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# Acid–base blend membranes based on 2-amino-benzimidazole and sulfonated poly(ether ether ketone) for direct methanol fuel cells

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## Abstract

Direct methanol fuel cells (DMFC) are attractive for portable and automobile power needs, but their commercialization is hampered by high methanol permeability and the high cost of the currently used Nafion membrane. We report here a novel, low-cost blend membrane consisting of polysulfone-2-amide-benzimidazole (a basic polymer) and sulfonated poly(ether ether ketone) (an acidic polymer), which facilitates proton conduction through acid–base interactions while preserving excellent chemical and mechanical stabilities. The blend membrane exhibits performance in DMFC much higher than that of Nafion 115 and similar to that of Nafion 112, but with a remarkably superior long-term performance than Nafion 112 due to significantly reduced methanol crossover, enhancing the commercialization prospects of DMFC.

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**Keywords:** Fuel cell; Proton exchange membrane; Blend membrane; Direct methanol fuel cell; Methanol crossover

## 1. Introduction

Portable electronic devices such as laptop computers and cell phones have revolutionized modern society. Portable electronic devices are currently powered by lithium ion batteries, but they require a time consuming recharge process with an electrical outlet. Direct methanol fuel cells (DMFC), employing liquid methanol as a fuel, offer an attractive option to replace lithium ion batteries in portable devices, eliminating the necessity of electrical outlet [1,2]. The use of a liquid fuel also makes DMFC attractive for transportation applications, overcoming the difficulties related to safe and economical production, storage, and transportation of hydrogen fuel and the associated infrastructure issues. However, the high electro-osmotic drag coefficient of the currently used proton conducting electrolyte membrane Nafion (a fluorinated polymer) results in a

high methanol crossover from the anode to the cathode through the membrane and a consequent performance loss in DMFC [3,4]. Additionally, Nafion is expensive. Thus, development of low-cost, alternative membranes with acceptable long-term performance remains a critical barrier for the commercialization of DMFC for portable and transportation applications.

Several non-fluorinated polymeric materials have been investigated as replacements for Nafion due to low cost and ease of synthesis [5–12], but they are generally based on free sulfonic acid groups and experience severe dimensional swelling in DMFC at high degree of sulfonation, resulting in mechanical instability problems [1,12,13]. Cross-linked ionomers have been pursued to overcome this problem, but they usually lead to a sacrifice in fuel cell performance and microphase-separation is easy to occur in such blends due to different, incompatible acidic (aromatic) and basic (polybenzimidazole) polymer structures [14,15].

Tethering of N-heterocycles to a polymer backbone followed by its blending with a sulfonic acid polymer is an attractive strategy to achieve high proton conduction

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through acid–base interactions involving the sulfonic acid groups in one polymer (acidic polymer) and the basic N-containing groups in the other polymer (basic polymer) [14–17]. However, this strategy has been pursued with basic polymers having only one or two nitrogen atoms acting as proton donors or acceptors (e.g. pyridine, imidazole, or benzimidazole), limiting the extent of promotion of proton conduction and the fuel cell performance. We report here the identification of a novel N-heterocycle unit (2-amino-benzimidazole) with three nitrogen atoms, which could greatly promote proton conduction in the presence of a sulfonic acid polymer. The three nitrogen atoms of the 2-amino-benzimidazole unit could act equally as proton donors or acceptors as shown in Fig. 1, increasing the probability of proton transfer compared to one nitrogen atom of the pyridine- and two nitrogen atoms of the imidazole- or benzimidazole-doped systems [18].

