Proton-Exchange Membranes from Sulfonated Polyphosphazene Blends

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INTRODUCTION

Polyorganophosphazenes offer new possibilities as potential membrane materials. These polymers belong to a class of hybrid polymers; their backbone is inorganic while the side groups are of organic nature. Numerous papers have been published on various aspects of polyphosphazene synthesis, properties and applications but there are only a few reports on their use as ion-exchange or proton-exchange membranes (1).

Our previous studies (2-4) have shown that ion-exchange membranes composed of sulfonated and crosslinked poly[bis(3-methylphenoxy)phosphazene] possess high proton conductivity (0.01-0.1 S/cm) and low methanol diffusivity (10^{-8}-10^{-7}cm^2/s), the properties required of a candidate membrane for use in direct methanol fuel cells. Additionally, at low and moderate sulfonation degrees, the polymer had acceptable mechanical properties and it could be crosslinked using benzophenone (BP) and UV irradiation. However, at ion-exchange capacities greater than 1.2 mmol/g, there appeared brittleness which rendered the membranes difficult to handle and electrodes for fuel cell testing could not be hot-pressed to them. Blending of the sulfonated polyphosphazene with a tough and strong inert polymer was thought to give membrane material with improved mechanical properties that will allow for MEA fabrication. Besides the mechanical characteristics alone, blending with an appropriate polymer could also improve the material's transport properties (reduce water and methanol flux). After the initial screening, based on analysis of miscibility, three polymers were selected for blending with sulfonated polyphosphazene: Kynar Flex (a copolymer of vinylidene fluoride and hexafluoropropylene), polyacrylonitrile (PAN), and polybenzimidazole (PBI).

EXPERIMENTAL

Sulfonation of the polyphosphazene. A known weight (2g) of poly[bis(3-methylphenoxy) phosphazene] (MW=700,000) was dissolved in 80 ml of 1,2-dichloroethane (DCE). An appropriate amount (0.3-2.0 ml) of SO_3 in DCE was then added to the polymer solution at $0^\circ C$ in a dry nitrogen atmosphere. The resulting precipitate was stirred for ca. 3 hours, followed by the addition of NaOH dissolved in a water/methanol mixture to terminate the reaction. After solvent evaporation, the sulfonated polymer was soaked in water and then treated sequentially with 0.01 M NaOH, water, 0.1 M HCl and water. Next, the sulfonic acid groups were converted into the sodium salt form using 0.1M NaOH, followed by thorough washings with water. In the final step the SPOP was dried at $60°C$.

Blending and membrane preparation. SPOP and the second componentt (FLEX, PAN or PBI) were dissolved separately in dimethylacetamide (DMAc). Both solutions were combined and mixed for 2 hours. Benzophenone was added to appropriate solutions. The solution was filtered and cast into a polypropylene dish. The solvent was evaporated by heating in an oven at $60°C$ for 48 hours. Those dried blends that required photocrosslinking were irradiated under nitrogen with UV light of wavelength 365 nm for 12 hours. Next the membranes were placed in 1M H_2SO_4 for 12 hours. Finally they were washed several times with de-ionized water.

Conductivity Measurements. Proton conductivity of water swollen membranes, with sulfonate groups in SO_3H form, was measured by an AC impedance method (real axis intercept of the impedance spectrum) in the frequency range 1 Hz to 100 kHz using a lock-in amplifier (EG&G Model 5210) and potentiostat (EG&G Model 273). The cell employed was a two-probe type. Measurements were taken at $25°C$.

Swelling Measurements. A membrane sample (in the SO_3H form) was equilibrated in water at $25°C$ for 24 h. After removal from the water bath, the membrane surface was blotted dry with filter paper and the sample was weighted on an electronic balance (m_w). After thorough drying under vacuum and over P_2O_5 for 24 h, the membrane was re-weighed (m_d). The equilibrium water swelling (S) was calculated according to the following formula:

$$S \text{ [g/g]} = (m_w - m_d)/ m_d$$

<u>MEA Fabrication.</u> MEAs with a geometric area of 5.0 cm^2 were prepared using fuel-cell-grade platinum-black (Alfa Aesar) and 1:1 platinum-ruthenium alloy powder (Alfa Aesar) as the cathode and anode catalysts, respectively (each at a loading of 4.0 mg/cm^2). MEA inks were prepared according to the methods of Wilson *et al.* (5), where 1.0 g catalyst, 4.0 g water, and 4.0 g isopropyl alcohol were mixed thoroughly followed by the addition of a 5 wt% Nafion solution (Aldrich). The final Nafion binder content in the inks was either 15 wt% (anode) or 10 wt% (cathode). Inks were painted onto 0.36 mm thick single sided carbon only ELAT gas diffusion electrodes (E-TEK), followed by solvent drying at 90°C.   The catalyst/carbon cloth anode and cathode were hot-pressed onto a blended/crosslinked SPOP membrane (or onto a Nafion 117 membrane) at 120°C and 125 psi for 5 minutes. Under these conditions, there was good adhesion of the electrodes to the membranes. The MEAs were then soaked in 1.0 M H$_2$SO$_4$ for 6 hours, followed by numerous washings with distilled water to flush out the acid.

<u>DMFC Tests.</u> Steady-state current density/voltage data were collected using a single cell DMFC test station (Scribner Series 890B) with mass flow, air pressure, and temperature control. The fuel cell was operated at 60°C, with 1.0 M methanol (at a flow rate of 20 ml/min) and humidified air (at 50°C and a flow rate of either 150 sccm at 30 psi back pressure or 540 sccm at ambient pressure). The methanol crossover flux was determined by measuring the carbon dioxide concentration in the cathode air exhaust at open circuit with a Vaisala GMM12B CO$_2$ detector.
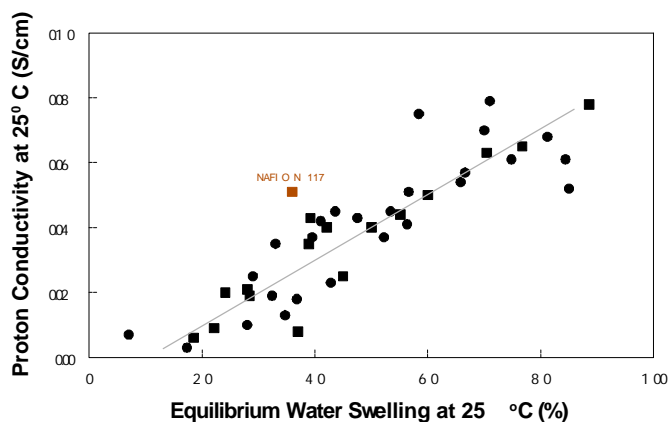
RESULTS AND DISCUSSION

Several batches of sulfonated poly[bis(3-methylphenoxy)phosphazene] (SPOP) were prepared with an IEC in the 1.4-3.5 range. They were blended with either: FLEX, PAN or PBI, by solution casting at 60 °C.

Fig. 1 shows a relationship between the ion-exchange capacity of the SPOP and its water affinity. The starting, unsulfonated material has IEC of 0 mmol/g. When half of the number of aromatic rings is mono-substituted with SO_3H, the IEC is 3 mmol/g. Finally when all the rings are mono-substituted, an IEC of 4.8 mmol/g is reached. The most important finding was that at an IEC greater than 2.1 mmol/g, the SPOP became water- soluble. Below that limit the polyphosphazene only swelled in water but did not dissolve.

Figure 1. The dependence between the sulfonation degree of SPOP and its water affinity.

It may be concluded, that using SPOP of IEC greater than 2.1 will require crosslinking or grafting not only to reduce swelling but, primarily, to prevent the sulfonated component from being leached out from the blend in aqueous solutions. Benzophenone assisted UV-crosslinking was used to prevent the polyphosphazene from dissolution and to reduce membrane swelling. Benzophenone crosslinking was studied earlier in our group (6-7).

Two groups of blended membranes were synthesized. The first group consisted of membranes containing SPOP of IEC=1.4-2.0 mmol/g and the second group consisted of membranes with SPOP of the IEC greater than 2.0 mmol/g. Membranes belonging to group 1 contained 50-80% of SPOP, those belonging to group 2 contained 30-50% of SPOP. It was found that, in general, either Kynar FLEX or PAN was immiscible on a molecular level with the SPOP. For certain compositions, SPOP IEC, and SPOP salt form, an acceptable degree of

compatibility was obtained and those blends showed no signs of macroscopic phase separation. The degree of compatibility increased with increasing IEC of the SPOP. Also, when the sulfonate groups of the SPOP were converted to tetrabutylammonium (TBA)-form, highly homogeneous, transparent blends were obtained, but these blends were unstable in hot aqueous solutions due to very low yields of crosslinking.

