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Fu, Y. -Z.; Manthiram, A.; Guiver, Michael



**Publisher's version / Version de l'éditeur:**
https://doi.org/10.1149/1.2434205
*Electrochemical and Solid-State Letters, 10, January 4, pp. B70-B73, 2007*

*Electrochemical and Solid-State Letters,* **10** (4) B70-B73 (2007)
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# Blend Membranes Based on Sulfonated Poly(ether ether ketone) and Polysulfone Bearing Benzimidazole Side Groups for DMFCs

**Y.-Z. Fu,[a,*] A. Manthiram,[a,**,z] and M. D. Guiver[b]**

[a]*Materials Science and Engineering Program, The University of Texas at Austin, Austin, Texas 78712, USA*
[b]*Institute for Chemical Process and Environmental Technology, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*

Blend membranes consisting of sulfonated poly(ether ether ketone) (SPEEK), which is an acidic polymer, and polysulfone bearing benzimidazole side groups (PSf-BIm), which is a basic polymer, have been prepared with various PSf-BIm contents (0–10 wt %). The blend membranes have been characterized by ion exchange capacity, proton conductivity, liquid uptake, methanol permeability, and polarization measurements in direct methanol fuel cell (DMFC). The membranes with an optimum PSf-BIm content of ~8 wt % exhibit electrochemical performance in DMFC better than that of plain SPEEK membrane due to an enhancement in proton conductivity through acid-base interactions and lower methanol crossover.
 [DOI: 10.1149/1.2434205] 

Manuscript submitted August 25, 2006; revised manuscript received November 14, 2006.
Available electronically January 19, 2007.

Direct methanol fuel cells (DMFCs) employing liquid methanol as a fuel are attractive to replace lithium-ion batteries in portable electronic devices as they do not require recharging with an electrical outlet. However, the high permeability of methanol fuel from the anode to the cathode (crossover) through the currently used perfluorinated sulfonic acid membrane (Nafion) and the sluggish oxidation kinetics of methanol at the cathode pose serious problems for the commercialization of the DMFC technology. Much effort has been paid in recent years to develop alternative fluorine-free membrane materials such as sulfonated poly(ether ether ketone) (SPEEK),[1-3] polybenzimidazole,[4-8] polyimide,[9-11] and polysulfone (PSf).[12-14] These materials generally exhibit lower methanol crossover and are less expensive than Nafion.[3,15] With an optimized degree of sulfonation, some of them show performance comparable to that of Nafion. However, high degrees of sulfonation to maximize the proton conductivity tend to lead to undesirable swelling of the membrane and mechanical integrity problems.

To reduce the swelling, covalently and ionically cross-linked polymer membranes have been investigated by Kerres and co-workers.[16-18] Swelling is greatly suppressed by covalent cross-linking, but the polymers usually become brittle on drying out. On the other hand, acid-base blends containing ionic cross-links show good flexibility and thermal stability, but the dimensional stability at $T > 70°C$ is inadequate with some blends like SPEEK/PBI and SPPO/PBI [PBI and SPPO refer, respectively, to poly(benzimidazole) and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)]. They also exhibit lower methanol crossover in DMFC.[17-21] Unfortunately, microphase-separation is easy to occur in such blends due to different, incompatible acidic (aromatic) and basic (PBI) polymer structures.[16]

Recently, we reported that polysulfone bearing benzimidazole side groups (PSf-BIm) could promote proton conduction in SPEEK under anhydrous conditions through acid-base interactions between the sulfonic acid groups of SPEEK and the nitrogen atoms of the benzimidazole group tethered to PSf backbone.[22] This blend membrane concept is based on industrially available, inexpensive polymer precursors that are compatible with each other due to similar aromatic backbones. In addition to SPEEK being known to exhibit lower methanol crossover compared to Nafion, the benzimidazole side groups tethered to the PSf backbone could also help to suppress methanol crossover further by inserting into the hydrophilic channels. We present here an investigation of the ion exchange capacity, proton conductivity, water uptake, electrochemical performance in DMFC, and methanol crossover as a function of the PSf-BIm content in the blend membranes, and compare the performance data with that of Nafion 112 membrane.