To demonstrate the feasibility of this concept, we present here the synthesis of a novel polymer, polysulfone-2-amide-benzimidazole (PSf-ABIm), using carboxylated polysulfone and 2-amino-benzimidazole and an electrochemical evaluation in DMFC of a blend membrane consisting of PSf-ABIm (basic polymer) and sulfonated poly(ether ether ketone) (SPEEK, an acidic polymer). Our strategy in selecting this system is based on the following: (i) polysulfone is a low-cost industrial polymer with good mechanical and chemical stabilities, (ii) carboxylated polysulfone precursor can be readily synthesized with a wide variation in the degree of carboxylation from 0.2 to 1.9 [19], offering the flexibility to tune the content of 2-amino-benzimidazole units in the polymer, (iii) polysulfone is an aromatic polymer and so the PSf-ABIm can be expected to have excellent compatibility with other aromatic sulfonic acid polymers like SPEEK and sulfonated polysulfone (SPSf), offering good long term stability, and (iv) the pendant 2-amino-benzimidazole group could ‘insert’ into the sulfonic acid group domains of SPEEK, promoting proton conduction through acid–base interaction as well as blocking methanol crossover.

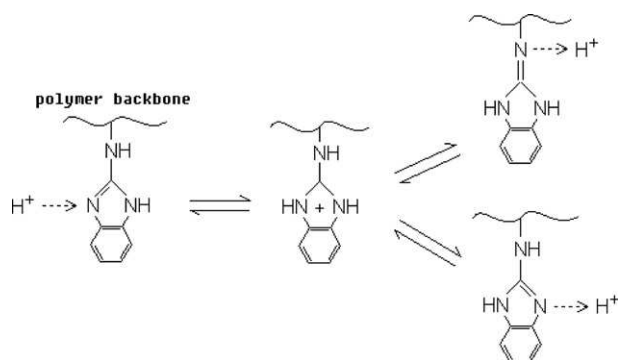


Fig. 1. Mechanism of proton transfer with 2-amino-benzimidazole units.

## 2. Experimental

### 2.1. Materials synthesis and membrane preparation

The synthesis of PSf-ABIm was carried out by a condensation reaction between carboxylated polysulfone and 2-amino-benzimidazole (ABIm) using triphenylphosphite (TPP) as a dehydration agent at 100 °C for 3 h to form the amide unit. Lithium chloride was used to enhance the dissolution of the reactants and product in dimethylformamide. The carboxylated polysulfones had a degree of carboxylation of 1.03, 1.58, and 1.90. The synthesis of SPEEK was carried out by sulfonating PEEK in concentrated sulfuric acid at room temperature for 42 h [3]. The formation of PSf-ABIm was confirmed by absorption bands in FT-IR spectra at 3400 and 1630 cm<sup>-1</sup>, corresponding to isolated N–H stretching and C=N stretching respectively.

The plain SPEEK and the blend membranes with different PSf-ABIm contents were prepared by casting onto a glass plate a *N,N*-dimethylacetamide solution of SPEEK or SPEEK + PSf – ABIm polymers (~10 wt.% polymer) and drying at 95 °C overnight, followed by boiling in deionized water for 2 h. Commercial Nafion 112 membrane with a thickness of 50 μm and Nafion 115 membrane with a thickness of 125 μm were selected for comparison, and they were pre-treated with a 5% solution of hydrogen peroxide, deionized water, and 0.5 M sulfuric acid at around 80 °C for 1 h.

### 2.2. Proton conductivity measurement

Proton conductivity values of the membranes were obtained from the impedance data, which were collected with a computer interfaced HP 4192A LF Impedance Analyzer in the frequency range of 5 Hz to 13 MHz with an applied voltage of 10 mV. The impedance measurement was carried out using a home-made two-electrode setup and stainless steel was used as the blocking electrodes.

