

Sulfonated PEEK Ion Exchange Membranes for Direct Methanol Fuel Cell Applications

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Abstract: Sulfonation of polyetheretherketones (PEEK) was carried out in order to fabricate commercial perfluorosulfonic acid membrane alternatives, which were characterized in terms of their ion exchange capacity, ionic conductivity, water swelling, methanol crossover and electrochemical performance in their direct application as a methanol fuel cell. A high ion exchange capacity, 1.88, was achieved with a sulfonation reaction time of 8 h, with a significantly low methanol crossover low compared to that of Nafion. However, the morphological stability was found to deteriorate for membranes with sulfonation reaction times exceeding 8 h. Electrochemical cell tests suggested that the fabrication parameters of the membrane electrode assembly based on the sulfonated PEEK membranes should be optimized with respect to the physicochemical properties of the newly prepared membranes.

Keywords: direct methanol fuel cell, sulfonated PEEK, methanol crossover, membrane, fuel cell.

Introduction

Direct methanol fuel cells fueled with aqueous methanol and air has been favored unanimously and has been developed extensively by many electronic companies and the secondary battery manufacturers due to their many potential benefits over the secondary battery like long operating time per a cartridge and hot swapping capability although several disadvantages such as low kinetic response time, high cost as a result of high precious metal catalyst loading, and methanol crossover in high methanol concentration are still to be solved.

There are a number of applications where the direct methanol fuel cell can provide real benefit based on its high energy density (pure methanol's energy density is 4,758 Wh/L, note that Li ion battery has around 471 Wh/L energy density) and instantaneous refueling time with the simple exchange of the fuel cartridge.¹

As potential applications, the next generation of high bandwidth mobile devices, battery charger and military applications are good introductory markets for DMFC since these applications require the supply of higher power density than existing batteries can provide.

Perfluorosulfonic acid membranes such as Nafion of

Dupont have been a standard membrane in fuel cell area as well as chloro-alkali industry. Its fuel cell performance, ionic conductivity, longevity, physical and chemical properties became a unanimous benchmark to the membrane developers. However, its successful adoption in proton exchange membrane fuel cell was hesitated in direct methanol fuel cell application because of the methanol crossover, which is the problem that anode fuel, the mixture of methanol and water, diffuses through the ion exchange membrane and reacts with the cathode catalysts as shown below in eq. (1) under the electrochemical operating condition so that overall fuel efficiency reduces significantly.



Now there are numerous research activities in fuel cell arena developing novel membranes satisfying the operating condition of the direct methanol fuel cell at low expense. Especially hydrocarbon based ionic polymers with high thermal and electrochemical stabilities are expected to have potential for lowering the methanol crossover and material cost and providing different characteristics for the proton exchange membrane (PEM) and direct methanol (DM) fuel cells.

Driving forces for methanol crossover are the methanol concentration gradient through the membrane involving the higher fuel concentration the larger crossover and the elec-

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tro-osmotic drag related to the proton transport from anode to cathode which becomes substantial at high current densities. Based on the operating conditions of direct methanol fuel cell systems, the following requirements for the membranes should be met;

- High ionic conductivity (equivalent to or over that of Nafion, 0.1 S/cm) with significantly lowered methanol crossover
- Dimensional stability in the methanol concentration of 0.5 M to neat methanol
- Easy hydration after storing periods
- Stability in temperature range from sub-zero to 80 °C (for laptop or mobile handset applications lower temperature is preferred)

Post-sulfonation of engineering plastics such as poly(arylene ether) is the easy and fast approaches adopted by many developers since they have been known to be chemically and mechanically stable among many commercially available polymers.

Poly(arylether ketones) is an engineering plastic having phenyl ring between ether and carbonyl linkages. It is a thermoplastic with extraordinary mechanical properties and is highly resistant to thermal degradation.

