voltage of 0.7 V. For DMFC testing, the cell was held at 80°C; 0.5 and 2 M aqueous methanol solution was fed to the anode with a flow rate of 1.8 mL/min; 90°C humidified air was fed at 500 sccm without back pressure (high humidification and stoichiometry were used to minimize ohmic and mass transfer effects). HFR was measured by applying a sinusoidal wave perturbation of 2 kHz where capacitive contributions to cell impedance were found to be minimized. Both limiting methanol crossover current densities and HFR measurements exhibited experimental reproducibility of approximately ±5%.

### Results and Discussion

**Membrane properties.**— Table I compares the density, IEC, and WU of the m-SPAEENs, BPSHs, and Nafion. Volume-based quantities under operating conditions (hydrated membranes) have been reported to be the most appropriate comparison basis, because electrochemical properties such as proton conductivity and permeability occur over length scales under operating conditions independent of mass.<sup>18</sup> Still, dry, weight-based measurements are most often quoted in the literature and appear in Table I for comparison purposes.

The WU directly affects the proton-exchange concentrations within the polymer matrix under hydrated conditions, which can be gauged by comparing wet-volume-based IEC [IEC<sub>V</sub> (wet)] values with IEC<sub>W</sub> values. The IEC<sub>V</sub> (wet) of m-SPAEEN increased from 1.45 to 1.69 mequiv/cm<sup>3</sup> as IEC<sub>W</sub> changed from 1.60 to 1.91 mequiv/g. The IEC<sub>V</sub> (wet) of BPSH decreased from 1.40 to 1.12 mequiv/cm<sup>3</sup> as IEC<sub>W</sub> changed in a similar range (i.e., 1.54 to 1.92 mequiv/g). In the case of m-SPAEEN, even when a high concentration of sulfonic acid groups was present in the dry state, it was not greatly reduced when the membrane was equilibrated in water, because the dimensional swelling was restrained. This is in contrast with BPSH membrane after equilibration with water, where excessive WU and dimensional swelling occurred, ef-

**Table I. Properties of the m-SPAEEN, BPSH, and Nafion.**

Copolymer	Density <sup>a</sup> (g/cm <sup>3</sup> )	IEC <sub>w</sub> <sup>b</sup> (mequiv/g)	IEC <sub>v</sub> <sup>c</sup> (mequiv/cm <sup>3</sup> )		WU				Proton conductivity (mS/cm <sup>2</sup> )
			dry	wet	wt % <sup>d</sup>		vol% <sup>e</sup>		
					20°C	80°C	20°C	80°C	
m-SPAEEN-50	1.15	1.60	1.83	1.45	23	27	26	31	50
m-SPAEEN-60	1.18	1.91	2.26	1.69	28	38	33	45	115
BPSH-30	1.30	1.34	1.74	1.26	24	38	31	49	40
BPSH-35	1.34	1.54	2.06	1.40	35	50	47	67	72
BPSH-40	1.38	1.72	2.37	1.38	52	84	72	116	104
BPSH-45	1.41	1.92	2.70	1.22	85	~140	120	~197	140
Nafion	1.98	0.90	1.78	1.29	19	29	38	57	125

<sup>a</sup> Based on dry state.<sup>b</sup> Based on weight of dry membrane.<sup>c</sup> Based on volume of dry and/or wet membranes [ $IEC_v(\text{wet}) = IEC_v(\text{dry})/(1 + 0.01 \text{ WU})$ ].<sup>d</sup> WU (mass %) =  $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100$ .<sup>e</sup> WU (vol %) =  $[(W_{\text{wet}} - W_{\text{dry}})/\delta_w]/[(W_{\text{dry}}/\delta_m)] \times 100$ ;  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the wet and dry membranes, respectively,  $\delta_w$  is the density of water (1 g/cm<sup>3</sup>), and  $\delta_m$  is the membrane density in the dry state.

