

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE May 15, 2000	3. REPORT TYPE AND DATES COVERED Final	
4. TITLE AND SUBTITLE PTFE/Polyphosphazene Composite Fuel Cell Membranes		5. FUNDING NUMBERS DAAG55-98-1-0377		
6. AUTHOR(S) Peter N. Pintauro		7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Tulane University, Office of Research, 327 Gibson Hall, New Orleans, LA 70118		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		8. PERFORMING ORGANIZATION REPORT NUMBER		
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.		10. SPONSORING / MONITORING AGENCY REPORT NUMBER <i>ARO 38973.2CH</i>		
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Polyphosphazene-based cation-exchange membranes were fabricated and evaluated for possible use in proton exchange membrane (PEM), direct liquid methanol fuel cells. Two types of membranes were prepared: (1) A composite PTFE/sulfonated-polyphosphazene membrane and (2) homogeneous membranes composed of either a single sulfonated phosphazene polymer or blends of a sulfonated polyphosphazene and a non-sulfonated polymer. The phosphazene polymer used for all membranes was poly[bis(3-methylphenoxy)phosphazene], which was sulfonated with SO ₃ . To control water/methanol swelling and methanol crossover, the polymer was either chemically crosslinked (using UV light and a photo-initiator or electron beam radiation) or blended with a hydrophobic polymer. Methanol crossover was high in membrane-electrode-assemblies with PTFE/polyphosphazene composite membranes (that were fabricated at W. L. Gore and Associates, Inc.) due to pore impregnation of the polyphosphazene in the PTFE matrix. Homogeneous crosslinked and blended membranes with sulfonated polyphosphazene exhibited an acceptably				
14. SUBJECT TERMS Polyphosphazene membranes, direct liquid methanol fuel cells, proton-exchange membrane, proton conductivity, methanol crossover		15. NUMBER OF PAGES 9		16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Army Research Office Final Report

for

PTFE/POLYPHOSPHAZENE COMPOSITE FUEL CELL MEMBRANES

Grant No. DAAG55-98-1-0377

**Peter N. Pintauro, Principal Investigator
Department of Chemical Engineering
Tulane University
New Orleans, LA 70118
VOICE: (504) 865-5872
FAX: (504) 865-6744
e-mail: peter.pintauro@tulane.edu**

20000628 174

Statement of the Problem Studied

The objective of this project was to fabricate and evaluate polyphosphazene-based cation-exchange membranes for possible use in proton exchange membrane (PEM), direct liquid methanol fuel cells. Two types of membranes were prepared and tested: (1) a composite PTFE/sulfonated-polyphosphazene membrane and (2) homogeneous membranes composed of either a single sulfonated phosphazene polymer or blends of a sulfonated polyphosphazene and a non-sulfonated polymer. The phosphazene polymer used for all membranes was poly[bis(3-methylphenoxy)phosphazene], which was sulfonated to varying extents using SO_3 . To control water/methanol swelling and methanol crossover, the polymer was either chemically crosslinked (using UV light and a photo-initiator or electron beam radiation) or blended with a hydrophobic polymer. PTFE/polyphosphazene composite membranes were fabricated at W. L. Gore and Associates, Inc. and tested at Los Alamos National Laboratory. All other work was performed at Tulane University.

Summary of Important Results

1. PTFE/Polyphosphazene Composite Membranes

Poly[bis(3-methylphenoxy)phosphazene], purchased from technically, Inc., Woburn, MA, was dissolved in dichloroethane and sulfonated in solution with SO_3 . A membrane casting solution was prepared using sulfonated poly[bis(3-methylphenoxy)phosphazene] polymer (1.1 mmol/g ion-exchange capacity) in dimethylacetamide solvent (approximately 30 ml of a 3 wt% solution) with 15 wt% benzophenone photo-initiator (for UV crosslinking). The solution was sent to W. L. Gore & Associates for impregnation into microporous PTFE. Composite membranes were then returned to Tulane and some films were exposed to UV light to photo-crosslink the phosphazene polymer. Crosslinked and non-crosslinked membranes were sent to Los Alamos National Laboratory for construction of membrane-electrode-assemblies (MEAs) and direct methanol fuel cell testing. The preliminary results were not encouraging; the IR drop across the MEAs was high and the methanol crossover rate was essentially the same as that for Nafion 117. We believe that the poor results were due to improper polyphosphazene impregnation at W. L. Gore, i.e., there were numerous pin-holes and void spaces in the composite membrane, through which methanol would pass but no current (H^+) would flow during a fuel cell test. As a consequence of these results, work at Tulane focused on fabricating and characterizing homogeneous polyphosphazene membranes. Only after showing that such membranes work well in direct methanol fuel cells would the work proceed to fabricating and testing composite membranes.