Sulfonated poly(arylether ketone) membranes of various types were developed by the industries.^{2,3} It has been known that sulfonation reaction is preferentially taking place in aromatic ring of -O-phenyl-O- unit since electron density is relatively high in this site.⁴ But with long reaction time and high temperature condition sulfonation reaction in electron withdrawing phenyl site of -O-phenyl-CO- group can be achieved although excessive sulfonation results in the loss of dimensional integrity of the membranes in the direct methanol fuel cell application. Thus sulfonation degree should be carefully controlled to meet all the requirements mentioned above.

There are many promising results in the viewpoint of the commercialization, especially Soczka-Guth *et al.*⁵ demonstrated a sulfonated PEEK with ion exchange capacity in the range of 1.35 to 1.94 mmol (-SO₃H/g polymer) and with the durability of at least 1,000 h in the proton exchange membrane fuel cell. There are two ways of sulfonation of polyetheretherketones (PEEK). One is to add the sulfonic acid group directly to the backbone of the polymer as mentioned above, the other is to polymerize the sulfonated monomers.^{5,6} Previous studies revealed the sulfonated PEEK's physiochemical properties such as controllable proton conductivity, water uptake behavior according to the sulfonation degree,⁷ lower methanol permeability than its perfluorosulfonic acid competitor,^{5,8} and the fuel cell performances of the proton exchange membrane fuel cell (PEMFC),^{12,13} direct methanol fuel cell (DMFC).^{14,15}

After the sulfonation of PEEK, blends with poly(vinylidene fluoride) (PVDF)⁹ and polysulfone¹⁰ as well as the composite¹¹ were also studied to enhance the chemical stability and to

reduce the methanol crossover further.

In addition to PEEK, many other aromatic polymers like polyether sulfone,^{16,17} polysulfone,^{18,19} polyether imide,²⁰ polyimide²¹⁻²³ were sulfonated and evaluated for the purpose of fuel cell applications.

In this experiment we intend to check the feasibility of sulfonated PEEK in the direct methanol fuel cell applications. Sulfonation of PEEK is carried out and the membranes fabricated from sulfonated polyetheretherketones (S-PEEK) were characterized in terms of equivalent weight, ion conductivity, methanol crossover and I-V performance.

Experimental

Materials. Victrex PEEK (450PF) was obtained from the Victrex US Inc in the form of powder with a molecular weight M_w 39,200 and density 1.26-1.32 g/cm³.

Concentrated sulfonic acid of 96 wt% was provided by Fisher Scientific. *N,N*-Dimethylformamide (DMF) and dimethylacetamide (DMAc) were purchased from Aldrich Chemical Company. Catalysts of 50/50 PtRu black from Johnson Matthey and 40% Pt/C from Tanaka were used for the membrane electrode assemblies (MEA) fabrication.

Carbon paper was acquired from SGL Carbon.

Sulfonation and Membrane Preparation. 15 g of dried PEEK is introduced into 156 mL of concentrated sulfuric acid at 50 °C with vigorous stirring. Reaction is taking place in nitrogen environment. Sulfonation degree is controlled by the reaction time. When the certain sulfonation time is reached, the solution is cooled down to the room temperature and then is poured into the DI ice water to recover the sulfonated PEEK. Sulfonated PEEK was washed repeatedly in DI water to remove the unreacted sulfuric acid and low molecular weight polymers which are detrimental during the fuel cell operation. The recovered polymer was dried in the oven for several days and stored in desiccators before the membrane fabrication and further characterization.

The dried SPEEK was dissolved in DMF and the membranes were prepared by solution casting on the glass substrates. Thickness was $\approx 75 \mu\text{m}$.

Equivalent Weight Measurement. Equivalent weight was determined according to a base titration procedure. The samples dried and kept in desiccator were weighed and placed into 2 M HCl solution in order to convert into acid (H⁺) form. The samples were rinsed with DI water several times. After removing excess HCl, the 2 M NaCl was added and let stand for 30 min to liberate H⁺ ions. With gentle swirling, the solution was titrated with 0.25 N NaOH to the phenolphthalein endpoint.