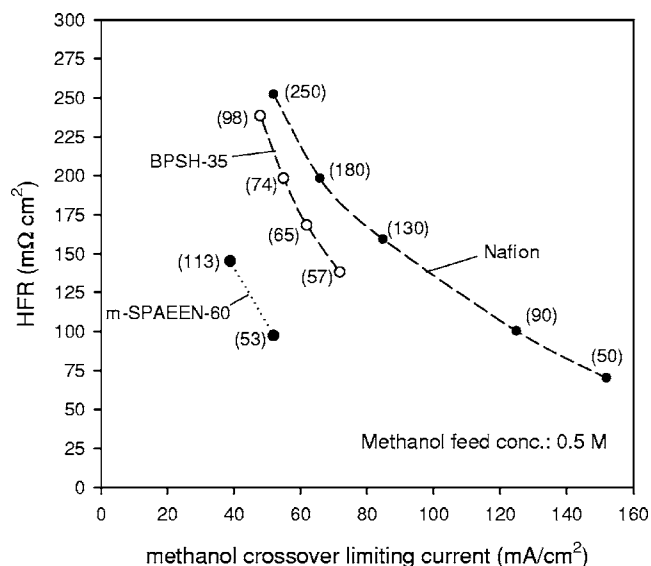
fectively resulting in a dilution of the ion concentration. This is a striking property difference which has major advantages for utilizing nitrile copolymers in fuel cell applications, in that increased levels of protogenic acid groups can be incorporated into the polymer without excessively increasing WU. Note that m-SPAEEN copolymers have lower WU than BPSH copolymers when compared at similar  $IEC_v(\text{wet})$ . For example, the WU at 80°C of m-SPAEEN-50 [ $IEC_v(\text{wet}) = 1.45$  mequiv/g] was 31 vol %, less than half of the WU of BPSH-35 [ $IEC_v(\text{wet}) = 1.40$  mequiv/g], 67 vol %. The reduced WU of m-SPAEENs could be due to a number of factors. One plausible explanation is the presence of nitrile–nitrile dipole interactions that combine to limit swelling. In addition, the nitrile-sulfonic acid group may be important as nitrile groups have been found to associate with sulfonic acid groups through bridging water molecules bridged in specific spectroscopic studies.<sup>19</sup> Finally, Nafion, which has a relatively low  $IEC_w$  due to its relatively high density, appears much closer to the other polymers when compared on an  $IEC_v(\text{wet})$  basis.

Table I also shows the proton conductivity of m-SPAEENs, BPSHs and Nafion that were measured on freestanding membranes at 30%. The m-SPAEEN-60 and BPSH-40 and -45 had good conductivity (104–140 mS/cm), comparable to Nafion (125 mS/cm), BPSH-35 showed moderate conductivity (72 mS/cm), and m-SPAEEN-50 and BPSH-30 had relatively low conductivity (40–50 mS/cm). Conductivity below 50 mS/cm can lead to significant ohmic losses under operation, as minimum membrane thickness is often practically limited due to membrane fabrication or mechanical properties.<sup>20</sup> A comparison of the hydrocarbon PEMs with similar WU values reveals that the conductivity of m-SPAEENs is significantly higher than that of BPSHs. For example, the conductivity of m-SPAEEN-60 (WU at 20°C: 33 vol %) was 115 mS/cm, which was almost three times higher than that of BPSH-30 (WU at 20°C: 31 vol %), showing the practical advantages of nitrile containing PEMs on improving conductivity while effectively restraining WU and swelling.

**MEA properties.**—Based on membrane properties presented in Table I, one membrane from each family of copolymers was selected for further study, m-SPAEEN-60, BPSH-35, and Nafion. These three were chosen based on a favorable combination of WU and proton conductivity. Membranes with excessive water swelling tend to be (i) less effective in proton conduction and (ii) mechanically fragile and subject to dimensional changes under dehydration/hydration cycling. The decreased effectiveness of proton conduction at high WUs has been demonstrated in these systems.<sup>15,18,21</sup> Mechanical fragility of highly water swollen membranes has been demonstrated during MEA fabrication and fuel cell testing.<sup>6</sup> Due to their

high WUs, BPSH-40 and -45 copolymers were excluded from fuel cell testing in the present work, although their fuel cell performance was reported elsewhere.<sup>9,22</sup> BPSH-35 and m-SPAEEN-60 were selected as representative membranes for sulfonated polysulfones and polynitriles because they had the highest proton conductivity with reasonably low WU. Nafion was tested as a reference.