* Electrochemical Society Student Member.
** Electrochemical Society Active Member.
z E-mail: rmanth@mail.utexas.edu

## Experimental

The details of preparation of SPEEK and PSf-BIm are available elsewhere.[3,22] PSf-BIm was prepared by a condensation reaction between carboxylated polysulfone (CPSf) having a degree of carboxylation (DC) of 1.90 and 1,2-diaminobenzene in the presence of triphenylphosphite (TPP) in dimethylformamide (DMF) in a three-necked flask. The solution was stirred at 100°C for 3 h and then at 150°C for 10 h under nitrogen atmosphere before precipitating the product by adding methanol, followed by filtering and drying in a vacuum oven at 110°C overnight. SPEEK with an ion exchange capacity (IEC) of 1.52 meq/g and a degree of sulfonation (DS) of 51% was used in this study. The blend membranes with different PSf-BIm compositions were obtained by casting onto a glass plate a *N,N*-dimethylacetamide solution of the SPEEK and PSf-BIm polymers (~10% w/w) and drying at 95°C overnight, followed by boiling in de-ionized water for 2 h. The thicknesses of all the membranes were kept at around 50 μm. Commercial Nafion 112 membrane with a thickness of 50 μm was selected for comparison, and it was pre-treated with a 5% solution of hydrogen peroxide, deionized water, and 0.5 M sulfuric acid at around 80°C for 1 h.

The ion exchange capacity was determined by suspending ~0.3 g of SPEEK or SPEEK/PSf-BIm blend membranes in 20 mL of a saturated aqueous solution of sodium chloride for 4 days to liberate the $H^+$ ions and then titrating with 0.1 M NaOH solution using phenolphthalein as an indicator. The mole ratio of $[-SO_3H]/[BIm]$ in the SPEEK/PSf-BIm blend membranes was determined based on the weight fraction of PSf-BIm and SPEEK.

The percent liquid uptake was obtained from the weight change before and after equilibrating the dry membrane in de-ionized water or methanol solution at 65 and 80°C for 30 min. Proton conductivity values were determined from the impedance data collected with an HP 4192A LF impedance analyzer in the frequency range of 5 to 13 MHz with an applied voltage of 10 mV after equilibrating the membranes with water vapor at 100% relative humidity (RH). The error bar in proton conductivity values is ±5%.

The electrodes for testing in DMFC were prepared as reported elsewhere.[23] The anode consisted of commercial 40 wt % Pt-Ru (1:1) in Vulcan carbon (E-TEK) with a metal loading of 0.6 mg/cm$^2$ on carbon cloth with gas diffusion layer. The cathode consisted of commercial 20 wt % Pt in Vulcan carbon (Alfa Aesar) with a metal loading 1.0 mg/cm$^2$ on carbon cloth with gas diffusion layer. The electrodes prepared were impregnated with Nafion solution (5 wt %

**Table I. Comparison of the ion exchange capacity (IEC), proton conductivity (σ), and liquid uptake of the SPEEK/PSf-BIm blend membranes for various [–$SO_3H$]/[BIm] mole ratios with those of plain SPEEK membrane.**

| wt % PSf-BIm | Ratio of [–$SO_3H$]/[BIm] | IEC (meq/g) | σ × $10^3$ (S/cm) | | Methanol Concentration (M) | Liquid uptake (wt %) | |
|---|---|---|---|---|---|---|---|
| | | | 65°C | 80°C | | 65°C | 80°C |
| 0 | — | 1.52 | 1.7 | 2.1 | 0 | 11.6 | 20.6 |
| | | | | | 1 | 15.7 | 22.4 |
| | | | | | 2 | 24.5 | 28.9 |
| 5 | 7.67 | 1.35 | 1.8 | 2.4 | 0 | 10.6 | 18.3 |
| | | | | | 1 | 15.2 | 19.2 |
| | | | | | 2 | 23.0 | 26.6 |
| 8 | 4.64 | 1.23 | 2.3 | 2.8 | 0 | 8.1 | 15.5 |
| | | | | | 1 | 13.1 | 16.2 |
| | | | | | 2 | 21.8 | 24.8 |
| 10 | 3.57 | 1.13 | 1.3 | 1.6 | 0 | 7.6 | 14.4 |
| | | | | | 1 | 12.4 | 15.1 |
| | | | | | 2 | 19.8 | 22.9 |

solution, DuPont Fluoro-products) by a spray technique and dried at 90°C for 30 min; the Nafion loading for both the anode and cathode catalysts was 0.35 mg/cm$^2$.