2. Measurement of Methanol Oxidation Limiting Current in Homogeneous Membranes of Sulfonated Polyphosphazene

The methanol diffusion limiting current density was measured in membrane-electrode-assemblies prepared with a sulfonated and non-crosslinked polyphosphazene-based ion-exchange

membrane. The limiting current density is proportional to the methanol diffusion coefficient and methanol solubility in the membrane and thus these experiments were used to evaluate the ability of the polyphosphazene membrane to inhibit methanol crossover. Membrane-electrode-assemblies (MEAs) were prepared by hot pressing gas diffusion electrodes to a sulfonated polyphosphazene membrane (the hot pressing conditions were very mild, with a temperature of about 50°C, to avoid damage to the membrane). One side of the MEA (cathode side) was exposed to a methanol/water solution and the anode was exposed to humidified nitrogen gas. A methanol mass transfer limiting current density at the anode was obtained from galvanostatic polarization experiments. This technique for determining methanol crossover rates has been published by the fuel cell group at Los Alamos National Laboratory [X. Ren, A. Zawodzinski, F. Uribe, H. Dai, and S. Gottesfeld, in Proton Conducting Membrane Fuel Cells I, Electrochemical Society Proceedings, Vol 95-23, pp. 284-298, (1995)]. In preliminary experiments at Tulane, the methanol limiting current density in MEAs with a Nafion 117 membrane was measured as a function of temperature (40-70°C) and was found to be within 20% of data in the literature.

Next, an MEA was tested with a non-crosslinked, sulfonated poly[bis(3-methylphenoxy)phosphazene] membrane. The ion-exchange capacity (IEC) of the membrane was 1.05 mmol/g, its dry thickness was 130 µm, its equilibrium swelling in water at 25°C was 37%, and the proton conductivity in a water-equilibrated film (as measured by AC impedance) was 0.05 S/cm at 70°C. Methanol crossover in the phosphazene polymer was qualitatively evaluated by comparing methanol limiting current densities at different temperatures and a 1.0 M methanol feed solution with limiting currents with a Nafion 117 membrane. For temperatures between 40°C and 70°C, the limiting current density for methanol in the sulfonated polyphosphazene film ranged from 4.5 mA/cm² to 10 mA/cm² and was more than one-order of magnitude lower than that for Nafion 117 (see the polarization plots in Figure 1 and the values of the limiting current density in Table 1). These results are consistent with prior water diffusion coefficient measurements in sulfonated polyphosphazene membranes, which were also much lower than those in Nafion 117.

Table 1
Experimentally Measured Methanol Oxidation Limiting Current Densities
in Fuel Cell Membrane-Electrode Assemblies
with Nafion 117 and Non-Crosslinked Polyphosphazene Membranes
(with a 1.0 M methanol)

Temperature (°C)	Methanol Limiting Current Density (mA/cm ²)	
	Nafion 117 (180 µm thickness)	1.05 IEC Polyphosphazene (130 µm thickness)
40	60	4.5
50	80	6.0
60	97	7.9
70	119	10.0