Figure 2 shows a plot of HFR vs methanol crossover limiting current of MEAs using the selected membranes as a function of membrane thickness under 80°C, 0.5 M methanol feed concentration. As would be expected, HFR increases and methanol crossover limiting current decreases as a function of increasing membrane thickness within a copolymer family. The comparison of membranes in this way allows the effects of methanol crossover and ohmic losses to be considered together when evaluating performance potential of a DMFC. This MEA comparison is similar to selectivity, a ratio of proton conductivity to methanol permeability suggested as a basis for qualitatively evaluating membranes as DMFC electrolytes.<sup>23</sup> However, unlike membrane selectivity, this MEA comparison takes membrane thickness issues into account as well. A



**Figure 2.** HFR vs methanol crossover limiting current of m-SPAEEN-60, BPSH-35, and Nafion as a function of membrane thickness measured in DMFC mode at 0.5 M methanol feed concentration (cell temperature: 80°C); numbers in parentheses denote membrane thickness in micrometers.



**Table II.** HFR, methanol limiting current densities, and maximum power densities of three different membranes under various operating conditions: m-SPAEEN-60 (53  $\mu\text{m}$  thick), Nafion (50  $\mu\text{m}$  thick), and Nafion (250  $\mu\text{m}$  thick).

Operating conditions		m-SPAEEN-60 (53 $\mu\text{m}$ thick)			Nafion 112 (50 $\mu\text{m}$ thick)			Nafion 1110 (250 $\mu\text{m}$ thick)		
Temperature ( $^{\circ}\text{C}$ )	MeOH conc. (M)	HFR ( $\text{m}\Omega\text{ cm}^2$ )	MeOH limiting current ( $\text{mA}/\text{cm}^2$ )	Maximum power density ( $\text{mW}/\text{cm}^2$ )	HFR ( $\text{m}\Omega\text{ cm}^2$ )	MeOH limiting current ( $\text{mA}/\text{cm}^2$ )	Maximum power density ( $\text{mW}/\text{cm}^2$ )	HFR ( $\text{m}\Omega\text{ cm}^2$ )	MeOH limiting current ( $\text{mA}/\text{cm}^2$ )	Maximum power density ( $\text{mW}/\text{cm}^2$ )
40	0.5	128	22	34	96	75	36	326	20	29
60	0.5	103	37	80	82	112	87	260	35	60
80	0.5	97	52	151	70	152	147	252	52	120
80	1	98	105	240	78	298	168	256	99	153
80	2	99	201	216	85	524	132	263	182	141
80	5	101	325	128	110	902	25	282	322	96

polymer with ideal properties would appear in the bottom left corner of this graph as one having low HFR (ohmic losses) and low methanol crossover (low crossover losses).

Of the three polymers shown, Nafion shows the poorest DMFC properties, being in the top right corner of the graph. This is not surprising, because Nafion is known to be a relatively poor DMFC polymer electrolyte, possessing rather low selectivity.<sup>20,23</sup> While BPSH-35 shows slightly improved DMFC potential, m-SPAEEN-60 shows significantly improved potential, having much lower methanol crossover limiting current at comparable high-frequency resistance. From these results, one would expect slightly improved DMFC performance using BPSH-35 compared to Nafion but a much more significant improvement in performance using m-SPAEEN-60. By plotting the data as we have in Fig. 2, the tradeoffs between different membrane classes and membrane thickness can be more easily evaluated. For example, the low conductivity of BPSH-35 limited the use of membranes to less than 100  $\mu\text{m}$  in order to keep HFR below 250  $\text{m}\Omega\text{ cm}^2$ , in order to limit ohmic losses. Nafion could be much thicker (up to 250  $\mu\text{m}$ ) before reaching a similar HFR.