Equivalent weight (EW) of sulfonated PEEK was determined using following formula;

$$\text{EW}(\text{Na}^+, \text{g/mol}) = \frac{\text{Dry weight (g)}}{V_{\text{NaOH}} (\text{L}) \times [\text{NaOH}] (\text{M})}$$

EW in the acid form was determined as follows;

$$\text{EW (H}_3\text{O}^+, \text{ g/mol}) = \text{EW (Na}^+, \text{ g/mol}) - 4 \text{ g/mol}$$

EW values in the experiment were calculated in the H₃O⁺ acid form.

Ion exchange capacity was calculated by;

$$\text{IEC (meq/g)} = \frac{1000}{\text{EW (H}_3\text{O}^+ \text{ form)}}$$

Measurement of weight percent water was determined from the difference in weights between the dried and wet membranes using the following formula;

$$\text{Weight percent water} = \left(\frac{\text{wet weight}}{\text{dry weight}} - 1 \right) \times 100\%$$

Methanol Crossover and Ionic Conductivity. Methanol permeability was measured by the diffusion cell at 22 °C and the methanol concentration was detected by refractive index meter.

Proton conductivities of sulfonated PEEK membranes were measured by AC impedance spectroscopy using a Solatron over a frequency range of 1-10 MHz. Rectangular shaped membrane samples were fully hydrated and placed in four probe conductivity cell.

It is well known that the ionic conductivity strongly depends on the saturation level in the membrane and the temperature. Thus, the measuring cell was kept in a bath at room temperature. The conductivity was calculated from the membrane resistivity according to $\sigma = \kappa * L/A$, where κ is the resistivity, L is the membrane thickness in cm and A is the surface of the membrane in cm².

MEA Fabrication. Membrane electrode assemblies (MEA) used to evaluate the electrochemical performances of the sulfonated PEEK membranes were fabricated as follows. The electrodes consist of the uncatalyzed carbon papers, in other words, gas diffusion layers and catalyst layers coated directly on the membranes. Gas diffusion layers were hydrophobitized by soaking in liquid PTFE solution before the coating of carbon layer. 50% Pt/50% Ru black catalyst was used for the anode catalyst layer, 40 wt% Pt/C for the cathode catalyst layer. Catalyst solution is comprised of the polar solvents, water, catalyst and 30 wt% Nafion solution, which acts as a binder and an electron conductor in MEA geometry. It is widely accepted that Nafion with the electrode catalyst is located on catalyst particles and bridge among the active sites of catalysts as well as between the catalysts and the membranes in the interface. All components were mixed and sonicated thoroughly to be ensuring of the complete dispersion of nanosized catalyst particles. Spraying method was used to deposit the coating layer on the carbon paper. The five layer MEA was obtained by hot pressing gas diffusion layers on both sides of membrane at 120 °C. The amounts of catalyst deposited were 4 mg/cm²

for the anode and 4 mg/cm² for the cathode.

Prepared MEA was installed in the transparent acrylic single cell test fixture shown in Figure 1 in order to characterize the electrochemical I-V performance.

Results and Discussion

During the DMFC reaction in the anode 1 mol of methanol is consumed to produce 6 moles of proton and one mole of carbon dioxide. The gas effluent of carbon dioxide was observed through the transparent single cell fixture as shown in Figure 1. It is shown that the carbon dioxide bubble is still trapped in the channel of the right hand side of the single cell.

Equivalent weights or ion exchange capacities of various sulfonated PEEKs obtained from the different sulfonation time were measured by titration methods and the results are shown in Table I. According to the increase of reaction time, IEC was increased from 1.22 of 3 h reaction time to 1.88 of 8 h reaction time. Sulfonation reaction time was a convenient parameter to control the sulfonation degree. In comparison with 0.96 of Nafion 115, ion exchange capacity was doubled after 8 h of reaction time. It was proven that