The membrane-electrode assemblies (MEAs) were fabricated by uniaxially hot-pressing the anode and cathode onto the membrane at 140°C for 3 min. The electrochemical performances in DMFC of the MEAs were evaluated with a single-cell fixture having an active area of 5 cm$^2$ and feeding a preheated methanol solution into the anode at a flow rate of 2.5 mL/min by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of 200 mL/min with a back pressure of 20 psi. The temperatures of the preheated methanol solution and humidified oxygen were the same as that of the cell temperature (65 or 80°C).

Methanol crossover was evaluated by a voltammetric method in which methanol solution was fed at a flow rate of 2.5 mL/min into the anode side of the MEA while the cathode side was kept in an inert humidified $N_2$ atmosphere.[24] By applying a positive potential at the cathode side, the flux rate of permeating methanol was determined by measuring the steady-state limiting current density resulting from the complete electro-oxidation at the membrane/Pt catalyst interface at the cathode side.

## Results and Discussion

Table I summarizes the [–$SO_3H$]/[BIm] mole ratio, ion exchange capacity (IEC), proton conductivity (σ) at 65 and 80°C and 100% RH of the SPEEK/PSf-BIm blend membranes for various PSf-BIm contents. The IEC values of the blend membranes are lower than that of plain SPEEK, indicating the occurrence of acid-base interaction in the blend membranes, which reduces the amount of $H^+$ ions dissociating from sulfonic acid groups. As the PSf-BIm content increases, the IEC value decreases due to an increase in the degree of acid-base interaction. The conductivity of the SPEEK/PSf-BIm blend membranes increases with increasing temperature from 65 to 80°C similar to that found with the SPEEK membrane. At a given temperature, the conductivity increases as the PSf-BIm content increases from 0 to 8 wt % due to the enhancement of proton conduction in the presence of benzimidazole side groups tethered to polysulfone through acid-base interactions. However, as the PSf-BIm content increases to 10 wt %, the proton conductivity decreases significantly and is lower than that of plain SPEEK, indicating an optimum PSf-BIm content of 8 wt % maximizes the proton conductivity. This decrease in proton conductivity at higher BIm contents (or for –$SO_3H$/BIm molar ratio $<$4.5 in Table I) despite the availability of –$SO_3H$ groups still for further acid-base interactions suggests that the acid-base interaction between the sulfonic acid and the pendant benzimidazole units may be more complex than in other acid-base systems.[16-18] We believe that the morphology and the microscopic distribution of the sulfonic acid and pendant benzimidazole groups will be a critical factor in maximizing the acid-base interaction and enhancing the proton conductivity in this kind of blend membranes. Optimization of the microstructure and a uniform distribution of the sulfonic acid and pendant benzimidazole groups could increase the proton conductivity and lower the methanol crossover (see later) further.

Table I also compares the percent liquid uptake at different temperatures and methanol concentrations for various PSf-BIm contents. For a given PSf-BIm content, the liquid uptake increases as the temperature or the methanol concentration increases. At a given temperature or methanol concentration, the liquid uptake decreases with increasing PSf-BIm content. The membrane swelling, which is a critical issue for MEA stability in fuel cells, generally trends with liquid uptake. All the SPEEK/PSf-BIm blend membranes in Table I exhibit lower liquid uptake than plain SPEEK membrane, irrespective of water or methanol is being used, indicating a lower swelling and better stability. The lower hydrophilicity of PSf-BIm compared to that of SPEEK and the acid-base interactions (similar to the ionic cross-linking occuring in other acid-base systems like SPEEK/PBI) between the sulfonic acid and benzimidazole groups lead to lower liquid uptake. The lower liquid uptake could also help to lower the methanol crossover as the crossover is known to trend with the liquid uptake in the SPEEK membrane.[3]