### 2.3. Membrane-electrode assembly (MEA) preparation and fuel cell evaluation

The electrodes for single-cell testing in DMFC consisted of gas-diffusion and catalyst layers. The anode catalyst was a commercial 40 wt.% Pt–Ru (1:1) in carbon (E-TEK) and the cathode catalyst was a commercial 20 wt.% Pt in carbon (Alfa Aesar). The electrodes were impregnated with Nafion solution (5 wt.% solution, DuPont Fluoro-products) by a spray technique and dried at 90 °C under vacuum for 30 min. The loadings for cathode (Pt) and anode (Pt–Ru) were 1.0 and 0.6 mg cm<sup>-2</sup>, respectively, and the Nafion loading for both the anode and cathode catalysts were 0.35 mg cm<sup>-2</sup>. 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  $5\text{ cm}^2$  and feeding a preheated methanol solution into the anode at a flow rate of  $2.5\text{ mL cm}^{-1}$  by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of  $200\text{ mL min}^{-1}$  with a back pressure of 20 psi. The temperatures of preheated methanol solution and humidified oxygen were same as that of the cell (65 or  $80^\circ\text{C}$ ).

#### 2.4. Methanol crossover current density measurement

Methanol crossover was evaluated by a voltammetric method in which methanol solution was fed at a flow rate of  $2.5\text{ mL min}^{-1}$  into the anode side of the MEA while the cathode side was kept in an inert humidified  $\text{N}_2$  atmosphere. 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 complete electro-oxidation at the membrane/Pt catalyst interface at the cathode side [17].

### 3. Results and discussion

SPEEK with an ion exchange capacity (IEC) of  $1.52\text{ mequiv. g}^{-1}$  and a degree of sulfonation (DS) of 51% was selected in this study, and it has good dimensional stability [3]. Carboxylated polysulfone with a degree of carboxylation (DC) of 1.03, 1.58, and 1.90 were used, but the data with a DC of 1.90 are presented here. The thicknesses of the SPEEK and SPEEK/PSf-ABIm blend membranes were held constant at  $\sim 50\text{ }\mu\text{m}$ , which is same as that of the Nafion 112 membrane.

Table 1 summarizes the  $[-\text{SO}_3\text{H}]/[\text{ABIm}]$  mole ratio in the SPEEK/PSf-ABIm blend membranes, which was determined based on the weight fraction of PSf-ABIm and SPEEK, and also compares the percent liquid uptake at

different temperatures and methanol concentrations for various PSf-ABIm contents of the SPEEK/PSf-ABIm blend membranes. The liquid uptake increases as the temperature or the methanol concentration increases at a given PSf-ABIm content, and decreases with increasing PSf-ABIm content at a given temperature or methanol concentration. Membrane swelling is a critical issue for MEA stability in fuel cells, and it generally trends with liquid uptake. Irrespective of water or methanol is being used, the SPEEK/PSf-ABIm blend membranes exhibit lower liquid uptake than plain SPEEK and Nafion 115 membranes [12], indicating a lower swelling and better stability. The lower liquid uptake is due to the lower hydrophilicity of PSf-ABIm compared to that of SPEEK and the acid–base interactions between the sulfonic acid and 2-amino-benzimidazole groups. 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].

Fig. 2 compares the proton conductivities of SPEEK and the blend membranes obtained with SPEEK and PSf-ABIm under anhydrous condition. While the proton conductivity of SPEEK decreases with increasing temperature as the proton conduction becomes difficult at high temperatures in such acid-based polymers, the conductivity of the SPEEK/PSf-ABIm blend membranes increase with increasing temperature due to the presence of pendant 2-amino-benzimidazole tethered onto polysulfone. Compared to the pendant benzimidazole groups [16], the pendant 2-amino-benzimidazole groups could act as a better ‘bridge’ to promote proton conduction between sulfonic acid groups under low relative humidity conditions. Also, the proton conductivity increases as the content of PSf-ABIm increases, confirming the role played by 2-amino-benzimidazole on proton conduction. We believe optimization of the microstructure and a uniform distribution of the sulfonic acid and pendant 2-amino-benzimidazole groups could increase the proton conductivity and lower the methanol crossover (see later) further.