Swelling and proton conductivity are among the most important characteristics of the proton-exchange membrane. These parameters were measured in water at 25°C and the results are presented in Fig. 2.

Figure 2. Correlation between eqilibrium water swelling and membrane proton conductivity (in water at 25°C). Circles are from SPOP/Kynar FLEX blended membranes and squares are from SPOP/PAN blended membranes.

It can be seen that there exists, approximately, a linear correlation between the swelling of the membranes and proton conductivity. A swelling increase from 20 to 90% is accompanied by an increase in conductivity from 0.01 to 0.08 S/cm. No correlation was observed between the effective IEC of the blended membranes and their proton conductivity, although membranes of the same swelling but prepared from SPOP with higher IEC showed a higher conductivity. It can also be seen from Fig. 2, that there was no significant difference in

the swelling vs. conductivity behavior of membranes prepared from Kynar Flex blends and those prepared from PAN blends. It should be stated, however, that membranes prepared from the SPOP of the highest IEC (3.5 mmol/g) and to lesser extent those prepared from SPOP of IEC=2.1 mmol/g were unstable. When placed in an aqueous solution, the SPOP leached out which resulted in a gradual loss of membrane conductivity. This was an indication of insufficient crosslinking of the highly sulfonated polyphosphazene.
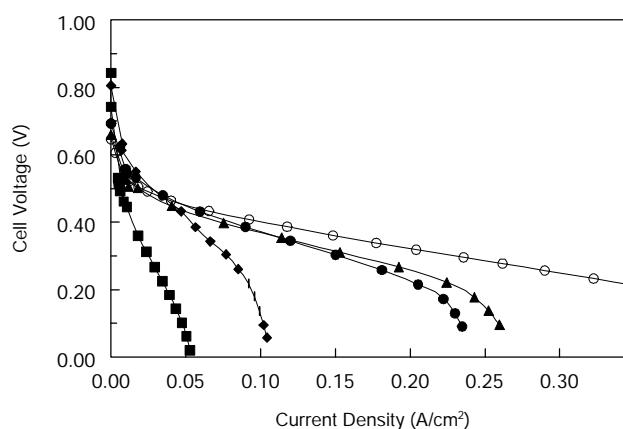
Initial studies targeting MEA preparation showed that blended membranes containing PAN gave much better current characteristics during actual DMFC tests than membranes with PVDF. Therefore, most of our fuel cell experiments were performed with SPOP/PAN blends. An example of one set of fuel cell experiment is described below. Four UV-crosslinked SPOP/PAN membranes with different effective ion-exchange capacities, ranging from 0.95 to 1.15 mmol/g, were used. The properties of these membranes (thickness, water swelling, proton conductivity, and methanol crossover) are contrasted with those of Nafion 117 in Table I.

Table I. Properties of Blended and Crosslinked SPOP/PAN Membranes for DMFC Tests

Membrane Composition	Membrane Effective IEC (mmol/g)	Wet Thickness (μm)	% Swelling in 25°C Water (g/g x 100)	Proton Conductivity in 25°C Water (S/cm)	Methanol Crossover at Open Circuit (mol/cm^2-min)
55% 2.1 IEC SPOP 40% PAN +5% BP	1.15	148	60%	0.050	3.3×10^{-6}
52% 2.1 IEC SPOP 43% PAN + 5% BP	1.10	137	50%	0.040	2.1×10^{-6}
48% 2.1 IEC SPOP 47% PAN + 5% BP	1.0	151	45%	0.025	1.4×10^{-6}
45% 2.1 IEC SPOP 50% PAN + 5% BP	0.95	158	37%	0.008	0.75×10^{-6}
Nafion 117	0.909	220	35%	0.06	9.0×10^{-6}

The SPOP/PAN membranes were thinner than Nafion, with lower proton conductivity, greater water swelling, and lower methanol crossover flux (as measured during fuel cell

performance tests). The DMFC current density/voltage curves for MEAs containing these membranes are shown in Figure 3. Fuel cell performance with the 1.10 and 1.15 effective IEC SPOP/PAN membranes was very good, with a high open circuit potential (0.66 V and 0.69 V for the 1.15 and 1.10 IEC membranes, respectively), current density/voltage curves that were only slightly lower than that with Nafion 117 (for current densities < 0.15 A/cm^2), and methanol crossover fluxes 3-4 times lower than that in Nafion 117.