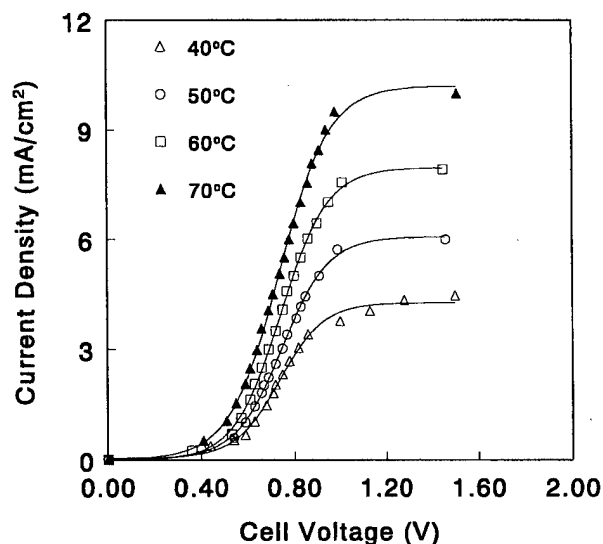


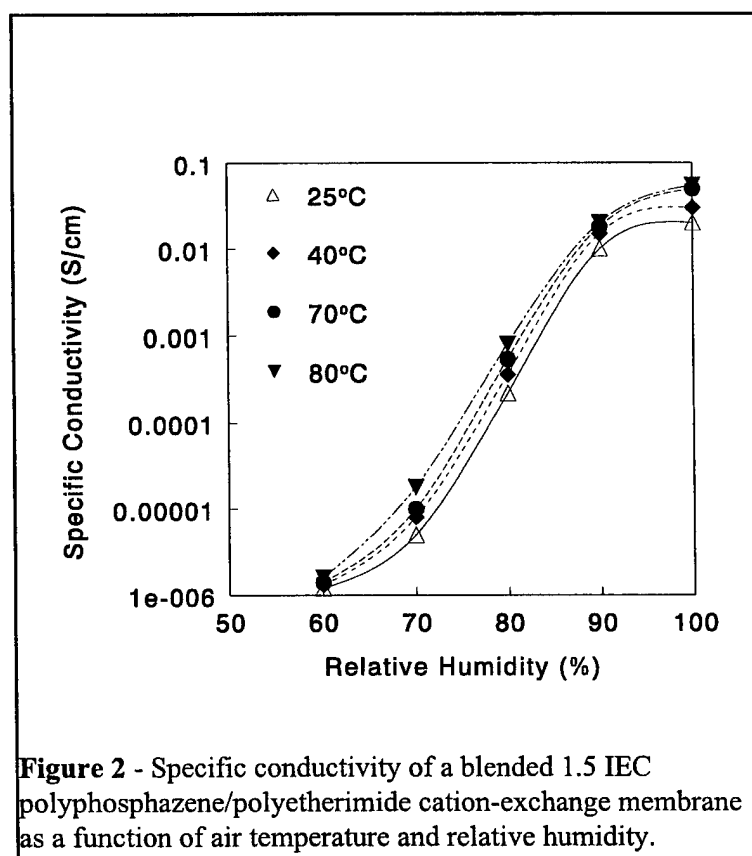
Figure 1 - Limiting current density polarization curves for methanol oxidation in a MEA containing a non-crosslinked 1.05 IEC polyphosphazene cation-exchange membrane (1.0 M methanol feed)

3. Polyphosphazene/Polyetherimide Blended Membranes

A new method of fabricating polyphosphazene cation-exchange membranes with controlled swelling has been devised, where a sulfonated bis-methylphenoxy polymer was blended with a glassy polyetherimide. This scheme is attractive because: (i) The polyetherimide is chemically inert, with excellent thermal and mechanical stability, (ii) methanol and water do not swell the polyetherimide, (iii) when blended with a sulfonated polyphosphazene, the polyetherimide provides physical crosslinks that controls membrane swelling, and (iv) the blending of an inexpensive polyetherimide material with the higher-priced polyphosphazene will lower the cost of the resulting ion-exchange membrane.

Polyphosphazene/polyetherimide blended membranes were prepared by a three-step procedure: (1) Sulfonated poly[bis(3-methylphenoxy)phosphazene] and the polyetherimide poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,2-phenylenediamine) were separately dissolved in dimethylacetamide solvent at a concentration of about 3 wt/vol%, (2) the appropriate

amounts of each polymer solution were then mixed together, and (3) the resulting solution was cast on a Teflon disk and dried at 70°C for 2 days. To date, small, 100 μm thick, blended membrane samples have been prepared from 1.5 mmol/g ion-exchange capacity phosphazene polymer (70 wt%) and polyetherimide (30 wt%). The effective ion-exchange capacity of the blended membrane was 1.05 mmol/g and its equilibrium swelling in water at 25°C was $\approx 35\%$. This swelling was significantly less than that of a non-crosslinked 1.5 mmol/g polyphosphazene membrane (100% swelling in water) and indicated that the polyetherimide was controlling water uptake. In water at 70°C, the conductivity of protons (as measured by AC impedance) in the blended membrane was good, at 0.050 S/cm. The conductivity in a blended film exposed to air at different temperatures (25°C-80°C) and different relative humidities (60-100%) is shown in Figure 2. Below 90% humidity (a water vapor activity of 0.90), there was a significant drop in the conductivity (for all temperatures).