Table 1

Comparison of the liquid uptake of the SPEEK/PSf-ABIm blend membranes for various  $[-\text{SO}_3\text{H}]/[\text{ABIm}]$  mole ratios with those of plain SPEEK membrane

PSf-ABIm (wt.%)	Ratio of $[-\text{SO}_3\text{H}]/$ $[\text{ABIm}]$	Methanol Concentration (M)	Liquid uptake (wt.%)	
			65 $^\circ\text{C}$	80 $^\circ\text{C}$
0	–	0	11.6	20.6
		1	15.7	22.4
		2	24.5	28.9
3	18.9	0	10.9	19.8
		1	15.3	21.4
		2	23.5	27.3
5	11.1	0	10.2	18.2
		1	15.0	20.4
		2	22.8	25.9
8	6.7	0	9.5	16.1
		1	14.1	17.5
		2	21.6	24.3

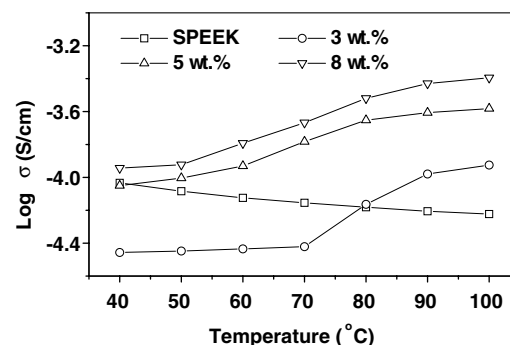


Fig. 2. Variations of the proton conductivities of the SPEEK and SPEEK/PSf-ABIm blend membranes with temperature under anhydrous condition. The wt.% values refer to the amount of PSf-ABIm in the SPEEK/PSf-ABIm blend membranes.

Fig. 3 compares the electrochemical performance data of the SPEEK/PSf-ABIm blend membranes with those of SPEEK and Nafion membranes in DMFC at 65 and 80 °C, collected with 1 M methanol solution. The plain SPEEK membrane exhibits higher polarization loss and lower power density compared to both the Nafion 112 and Nafion 115 membranes due to low proton conductivity [3]. Nafion 112 shows better performance than Nafion 115 because it is thinner. The SPEEK/PSf-ABIm blend membrane with 5 wt.% of PSf-ABIm shows performance much better than those of Nafion 115 and plain SPEEK and similar to or slightly better than that of Nafion 112 at 65 and 80 °C. Also, the blend membrane exhibits higher open circuit voltage (0.731 V and 0.733 V) than all the other three membranes (0.497–0.582 V), indicating lower methanol crossover. The better performance of the SPEEK/PSf-ABIm blend membrane compared to that of the plain SPEEK and Nafion membranes could be attributed, respectively, to the promotion of proton conduction through acid–base interaction and lower methanol crossover (see below). Furthermore, while it is difficult to get fuel cell performance data with membranes containing imidazole due to the poisoning of the Pt catalyst by imidazole [21], the tethering of N-heterocycles like 2-amino-benzimidazole to a polymer backbone prevents or suppresses such a poisoning.

Fig. 4 compares the methanol crossover current density for the membranes, which was measured by a procedure described elsewhere [20]. The crossover current density for the PSf-ABIm blend membrane is lower than that found with Nafion 115 at 65 and 80 °C and plain SPEEK membrane at 65 °C, but slightly higher than that found with the plain SPEEK membrane at 80 °C. This is consistent with the literature data that SPEEK exhibits lower methanol permeability than Nafion 115 [3]. The