While such comparisons are useful for evaluating membrane DMFC potential, they cannot take into account all the relevant factors (membrane-electrode interface, etc.) associated with DMFC performance.

**MEA performance.**— In this section, we compare the voltage-current characteristics (i.e., DMFC polarization curves) of MEAs using the three selected membranes. Although polarization curves are the most popular method for evaluating DMFC performance, making reasonable and relevant performance comparisons across different types of membranes is difficult because (i) cell properties depend on membrane thickness, (ii) methanol crossover (fuel utilization) is not fully interpreted by polarization curves, and (iii) optimum operating conditions (primarily methanol feed concentration but also factors such as temperature and cathode flow rate) may be different for different systems. In order to minimize the uncertainty caused by methanol crossover, we selected membranes having a thickness for which methanol crossover limiting currents were similar. Membranes of m-SPAEEN-60 (53  $\mu\text{m}$  thick), BPSH-35 (74  $\mu\text{m}$  thick), and Nafion (250  $\mu\text{m}$  thick) all had methanol crossover limiting currents of  $\sim 50\text{ mA}/\text{cm}^2$ , as shown in Fig. 2. This choice seems to be reasonable based on previous DMFC efficiency analyses, which indicated that cells using highly methanol-permeable membranes such as Nafion have better maximum efficiency with thick membranes while cells having low permeable membranes give better efficiency with thin membranes.<sup>20</sup> We have tested multiple membrane thicknesses in MEAs under several operating temperatures and methanol feed concentrations; although we present polarization curves for only two different methanol feed concentrations, the results are representative of a more complete data set (see Table II).

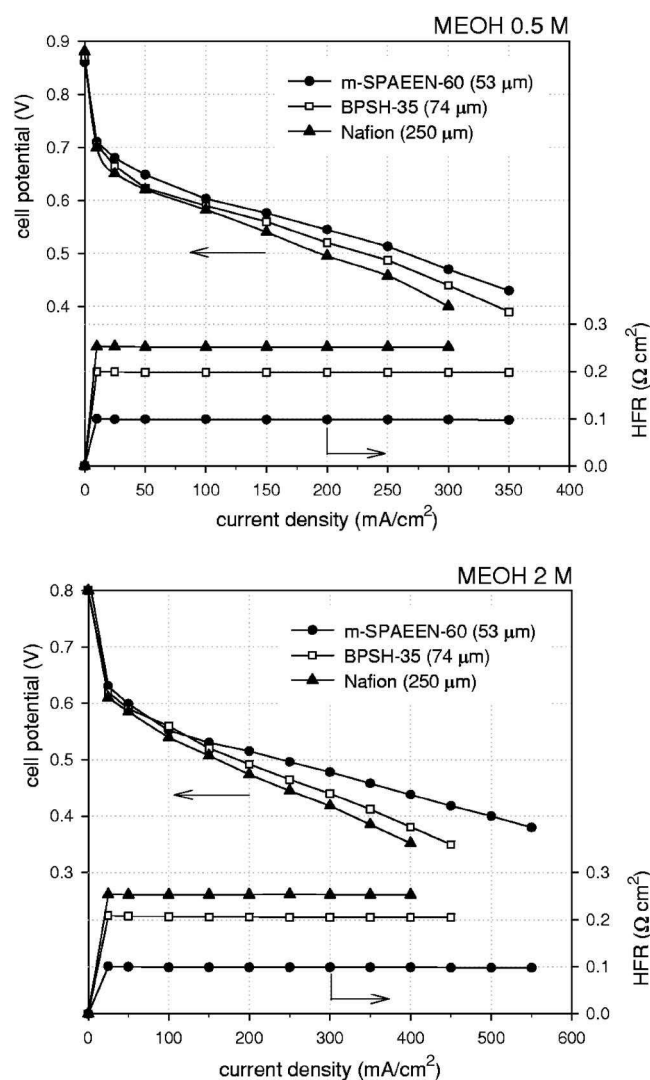
Table II reports the observed HFR, methanol limiting current densities, and maximum power densities of three different mem-