4. Small-Angle X-Ray Scattering Studies and Proton Conductivity Measurements

Wide and small-angle X-ray diffraction experiments were carried out on crosslinked and non-crosslinked membranes composed of sulfonated poly[bis(3-methylphenoxy)phosphazene]. The results of these measurements indicated the presence of two distinct phases in sulfonated

poly[bis(3-methylphenoxy)phosphazene] membranes, an amorphous phase and a two-dimensional ordered phase. The 2-D structure changed, depending on the polymer's ion-exchange capacity and extent of water swelling, but the presence of ionic fixed-charge groups did not disrupt completely the ordered morphology. The appearance of a reflection peak in Small-Angle X-ray Scattering scans of dry and hydrated sulfonated polymers with an IEC ≥ 0.6 mmol/g was evidence of ion clustering. The apparent Bragg spacing was about 30 Å for non-hydrated (dry) polymers of varying ion-exchange capacity (IEC) and varied from 50 Å to 90 Å for hydrated membranes. For hydrated films, the cluster size increased with both IEC and the extent of water swelling and decreased with the size (weight) of the cation associated with the SO_3^- fixed-charge sites. The specific conductivity of sulfonated membranes increased with the IEC of the polymer and with the degree of polymer swelling. From the variation of conductivity with water content, the percolation threshold for sulfonated phosphazene membranes with ion-exchange capacities in the range of 0.8 - 1.6 mmol/g was about 12.5%, which is similar to that for a Nafion 117 perfluorosulfonic acid cation-exchange membrane. The proton conductivity is mainly determined by the cluster size/polymer water content. The apparent activation energies for proton conduction in a fully hydrated phosphazene membrane (1.2 mmol/g IEC) was 36.7 kJ/mol (non-crosslinked) and 27.8 kJ/mol (for the crosslinked polymer), which are considerably larger than that in a Nafion membrane, suggesting a proton-hopping, Grothuss mechanism for proton conduction.