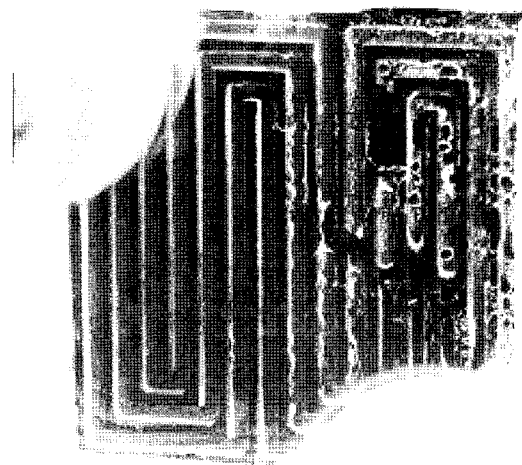


Figure 1. A transparent acrylic single cell test fixture, cathode side view.

Table I. Equivalent Weights According to the Time of Sulfonation Reaction

Reaction Time	Sulfonated PEEK				Nafion 115
	3 h	5 h	7 h	8 h	
EW (H ⁺), g/mol	820	752	608	530	1042
IEC, meq/g	1.22	1.33	1.64	1.88	0.96
Weight Percent Water (%)	30.4	36.9	37.1	41.3	16.5

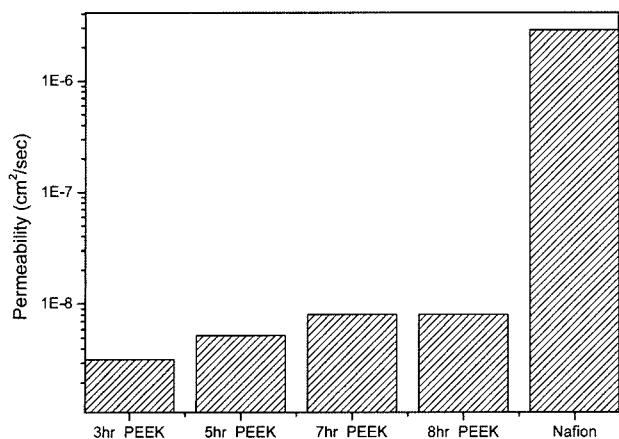


Figure 2. Methanol crossover behavior of sulfonated PEEKs for 10 M methanol solution.

the control of IEC for the bulk polymer by the post sulfonation method was straightforward and convenient. But it was also found that due to the random sulfonation reaction occurring in the reaction vessel the loss of low molecular weight portion during the recovery of the sulfonated polymer from the reaction vessel by the precipitation method was significant. Careful experimental conditions and setups are required in order to reduce the loss of raw material.

One of mechanical properties of the ion exchange polymers, water absorption behavior, was measured in Table I. According to the increase of the ion exchange capacity weight percent water was increased from 30.4 to 41.3% due to the increased swelling. Weight percent water property affects the dimensional stability of the membrane electrode assembly during the fuel cell operation.

In case of the proton exchange membrane fuel cells, the integrity of the membrane electrode assembly could be changed significantly for the high water swelling membrane when the membrane electrode assembly experiences the humidity change. For the direct methanol fuel cell operation, the water swelling behavior can affect the integrity of the membrane electrode assembly when the concentration of aqueous feed methanol solution fluctuates.

Methanol permeabilities of the sulfonated PEEK membranes and Nafion were measured and shown in Figure 2. It is clear from the experiment that methanol crossover is substantially suppressed with sulfonated PEEKs. This phenomenon is attributed to the narrower diffusion path in sulfonated PEEKs than that of Nafion,²⁴ which is typically known to be 4–5 nm. Methanol permeability increases slightly with the increase of sulfonation reaction time due to the increased amounts of hydrophilic sulfonic acid moieties. However, gaps among the methanol permeabilities of the sulfonated PEEKs are minimal compared to gap between 8 h sulfonated PEEK and Nafion, which is observed to be more than 100 times.