branes: m-SPAEEN-60 (53  $\mu\text{m}$  thick), Nafion (50  $\mu\text{m}$  thick), and Nafion (250  $\mu\text{m}$  thick), as a function of cell temperature and methanol feed concentration. From the data presented in Fig. 2 the superior properties of m-SPAEEN can be directly compared. While thin Nafion (50  $\mu\text{m}$  thick) has slightly lower HFR (except at high methanol concentration), methanol crossover rates are substantially higher. Thick Nafion (250  $\mu\text{m}$  thick) has essentially identical methanol crossover rates, with substantially increased HFR. Some variations of these properties exist with temperature and concentration, but the trends are fairly consistent. Finally, maximum power density, while not the ideal indicator of performance because efficiency is not properly weighted, shows that m-SPAEEN-60 compares favorably to that of Nafion.

Figure 3 shows the cell performance of the MEAs using m-SPAEEN-60, BPSH-35, and Nafion at methanol feed concentrations of 0.5 and 2 M. As would have been expected from the data in Fig. 2 and Table II, the performance of the MEA using m-SPAEEN-60 was superior to that of the MEAs using BPSH-35 and Nafion, with BPSH-35 being slightly improved compared to Nafion. For example, the current density of the MEA using m-SPAEEN-60 at 0.5 V and 0.5 M methanol was 265  $\text{mA}/\text{cm}^2$ , whereas the current densities of the MEAs using BPSH-35 and Nafion were 230 and 195  $\text{mA}/\text{cm}^2$ . At 2 M methanol, open-circuit potential and mass-transport limitations for all MEAs decreased but the performance trend remained remarkably similar to that at 0.5 M methanol. As these membrane thicknesses were chosen based on equivalent methanol crossover limiting currents, it is reasonable to suggest that performance differences could be largely attributed to changes in ohmic losses reflected in the HFR values, also shown in Fig. 3.

IR-corrected polarization curves, which comprise the measured cell voltage plus estimated ohmic losses (measured HFR multiplied by cell current density) vs cell current density, are shown in Fig. 4. These data allow cell performance to be compared independently of ohmic losses and show that indeed the performance differences shown in Fig. 3 are primarily the result of ohmic losses, as IR correction results in nearly equivalent performance from all three samples. The remaining small differences in performance can be attributed to differences in methanol crossover rates as a function of current density (due to issues such as membrane tortuosity and electro-osmotic drag), membrane-electrode interfacial variability, or other issues such as sample-to-sample variability of the electrodes of each specific sample or water transport issues through the membranes and flooding within the cathode backing. Of particular interest is membrane-electrode interfacial resistance, which has already been reported for BPSH-35 and Nafion under these operating conditions and is known to be small.<sup>7</sup> These results suggest the m-SPAEEN-60 membrane-electrode interface resistance is also likely small.

Along similar lines, a previous study indicated that MEAs using alternative membranes and Nafion-bonded electrodes often suffered from membrane-electrode interfacial failure during life testing, with-