5. A New NMR Method for Measuring Methanol Diffusion Coefficients in Sulfonated Polyphosphazene Membranes

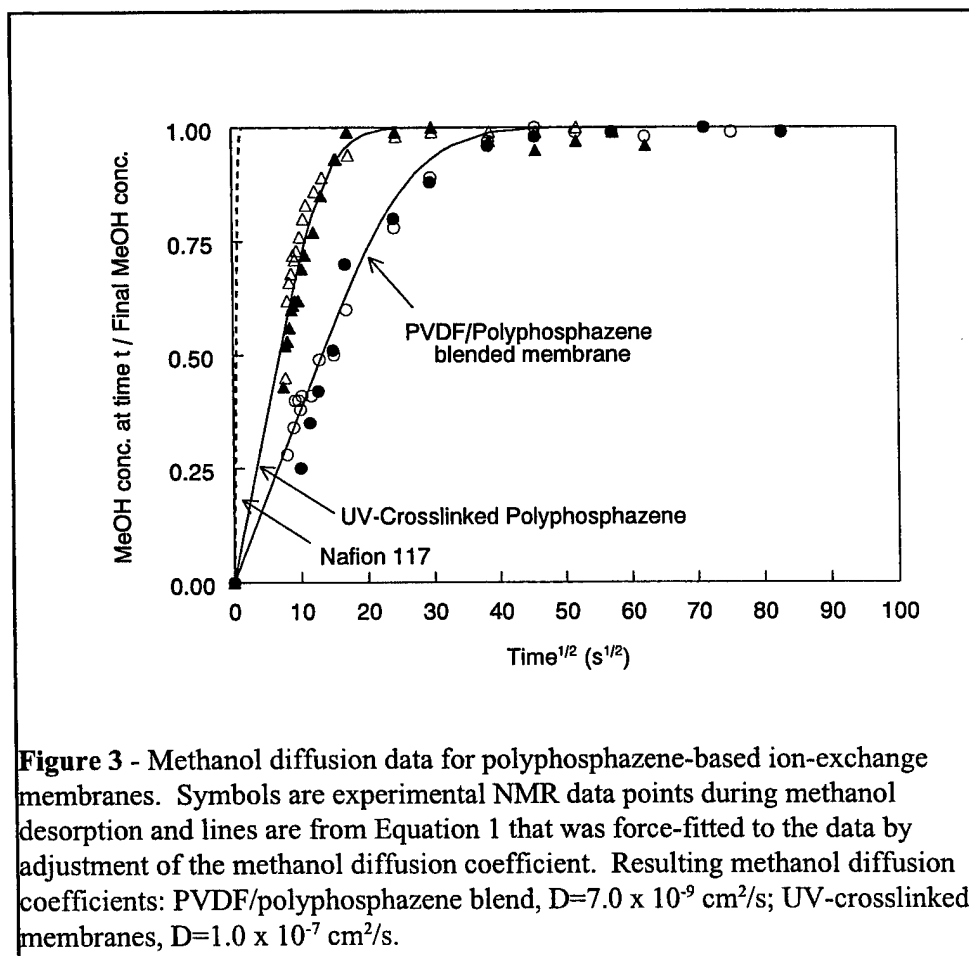
The growth of an NMR signal due to diffusion of deuterated methanol out of a thin polyphosphazene membrane has been investigated as a method for measuring methanol diffusion coefficients under conditions that are not suitable for accurate application of pulsed field gradient NMR methods. Such conditions include those where the internal solute (methanol) signal is either too small or too broad to be utilized or where the diffusion rate is too slow to yield observable attenuation of the NMR signal with commonly available gradient strengths or possible gradient application times. The method has been used to measure the diffusion coefficient of methanol in a series of sulfonated and sulfonated/crosslinked polyphosphazene membranes. The method is most useful for slow diffusion rates (diffusivities $\leq 10^{-7}$ cm²/s) and for membrane systems where the internal signal for the diffusing molecule is very weak or broad (as is the case for methanol in a sulfonated polyphosphazene film). Successful application of this approach requires that the external NMR signal be observable in a single pulse and that the membrane-phase diffusion rate of solute is much slower than that in bulk solution.

The method involves equilibrating a polyphosphazene ion-exchange membrane in a solution of deuterated methanol (CH_3OD) in D_2O , removing the membrane and wiping excess methanol from its surface, and then placing the membrane in an NMR tube filled with D_2O . Time-monitoring of the H^1 NMR spectrum of CH_3OD outside the membrane was used to quantify the process of transient desorption of methanol from the polyphosphazene membrane,

which is directly dependent on the methanol diffusion coefficient in the membrane. Separate NMR signals were observed for CH₃OD inside and outside the membrane. Typical experimental data are plotted in Figure 3 as the relative change in the external methanol concentration vs the square-root of time (where zero time denotes the start of the methanol desorption process). The data were then matched to a model for methanol diffusion/desorption, using the membrane-phase methanol diffusion coefficient as an adjustable parameter. The analytical solution to the diffusion model is [J. Crank, *The Mathematics of Diffusion*, Oxford, London, 1956]:

$$\frac{C_t}{C_\infty} = 2 \left(\frac{Dt}{l^2} \right)^{n_H} \left(\pi^{-n_H} + 2 \sum_{\zeta} (-1)^\zeta \text{ierfc} \left[\frac{n l}{(Dt)^{n_H}} \right] \right) \quad (1)$$

where C_t is the measured methanol concentration at any time t after desorption has begun, C_∞ is the final methanol concentration at the end of the desorption process, l is the membrane thickness, and d is the methanol diffusion coefficient in the membrane. The solid curves in Figure 3 are the fit of Equation 1 to the experimental desorption data with best fit values of D .



Also shown in Figure 3 is the hypothetical methanol diffusion/desorption curve (Equation 1) for a Nafion 117 membrane, where the diffusion coefficient was set equal to $6.5 \times 10^{-6} \text{ cm}^2/\text{s}$ (this diffusivity was reported in the literature by the Los Alamos group). This curve was included in Figure 3 to accentuate the difference in methanol diffusion rates for Nafion and the polyphosphazene membranes. In general, we found that methanol diffusion in sulfonated polyphosphazene membranes was always slower than that in Nafion 117, by as much as a factor of 100.