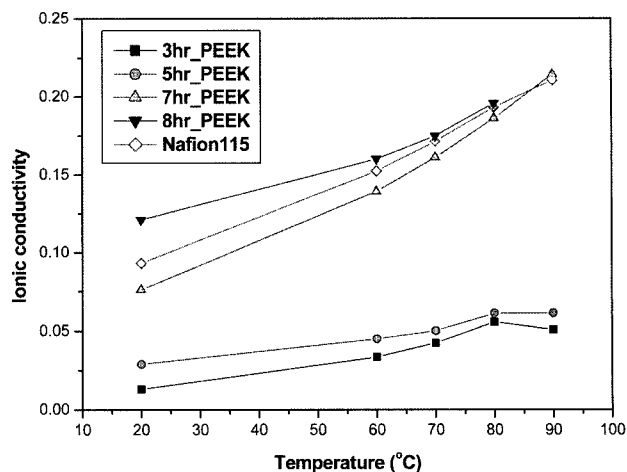


Figure 3. Ionic conductivities according to the sulfonation reaction time.

The effect of ionic conductivities of the sulfonated PEEK membranes on the temperature is shown in Figure 3. With the increase of the temperature ionic conductivities are increased for all membranes.

It is also recognized that the ionic conductivity increases with the increase of sulfonation reaction time for the sulfonated PEEK membranes. The difference in the conductivities for 8 and 7 h sulfonated membranes is getting narrow with the increase of temperature due to the facilitated ion transport in the increased temperature condition. At 20 °C ionic conductivity of 8 h sulfonated PEEK membrane is higher than that of Nafion 115 which is around 0.09 S/cm. This phenomenon is the same in the whole temperature range measured. However due to the failure in the dimensional integrity of 8 h sulfonated PEEK membrane the data was not obtained at 90 °C temperature.

In this experiment it was found that the ionic conductivity could be easily controlled to be high enough by controlling the sulfonation time, that is, the sulfonation degree. However the failure of the dimensional integrity for the highly sulfonated membranes, which are 8 and 7 h sulfonated membranes, is frequently observed during the experiments. Ideal fuel cell membranes have to possess the hydrophobic/hydrophilic balance in the structure. Hydrophobic backbone should contribute to the mechanical dimensional stability and chemical durability against water as well as methanol in the direct methanol fuel cell. On the other hand, hydrophilic parts are expected to contribute to proton and water transports. However when the hydrophilic sulfonic acid portions are excessive, certain domain in the membrane is dissolved in the water. Especially water transport through the hydrophilic pathway resulted from the electro-osmotic drag and diffusion is significant in DMFC condition and may originate the collapse of the morphological stability unless the hydrophobic backbone endures such environment.

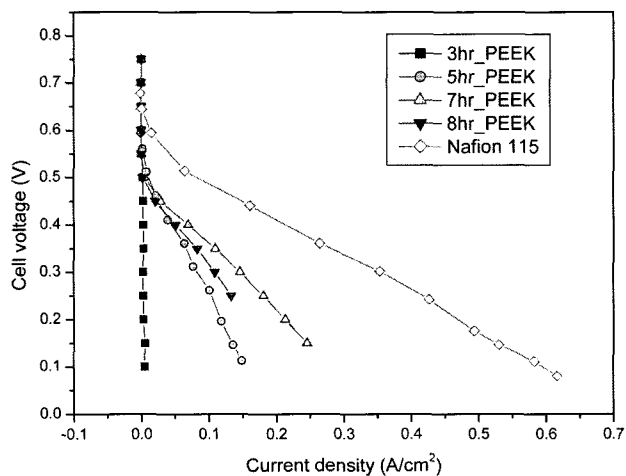


Figure 4. DMFC performance, current-voltage performance, 2 M methanol, 80°C, cathode 1 kgf pressure.

This trade-off phenomenon between high ionic conductivity and poor chemical/mechanical stabilities should be addressed in the preparation of post-sulfonated membranes.