Figure 3. Methanol fuel cell performance for blended SPOP/PAN membranes. Fuel cell operating conditions: 60°C, 1.0 M methanol, 50°C humidified air at 150 sccm and 30 psi back pressure. ○ Nafion 117; ▲ 1.15 IEC SPOP/PAN; ● 1.10 IEC SPOP/PAN; ♦ 1.0 IEC SPOP/PAN; ■ 0.95 IEC SPOP/PAN.

Since the SPOP/PAN membranes were thinner than Nafion 117, the thickness-corrected methanol permeability was significantly lower than that in Nafion; 4.1 times lower for the 1.15 IEC blended film and 6.9 times lower for the 1.10 IEC film. This result is particularly striking, given the fact that the two blended membranes swelled considerably more than Nafion 117 in water (50-60% vs. 35% for Nafion) and would presumably swell to an even greater extent in 1.0 M methanol (such measurements were not performed in the present study).
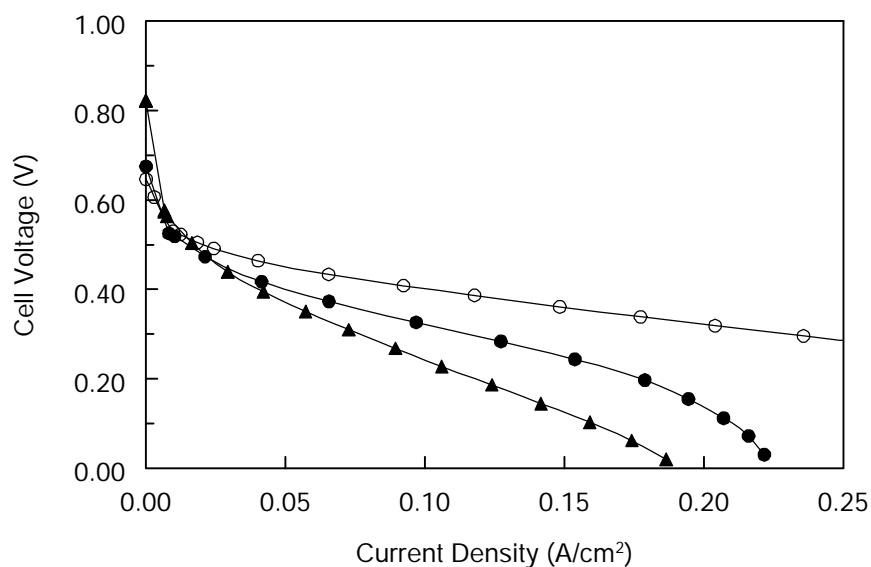
The electrochemical performance of the two low IEC blended membranes (at 0.95 and 1.0 effective IEC) was poor, although the methanol crossover was very low (e.g., 12 times lower than Nafion 117 for the 0.95 IEC blended membrane). The low power output was attributed to the combined effects of the membranes' lower proton conductivity (especially for the 0.95 IEC film) and a high contact resistance between the membrane and catalyst powder electrodes. Proper adjustment of the catalyst binder type/amount and/or identification of the optimum MEA hot pressing conditions may minimize this contact resistance. As follow-up experiments to those in Figure 3, the MEA fabrication conditions were kept unchanged and we focused our attention on fabricating a multi-layered membrane MEA, where the most desirable properties of both the high and low IEC SPOP/PAN blends were combined.

Based on the data in Figure 3, the preferred SPOP membrane would have an inner methanol barrier layer composed of a low effective IEC blend that is sandwiched between outer layer blends of high IEC, which would contact the anode and cathode. Such a multi-layered MEA construct was prepared as follows (8): Two thin 1.15 effective ion-exchange capacity SPOP/PAN membranes were prepared from 55% 2.1 IEC SPOP + 37.5% PAN + 7.5% benzophenone. A standard 5.0 cm^2 Pt-Ru + Nafion binder anode was hot pressed onto one film and a 5.0 cm^2 Pt-black + Nafion binder cathode was pressed onto the second membrane (hot pressing conditions were 120°C and 125 psi for 5 minutes).