6. Blended Membranes Composed of PVDF and Sulfonated Polyphosphazene

A new type of blended polyphosphazene-based cation-exchange membrane has been fabricated from a mixture of PVDF and sulfonated poly[bis(3-methylphenoxy)phosphazene]. Membranes were made with either 1.4 mmol/g or 1.8 mmol/g IEC polyphosphazene and between 50 and 80 wt% Kynar[®] polyvinylidene fluoride (PVDF) with an average molecular weight of 572,000. The resulting membranes were tested for equilibrium water swelling, proton conductivity in water-equilibrated membranes, and methanol diffusivity (measured using the NMR technique described above in Item #5). For a 50/50 PVDF/polyphosphazene blend (starting with a 1.4 IEC polyphosphazene), the membrane swelling in water was very low (approximately 10%), as was the proton conductivity ($1.0 \times 10^{-4} \text{ S/cm}$ at 25°C) and the methanol diffusion coefficient ($7.0 \times 10^{-9} \text{ cm}^2/\text{s}$ for 2.0 M methanol at 25°C). When the membrane contained a higher percentage of phosphazene polymer (80% polyphosphazene with 20% PVDF) with a higher ion-exchange capacity of the polyphosphazene component (1.8 mmol/g), there was more water swelling of the film (approximately 25%) and the proton conductivity was acceptable for fuel cell applications (0.02 S/cm at 25°C). Further testing of this membrane is being carried out, including the measurement of methanol diffusion coefficients.

7. Radiation-Crosslinked Membranes Composed of Sulfonated Polyphosphazene

As an alternative to UV-light crosslinking, sulfonated polyphosphazene membranes (1.4 mmol/g ion-exchange capacity) were crosslinked in dry-film form using electron beam radiation (membranes were irradiated at Science Research Laboratory, Inc., Somerville, MA). Membranes were irradiated at 5 MeV with a dosage rate of approximately 1 megarad/min to a total dosage of between 5 and 80 megarads. Water swelling, proton conductivity, and methanol diffusivity data for four different e-beam-crosslinked membranes are listed in Table 2. Methanol diffusion coefficients were measured using the NMR method described in Item #5, above. The membranes have attractive properties of a reasonably high proton conductivity (which is essentially independent of membrane water content for water swelling in the range of 28-46%) and a low methanol diffusivity (which does decrease with decreasing membrane swelling). The results are similar to those found using benzophenone and UV light for polymer crosslinking.

Table 2
Proton Conductivity and Methanol Diffusivity Data for Electron-Beam-Crosslinked Polyphosphazene Ion-Exchange Membranes (1.4 mmol/g IEC)

	Water Swelling (% of dry membrane weight)	Proton Conductivity (at 80°C, membranes in H ⁺ form, equilibrated in water)	Methanol Diffusion Coefficient (at 25°C and 2.0 M methanol)
10 MR ¹ film	46%	0.037 S/cm	2.4 x 10 ⁻⁷ cm ² /s
20 MR film	37%	0.041 S/cm	2.0 x 10 ⁻⁷ cm ² /s
40 MR film	32%	0.040 S/cm	1.2 x 10 ⁻⁷ cm ² /s
60 MR film	28%	0.038 S/cm	1.2 x 10 ⁻⁷ cm ² /s

1 - MR denotes megarad dosage of radiation.

Publications

H. Tang and P. N. Pintauro, "Polyphosphazene Membranes. IV. Polymer Morphology and Proton Conductivity in Sulfonated Poly[bis(3-methylphenoxy)phosphazene]," *Journal of Applied Polymer Science* (accepted).

R. Carter, R. Evilia, and P. N. Pintauro, "Tracer-Desorption H¹-NMR Measurement of Diffusion Coefficients in Membranes: A Compliment to Pulsed Field Gradient Methods" (in preparation).

H. Tang and P. N. Pintauro, "Water Structure and Water/Polymer Interactions in Sulfonated Polyphosphazene Ion-Exchange Membranes," (in preparation).

Scientific Personnel

Scientific Personnel Supported by this project are:

Dr. Hao Tang, Post-doctoral scholar (presently employed at Plug Power, Inc.,)

Mr. Roy Carter, Ph.D. graduate student (anticipated graduation date: September, 2001)

Report of Inventions

U.S. Patent: Peter N. Pintauro and Hao Tang, "Sulfonated Polyphosphazenes for Proton-Exchange Membrane Fuel Cells," (filed April 30, 1999).