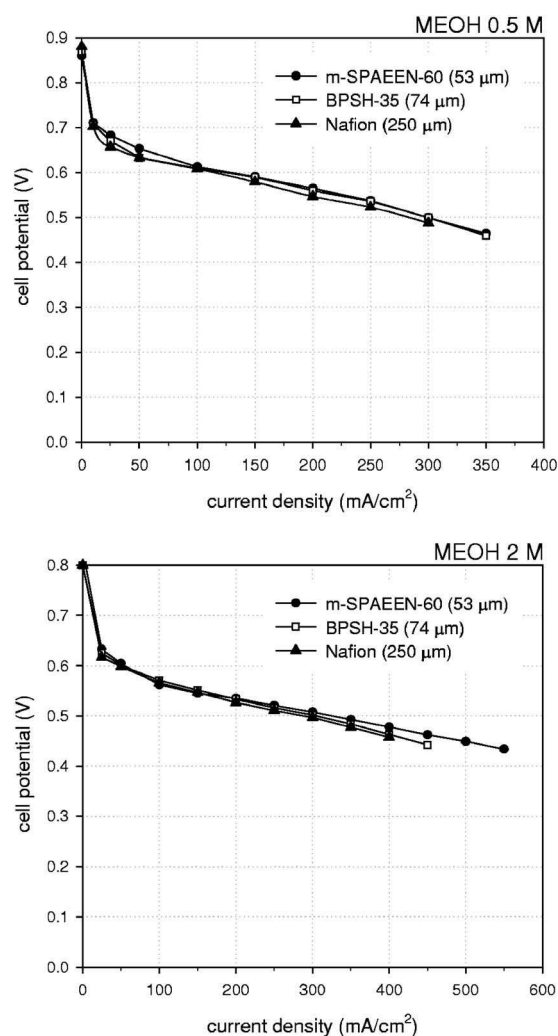


**Figure 3.** DMFC performance of m-SPAEEEN-60, BPSH-35, and Nafion at 0.5 and 2 M methanol feed concentration (cell temperature: 80°C).

out any discernable chemical degradation.<sup>10,22,24</sup> The interfacial failure was correlated with an increasing HFR and performance loss after 100 h. In order to verify the interfacial stability of the MEA using m-SPAEEEN-60, an extended life test (>100 h) was conducted. Figure 5 shows that the MEA using the m-SPAEEEN-60 had stable HFR and a moderate current density loss (approximately 40 mA/cm<sup>2</sup>) comparable to that of a Nafion MEA under the same operating conditions (with much higher performance throughout the life test).<sup>10</sup> The current density loss is thought to be primarily attributable to platinum oxidation at the high cathode potential and is largely reversible. These results indicate that the interfacial compatibility of m-SPAEEEN-60 is likely good using Nafion-bonded electrodes. These results clearly indicate the advantages of nitrile copolymers in DMFC operation.

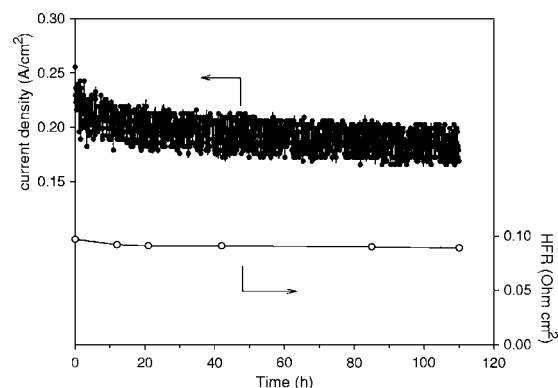
### Conclusion

MEAs using a nitrile copolymer (m-SPAEEEN-60) have been demonstrated with significantly improved performance in DMFC compared to the MEAs using sulfonated polysulfone analogs (BPSHs) and industrial standard Nafion membranes under optimized conditions. The nitrile copolymers have relatively low WU allowing relatively high ion concentrations in the hydrated polymer matrix. This increased hydrated acid concentration offers more effective proton conduction while providing improved mechanical stability.



**Figure 4.** IR-corrected polarization curves of m-SPAEEEN-60, BPSH-35, and Nafion at 0.5 and 2 M methanol feed concentration (cell temperature: 80°C).

The nitrile copolymer was found to be stable with Nafion-bonded electrodes in the practical window for DMFC operation. Further development of the nitrile copolymer electrolytes for H<sub>2</sub>/air fuel cells is being investigated and will be reported in the near future.



**Figure 5.** Current density and HFR changes of the MEA using m-SPAEEEN-60 (cell temperature: 80°C, 0.5 M methanol, electronic load: constant 0.5 V, cathode humidification: 90°C).

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