Figure 4 shows the I-V polarization curve of 2 M methanol fed anode and air fed cathode at 80°C for the single cells adopted the sulfonated PEEK membranes and Nafion 115. Whereas open circuit voltage (OCV) of Nafion was around 0.65 V, OCVs of sulfonated PEEKs were over 0.7 V except the single cell of 5 h sulfonated PEEK, which is presumably the defect in MEA fabrication. Current densities at 0.4 and 0.5 V for Nafion 115 were around 220 and 90 mA/cm², respectively. However current densities of sulfonated PEEK membranes at 0.4 and 0.5 V are significantly lower than those of Nafion.

Also the power density plot shown in Figure 5 indicates

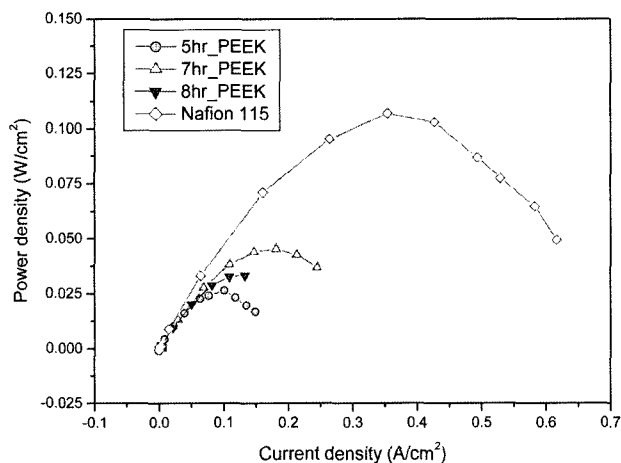


Figure 5. DMFC performance, power density at varied current density, 2 M methanol, 80°C, cathode 1 kgf pressure.

that the maximum power density of 7 h sulfonated PEEK membrane is only 44 mW/cm² compared to 110 mW/cm² of Nafion although the power density achieved was somewhat higher than those of other studies.^{14,15,17,20} These results are unusual considering the fairly low methanol crossover and relatively high ionic conductivities of 8 and 7 h sulfonated PEEK membranes. This output can be explained by mentioning fairly complicated fabrication process of the membrane electrode assembly. Catalyst coated electrodes are hot pressed onto the membrane at the temperature of 120°C for 5 min with the pressure of 0.1 ton. It is also notable that catalyst ink is composed of Nafion, platinum catalyst and polar solvent. Laminating condition was coined by considering the glass transition temperature of dry Nafion film, that is, 100-110°C and binding material, that is, Nafion.

It should be mentioned that all fabrication conditions of MEA was best optimized for the Nafion based membranes. Upon opening the single cell fixture after the fuel cell test, laminated electrodes were adhered to the membrane firmly in case of Nafion based MEA. However it was found that the MEAs based on sulfonated PEEK membranes did not maintain original laminated structure. The electrodes were separated upon opening the single cell fixture.

It suggests that the interface resistance between the electrode layer and the membrane was high. Thus it can be rationalized that the proton transport was greatly hindered in the interface between the electrode and sulfonated PEEK membranes. The future research has to be focused on the optimizing the laminating conditions and the catalyst ink formulation. It may be required that the binding material in the catalyst ink is changed to be the same material with the sulfonated PEEKs in order to enhance the affinity in the interface between the electrodes and the membrane.

In summary, it was demonstrated that sulfonated PEEK based membranes could be utilized as a proton exchange membrane in the direct methanol fuel cell application. However, it was recognized that several issues must be solved before its adoption in the real world applications. First, the sulfonation degrees of the PEEK differed from one reactor to another due to the agglomeration of PEEK powder in sulfuric acid medium. Considerable care for the reactor conditions should be paid to ensure the complete mixing of the sulfuric acid and PEEK powder. Second is the instability of the membrane throughout the MEA operation. One possible cause is low molecular weight portion of sulfonated PEEK molecules produced during the harsh mechanical mixing and long reaction time. Narrow molecular weight distribution should be guaranteed after the sulfonation, otherwise the crosslinking is one possible way to enhance the dimensional stability of the membrane.

Overall, physicochemical properties of post sulfonated PEEK membranes should be further tuned for the direct methanol fuel cell application.