The two "half cell" MEAs were inserted into a DMFC test cell and the two membrane sheets were physically pressed together when the cell was bolted shut. The performance of this MEA in a direct methanol fuel cell is compared to a Nafion 117 MEA in Figure 4. The measured current density vs. voltage curve is similar to the 1.15 IEC single membrane MEA plot in Figure 3, with a methanol crossover flux three-times lower than that with Nafion 117 (3.0 x 10^{-6} mol/cm^2-min at open circuit and 2.8 x 10^{-6} mol/cm^2-min at 0.1 A/cm^2). Next, a crosslinked, low IEC SPOP blended membrane was prepared from 56% 1.7 IEC SPOP + 36.5% PAN + 7.5% benzophenone. This film was 90 ìm thick with an effective IEC of 0.95 mmol/g. This methanol barrier layer was physically inserted between the two outer high IEC membrane/electrode half-cell MEAs, as shown schematically in Figure 3b. The three membrane layers were pressed together in the DMFC test cell and polarization data were

collected at 60°C and 1.0 M methanol (see Figure 4). The electrochemical performance of this MEA was lower than the two membrane MEA construct, presumably due to the combined effects of the additional IR drop within the low IEC inner membrane and the added contact resistance at the interfaces between the three membrane layers. The open circuit potential for the three-layer MEA, however, was very high (0.822 V) and the methanol crossover flux was about ten-times lower than that with Nafion 117 (0.97 x 10^{-6} mole/cm^2-min at open circuit and 0.95 x 10^{-6} mol/cm^2-min at 0.1 A/cm^2). Experiments are currently being carried out to identify: (*i*) the optimum composition and thickness for each layer of a composite SPOP/PAN DMFC membrane and (*ii*) methods for chemically attaching the layers to one another to form a single integral film.

Figure 4. Methanol fuel cell performance with the two-layer and three-layer SPOP/PAN MEAs. Fuel cell operating conditions: 60°C, 1.0 M methanol, 50°C humidified air at 540 sccm and ambient pressure. ○ Nafion 117 (methanol crossover flux = 9.0 x 10^{-6} mol/cm^2-min); ● two-layer SPOP/PAN MEA (methanol crossover flux = 3.0 x 10^{-6} mol/cm^2-min); ▲ three-layer SPOP/PAN MEA (methanol crossover flux = 0.97 x 10^{-6} mol/cm^2-min).

Polybenzimidazole (PBI) was shown to form acid-base complexes with many sulfonated polymers. Keres and coworkers performed the most extensive studies of various polymeric acid-base complexes and presented examples of their possible application as proton-exchange membranes in a fuel cell (9). Although PBI is claimed to significantly reduce swelling of the acidic polymer component of a blended membrane, its crosslinking advantage is achieved at the expense of a significant reduction in the number of protonic carriers. In fact, those sulfonic acid groups that participate in protonation of imidazole units can no longer contribute to proton conduction. Additionally, the acid-base complexes are reported to start decomposing at temperatures close to 100°C. Nonetheless, blending of sulfonated polymer with PBI may be regarded as a very convenient method of crosslinking and stabilizing the swelling properties of SPOP. Because the studies on SPOP/PBI blend were initiated at Tulane to be further continued at Case Western Reserve University, only brief description of the preliminary results will be given here.

A series of membranes composed of PBI and SPOP (of IEC in the range 1.4 – 3.5) was prepared. The effective IEC of the blended membrane was targeted at 1.0-1.2 mmol/g. Perfect miscibility with no macroscopic phase separations was achieved in all cases. With increasing PBI content, swelling of the blended membrane decreased but its conductivity decreased also as a result of the both reduced water content and a reduction in the number of available protons. Several MEAs were prepared and tested in a direct liquid methanol fuel cell. It was initially observed that fuel cell performance was slowly degrading to approximately half of the initial power density after ca. 7 hours. Further investigation revealed that the primary reason for this behavior was steady decrease in membrane swelling, due to continuing complexation of the PBI an SPOP. Drying the swollen membrane at 60°C for 8-10 hours helped to stabilize its performance in a DMFC. For example, a blend of 90% SPOP (IEC=1.8 mmol/g) and 10% PBI with an initial room temperature swelling of 107% and a conductivity of 0.06 S/cm (in water at 25°C) showed a reduction of swelling to 58% and a conductivity (to 0.03 S/cm) after thermal treatment. An MEA prepared from the membrane gave a very good I-V curve with only a small time-drift in power output and a MeOH crossover ca. 5 times smaller than that of Nafion 117.