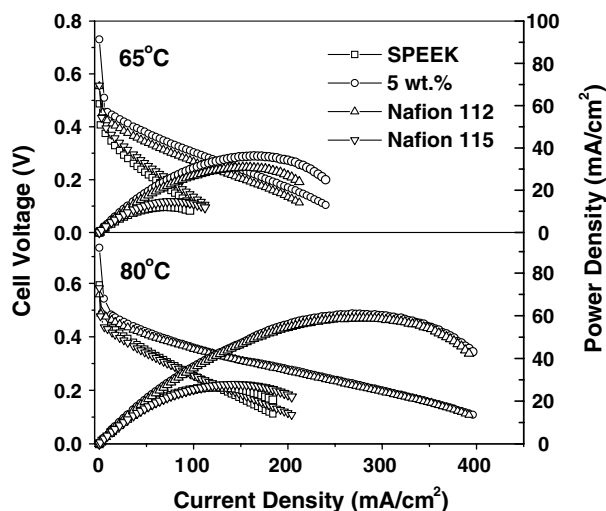


Fig. 3. Comparison of the polarization curves of the SPEEK/PSf-ABIm (5 wt.% of PSf-ABIm) blend membrane with those of SPEEK, Nafion 112, and Nafion 115 membranes in DMFC at 65 °C and 80 °C. The methanol concentration was 1 M.

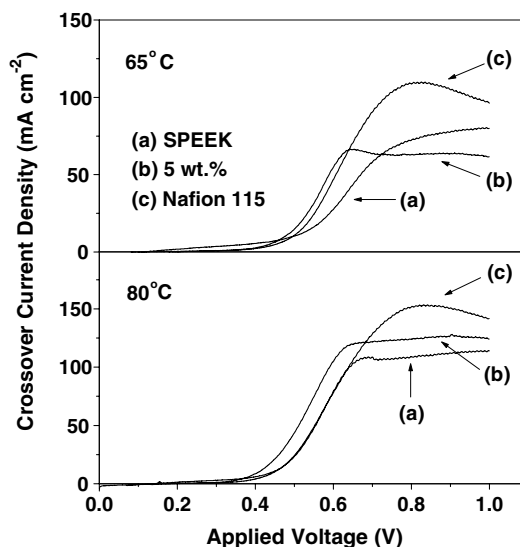


Fig. 4. Comparison of the methanol crossover current densities of the SPEEK/PSf-ABIm (5 wt.% of PSf-ABIm), SPEEK, and Nafion 115 membranes in DMFC at 65 °C and 80 °C. The methanol concentration was 1 M. Since the current exceeded the limit of our equipment, the data for Nafion 112 are not given.

crossover current density for Nafion 112 is not shown in Fig. 4 as it was too high to measure due to its lower thickness and exceeded the current limit of our equipment ( $200 \text{ mA cm}^{-2}$ ). The lower methanol crossover observed with the SPEEK/PSf-ABIm blend membrane compared to that with the Nafion membrane 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 smaller compared to that in Nafion, resulting in a stronger confinement of water/methanol in the narrow channels and significantly lower water/methanol permeation [22–24]. The 2-amino-benzimidazole side groups tethered to polysulfone and their interaction with the hydrophilic groups of SPEEK by Grotthuss-type mechanism helps to reduce the methanol crossover further.

Fig. 5 compares the electrochemical performance data of the SPEEK/PSf-ABIm blend membranes with various PSf-ABIm contents at 80 °C that were collected with 2 M methanol solution. The fuel cell performance increases initially with increasing PSf-ABIm content up to 5 wt.% and then decreases on going to 8 wt.%. The blend membrane with 5 wt.% PSf-ABIm offers the highest power density, suggesting that an optimum ratio between the sulfonic acid and 2-amino-benzimidazole groups may maximize the fuel cell performance. Also, in this type of acid–base blend membranes, proton conduction occurs through mixed mechanisms (vehicle and Grotthuss). Under anhydrous conditions (proton conductivity measurement), Grotthuss mechanism may be predominant and under humidified conditions (fuel cell evaluation), vehicle mechanism may be more significant than Grotthuss mechanism. Thus the degree of acid–base interac-