Conclusions

Sulfonated PEEK membranes with ion exchange capacities in the range of 1.22 to 1.88 were fabricated for the direct methanol fuel cell application. It was found that methanol crossovers with sulfonated PEEK membranes were significantly lower than that of Nafion membrane and ionic conductivities for 7 and 8 h sulfonated PEEKs were comparable to that of Nafion although the deterioration of the membrane dimension was found during the measurement of ionic conductivity at the elevated temperature. The electrochemical performances of sulfonated PEEK membranes were not reached to that of Nafion most probably due to the poor adhesion between the electrode and the membrane. It suggests that the optimization of the fabrication condition of the membrane electrode assembly should be carried out considering the material properties of sulfonated PEEK membranes.

References

- (1) G. Y. Moon and W. H. Lee, *Korean Membrane J.*, **5**, 1 (2003).
- (2) F. Helmer-Metzmann *et al.*, US Patent 5,438,082 (1995).
- (3) T. Soczka-Guth *et al.*, US Patent 6,355,149 (2002).
- (4) R. Y. M. Huang, P. Shao, C. M. Burns, and X. Feng, *J. Appl. Polym. Sci.*, **82**, 2651 (2001).
- (5) M. Gil, X. Ji, X. Li, H. Na, J. E. Hampsey, and Y. Lu, *J. Membrane Sci.*, **234**, 75 (2004).
- (6) X. Li, Z. Wang, H. Lu, C. Zhao, H. Na, and C. Zhao, *J. Membrane Sci.*, **254**, 147 (2005).
- (7) P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang, and S. Kaliaguine, *J. Membrane Sci.*, **229**, 95 (2004).
- (8) S. Xue and G. Yin, *Eur. Polym. J.*, **42**, 776 (2006).
- (9) J. Wootthikanokkhan and N. Seeponkai, *J. Appl. Polym. Sci.*, **102**, 5941 (2006).
- (10) J. Kerres, *Fuel Cells*, **6**, 251 (2006).
- (11) R. K. Nagarale, G. S. Gohil and V. K. Shahi, *J. Membrane Sci.*, **280**, 389 (2006).
- (12) A. Basile, L. Paturzo, A. Iulianelli, I. Gatto, and E. Passalacqua, *J. Membrane Sci.*, **281**, 377(2006).
- (13) R. Jiang, H. R. Kunz, and J. M. Fenton, *J. Power Sources*, **150**, 120 (2005).
- (14) S. Vetter, B. Ruffmann, I. Buder, and S. P. Nunes, *J. Membrane Sci.*, **260**, 181 (2005).
- (15) V. S. Silva, B. Ruffmann, S. Vetter, M. Boaventura, A. M. Mendes, L. M. Madeira, and S. P. Nunes, *Electrochim. Acta*, **51**, 3699 (2006).
- (16) L. Li and Y. Wang, *J. Membrane Sci.*, **246**, 167 (2005).
- (17) V. K. Shahi, *Solid State Ionics*, **177**, 3394 (2007).
- (18) F. Lufrano, V. Baglio, P. Staiti, A. S. Arico, and V. Antonucci, *Desalination*, **199**, 283 (2006).
- (19) S. L. Chen, A. B. Bocarsly, and J. Benziger, *J. Power Sources*, **152**, 27 (2005).
- (20) Y.-Z. Fu and A. Manthiram, *J. Power Sources*, **157**, 222 (2006).
- (21) B. P. Pinto, L. C. de Santa Maria, and M. E. Sena, *Materials Lett.*, submitted (2006).
- (22) J. M. Song, K. Miyatake, H. Uchida, and M. Watanabe, *Electrochim. Acta*, **51**, 4497 (2006).
- (23) X. Ye, H. Bai, and W. S. Winston Ho, *J. Membrane Sci.*, **279**, 570 (2006).
- (24) K. D. Kreuer, "Hydrocarbon membranes," in *Handbook of Fuel Cells*, 2003, Chapter 33, Vol. 3.