CONCLUSIONS

Ion-exchange membranes were prepared by blending sulfonated poly[bis(3-methylphenoxy)]phosphazene (SPOP) with either Kynar® FLEX, PAN or PBI. It was found that, in general, Kynar FLEX and PAN were immiscible on a molecular level with the SPOP. The polymers had, however, an acceptable degree of compatibility and no sign of macroscopic phase separation were observed for a relatively wide composition range. A linear correlation was observed between the conductivity and swelling of the blended membranes. A conductivity increase from 0.01 to 0.08 S/cm (water swollen films at 25°C) was accompanied by an increase in swelling from 20 to 90%. Additionally, membranes with the same swelling but prepared from SPOP with a higher IEC exhibited higher conductivity. No significant difference in the swelling vs. conductivity dependence was observed between membranes prepared with use of FLEX, PAN or PBI component.

Direct liquid methanol fuel cell tests were performed with MEAs fabricated with polyphosphazene-based proton-exchange membranes. MEAs worked best when a high ion-exchange capacity (high conductivity) polyphosphazene membrane contacted the electrodes, in which case the fuel cell power output was nearly the same as that with Nafion 117 (for current densities 0.15 A/cm ^{2}), with a methanol crossover that was three-times lower than Nafion 117. With a three-membrane composite MEA (a methanol-blocking film sandwiched between two high conductivity membranes), there was a significant decrease in crossover (ten-times lower than Nafion 117) with a modest decrease in current-voltage behavior. Long-term tests revealed that there was a slow decrease of the performance due to insufficient crosslinking of SPOP. MEAs made with heat-treated SPOP/PBI membranes showed good electrochemical performance and stability in DMFC with low methanol crossover.

FUTURE WORK
1. Investigation of new polyorganophosphazene for improved crosslinking
2. Further studies with acid-base blends (SPOP/PBI)
3. Multilayered membranes with a center methanol blocking layer

LITERATURE

1. R.Wycisk and P.N.Pintauro: Polyphosphazenes, in: Encyclopedia of Polymer Science and Technology, Wiley and Sons, 2003, in print.

2. Q.Guo, P.N.Pintauro, H.Tang and S.O'Connor, *J.Membrane Sci.* **154** (1999) 175.

3. H.Tang and P.N.Pintauro, *J.Appl.Polym.Sci*. **79** (2001) 49.

4. R.Carter, R.Evilia and P.N.Pintauro, *J.Phys.Chem. B,* **105** (2001) 2351.

5. M.Wilson, J.Valerio and S.Gottesfeld, *Electrochim.Acta*, **40** (1995) 355.

6. R.Wycisk, P.N.Pintauro, W.Wang and S.O'Connor, *J.Appl.Polym.Sci.* **59** (1996) 1607.

7. R.Graves and P.N.Pintauro, *J.Appl.Polym.Sci*. **68** (1998) 827.

8. R.Carter, R.Wycisk, H.Yoo and P.N.Pintauro, *Electrochem.Solid-State Lett*. **5** (2002) A195.

9. J.Keres,W.Zhang, L.Jorissen and V.Gogel, *J.New Mat.Electrochem.Syst*. **5** (2002) 97.

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13. ABSTRACT (Maximum 200 words)

Proton-exchange membranes for direct methanol fuel cells were prepared from sulfonated poly[bis(3-methylphenoxy)phosphazene], which was blended with either Kynar® Flex, polyacrylonitrile, or polybenzimidazole. In some cases the blended films were UV-crosslinked. The proton conductivity of the membranes was sufficiently high for fuel cell applications. The water swelling of the membranes was generally greater than that of Nafion 117, but the methanol crossover was lower than that of Nafion 117. Direct liquid methanol fuel cell tests were performed with MEAs fabricated with UV-crosslinked membranes containing sulfonated poly[bis(3-methylphenoxy)phosphazene] and polyacrylonitrile (crosslinking was carried out using benzophenone as the photo-initiator). MEAs worked best when a high ion-exchange capacity (high conductivity) polyphosphazene membrane contacted the electrodes, in which case the fuel cell power output was nearly the same as that with Nafion 117 (for current densities 0.15 A/cm^2), but the methanol crossover was 3-4-times lower than Nafion. With a three-membrane composite MEA (a lower conductivity methanol-blocking film sandwiched between two high conductivity membranes), there was a significant decrease in crossover (almost ten-times lower than Nafion 117) with a modest decrease in the fuel cell's current-voltage behavior.

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