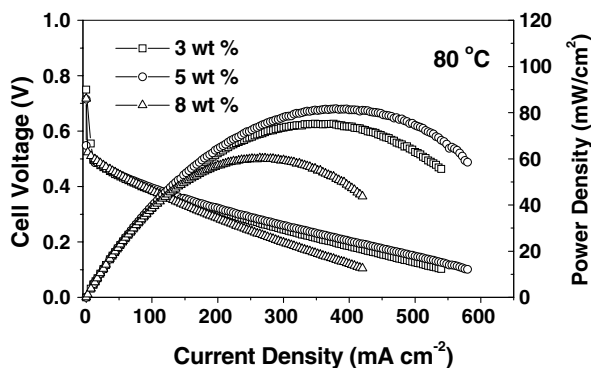


Fig. 5. Comparison of the polarization curves of the SPEEK/PSf-ABIm blend membranes with 3 wt.%, 5 wt.% and 8 wt.% PSf-ABIm in DMFC at 80 °C with a methanol concentration of 2 M.

tion may vary depending on the experimental conditions, causing apparent inconsistencies between the measured proton conductivity and fuel cell performance data.

In order to assess the long-term performance, the SPEEK/PSf-ABIm blend membrane with 3 wt.% PSf-ABIm was evaluated continuously for 120 h. Little or no decline in performance was found after 120 h with the PSf-ABIm blend membrane due to suppressed methanol crossover, while the Nafion 112 membrane exhibited a decline in performance due to a much higher amount of methanol crossover (Fig. 6). Thus, despite a similar initial performance in DMFC, the blend membrane exhibits much better long-term performance than Nafion 112. The superior performance of the blend membrane with lower methanol crossover compared to Nafion could also enable a lower Pt catalyst loading at the cathode, offering additional cost savings.

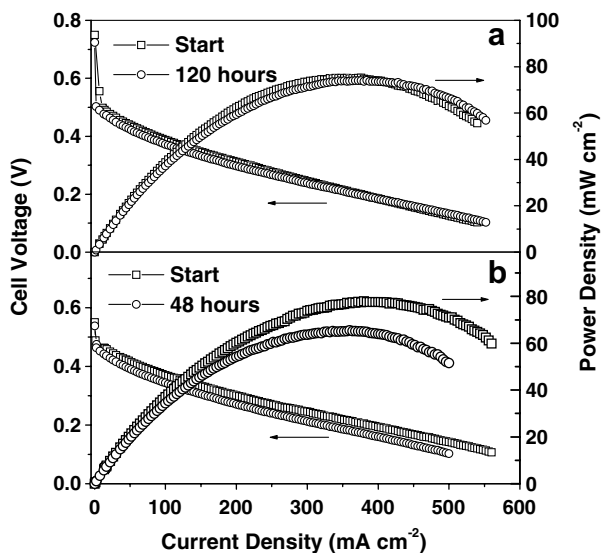


Fig. 6. Long-term performance tests carried out with the (a) SPEEK/PSf-ABIm (3 wt.%) blend membrane and (b) Nafion 112 membrane at 80 °C in DMFC. The methanol concentration was 2 M.

#### 4. Conclusions

In summary, we have designed and synthesized a novel polymeric membrane material based on 2-amino-benzimidazole units. Blend membranes consisting of polysulfone-2-amide-benzimidazole (basic polymer) and sulfonated poly(ether ether ketone) (acidic polymer) demonstrate a viable strategy to facilitate proton conduction through acid–base interactions and suppress methanol crossover, while preserving good mechanical and chemical stabilities. The blend membrane exhibits superior, long-term performance in DMFC with little or no decline with time due to a significant reduction in methanol permeability. These membranes based on acidic and basic polymer blends offer a promising strategy to replace lithium ion batteries in portable electronic devices like laptop computers and cell phones with DMFC. Although the concept is demonstrated here with polysulfone and SPEEK, the strategy could be applied with a wide variety and combination of other aromatic polymers. These membranes involving acid–base interactions also offer the possibility of exhibiting high proton conductivity and good performance in proton exchange membrane fuel cells (PEMFC) at higher temperatures (>100 °C) and low relative humidity, and our future work will focus on this.

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