Figure 1 compares the electrochemical performance data of the SPEEK/PSf-BIm blend membranes with those of SPEEK and Nafion 112 membranes in DMFCs at 65 and 80°C with 1 M methanol solution. The SPEEK and SPEEK/PSf-BIm blend membranes exhibit higher polarization loss than Nafion 112 membrane due to the lower proton conductivities of the former and a possible better membrane-electrode interfacial contact in the latter. The incorporation of PSf-BIm into SPEEK decreases the polarization loss initially at 5 wt % PSf-BIm and then increases it at a higher PSf-BIm content of 10 wt %. The increased polarization loss at 10 wt % PSf-BIm is due to the lower proton conductivity as seen in Table I. The blend membranes with 5 and 8 wt % PSf-BIm also show higher open circuit voltages (OCV) than plain SPEEK membrane. The better performance of the blend membrane with 8 wt % PSf-BIm could be attributed to the higher proton conductivity and lower methanol crossover, as indicated by a lower methanol crossover limiting current density compared to that for the SPEEK membrane in Fig. 2. Although the thickness of the SPEEK/PSf-BIm blend membranes is the same as that of SPEEK, the methanol crossover at 8 and 10 wt % PSf-BIm is only 70% of that found with plain SPEEK, indicating the effectiveness of the benzimidazole groups in suppressing the methanol permeability. Furthermore, the SPEEK/PSf-BIm blend membranes exhibit a much reduced methanol crossover than Nafion 112 membrane, offering better long-term performance

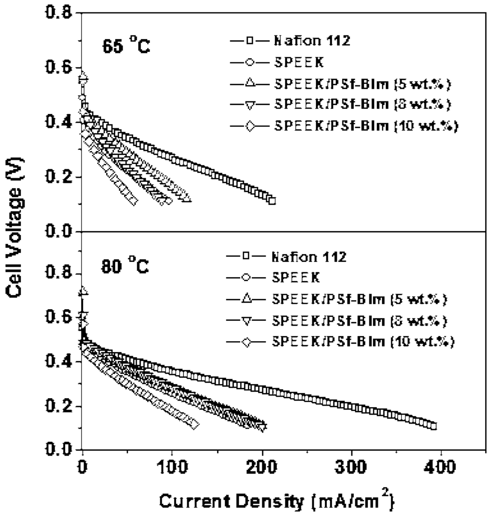


**Figure 1.** Comparison of the polarization curves of the SPEEK/PSf-BIm blend membranes with those of SPEEK and Nafion 112 membranes in DMFC. Anode: 0.6 mg $PtRu/cm^2$, cathode: 1.0 mg $Pt/cm^2$, and methanol concentration: 1 M.

in the fuel cell. The methanol crossover current for Nafion 112 is not shown in Fig. 2 as its high value exceeds the limit of our equipment.

Figure 3 compares the electrochemical performance data of the SPEEK/PSf-BIm blend membranes with those of SPEEK and Nafion 112 at a higher methanol concentration of 2 M. All the membranes in Fig. 3 show better performances than those found with 1 M methanol solution in Fig. 1 due to higher methanol flux. However, the blend membranes, for example, with 8 wt % PSf-BIm exhibit better performance than the SPEEK as with 1 M methanol in Fig. 1 due to lower methanol crossover as seen in Fig. 4. In Fig. 4, the plots of methanol crossover currents of Nafion 112, SPEEK and SPEEK/PSf-BIm with 5 wt % PSf-BIm at 80°C are not shown because they exceeded the current limit of our equipment.

The electrochemical data indicates that the SPEEK/PSf-BIm blend membranes with an optimum PSf-BIm content exhibits better performance than SPEEK due to lower methanol crossover and higher proton conductivity. The lower methanol crossover could be attributed to the narrower pathways for methanol/water permeation in the former. It has been found that the separation between the hydrophobic and hydrophilic groups in SPEEK is already smaller compared to that in Nafion, resulting in a stronger confinement of water/methanol in the narrow channels and significantly lower water/methanol permeation.[2,25,26] PSf-BIm with an aromatic backbone similar to that in SPEEK can be expected to have good compatibility with SPEEK at the molecular scale, and the insertion of the benzimidazole side groups into the hydrophilic groups of SPEEK can reduce methanol permeability further while enhancing proton conduction through acid-base interactions. Increase in the degree of sulfonation in SPEEK as well as optimization of the PSf-BIm content in SPEEK/PSf-BIm and the MEA fabrication process could improve the performance in DMFC further.

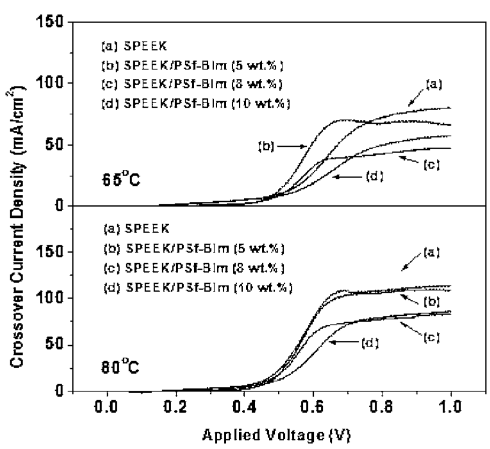


**Figure 2.** Comparison of the variations of the methanol crossover current density for the SPEEK/PSf-BIm and SPEEK membranes in DMFC at a methanol concentration of 1 M. Because the current exceeded the limit of our equipment, the data for Nafion 112 are not shown.

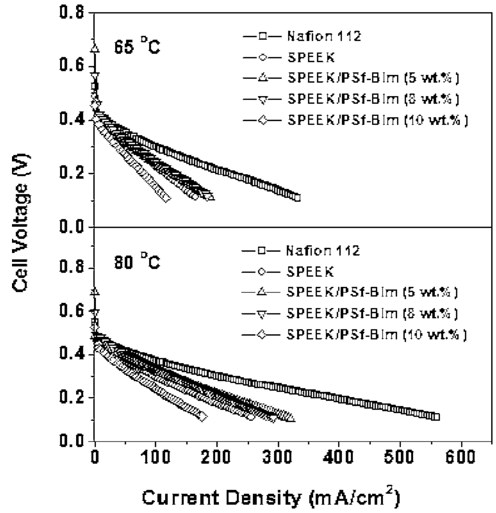


**Figure 3.** Comparison of the polarization curves of the SPEEK/PSf-BIm blend membranes with those of SPEEK and Nafion 112 in DMFC. Anode: 0.6 mg $PtRu/cm^2$, cathode: 1.0 mg $Pt/cm^2$, and methanol concentration: 2 M.

## Conclusions

The ion exchange capacity, proton conductivity, liquid uptake, electrochemical performance in DMFC, and methanol crossover of SPEEK/PSf-BIm blend membranes with different PSf-BIm contents (0–10 wt %) have been compared with those of plain SPEEK membrane. The blend membranes with an optimum PSf-BIm content like

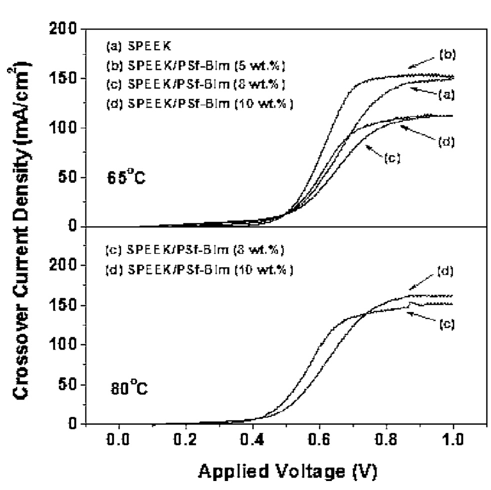


**Figure 4.** Comparison of the variations of the methanol crossover current density for the SPEEK/PSf-BIm and SPEEK membranes in DMF at a methanol concentration of 2 M. The data for Nafion 112, SPEEK, and SPEEK/PSf-BIm with 5 wt % PSf-BIm at 80°C are not shown because the current exceeded the limit of our equipment.

8 wt % exhibit better performance in DMFC than plain SPEEK due to an enhancement in proton conductivity through acid-base interactions and a reduction in methanol crossover. Although the performance of the SPEEK/PSf-BIm blend membranes in DMFC are lower than that of Nafion 112 due to lower proton conductivity, the former exhibits much reduced methanol crossover, offering better long term stability and performance. The novel blend membrane strategy presented here could be explored further with various combinations of a variety of aromatic polymers, and it has the potential to overcome some of the critical barriers associated with the DMFC technology.

## Acknowledgment

Financial support by the Welch Foundation Grant F-1254 is gratefully acknowledged.

*The University of Texas at Austin assisted in meeting the publication costs of this article.*

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