



N,N'-Bis-(1*H*-benzimidazol-2-yl)-isophthalamide as an additive in sulfonated polymer membranes for direct methanol fuel cells

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ABSTRACT

N,N'-Bis-(1*H*-benzimidazol-2-yl)-isophthalamide (BBImIP) has been synthesized using phosphorus pentoxide-methanesulfonic acid (PPMA) as a solvent and dehydrating agent and investigated as an additive in both sulfonated polysulfone (SPSf) membranes (up to 4.0 wt.% BBImIP) and sulfonated poly(ether ether ketone) membranes (up to 3.0 wt.% BBImIP). The SPSf/BBImIP blend membranes have been characterized by ion-exchange capacity and proton conductivity measurements as well as single cell and methanol crossover measurements in direct methanol fuel cells (DMFCs). Although the presence of BBImIP in the SPSf/BBImIP blend membranes lowers proton conductivity and cell performance compared to that of plain SPSf, it reduces methanol crossover significantly. On the other hand, the sulfonated poly(ether ether ketone) (SPEEK)/BBImIP blend membranes show cell performance comparable to or better than that of plain SPEEK membrane with reduced methanol crossover.

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1. Introduction

Direct methanol fuel cells (DMFCs) are attractive as a power source for portable electronic devices as they can provide continuous, uninterrupted power without requiring an electrical outlet to recharge them. However, the high methanol permeability through the Nafion[®] membrane remains to be a serious problem for their commercialization. The methanol crossover from the anode to the cathode through the membrane not only wastes the fuel but also poisons the cathode catalyst, resulting in performance loss [1]. In view of this, there has been considerable interest to develop new membrane materials that can suppress methanol crossover while offering acceptable proton conductivity [2–4].

Extensive efforts have been devoted to lower methanol permeability in Nafion[®] membranes, including incorporation of organic Si additives into Nafion[®] membrane [5], partial substitution of the sulfonic acid groups by Cs⁺ ions [6], sandwiching a Pd foil between two Nafion[®] 115 films [7], applying a plasma [8,9] or electron beam [10,11] to modify the surface structure of Nafion[®] and create a thin methanol impermeable barrier at the membrane surface, and adding polymers such as polypyrrole [12–14], polyaniline [15], and poly(1-methylpyrrole) [16] to form a composite membrane. These modified Nafion[®]-based membranes have shown potential for blocking the methanol crossover. However, they generally suffer

from a decrease in proton conductivity and some of them experience a loss in mechanical strength.

In parallel, many new membrane materials have been investigated as potential methanol blockers, including sulfonated derivatives of polyphosphazene, poly(ether ether ketone), polysulfone, and polyimide [17–21] as well as phosphoric acid-doped polybenzimidazole [22]. Additionally, some sulfonated copolymers have also been considered as substitutes for Nafion[®] in DMFC [23]. Recently, we reported polymeric blend membranes consisting of an acidic aromatic polymer like sulfonated poly(ether ether ketone) (SPEEK) and a basic polymer like polysulfone containing pendant benzimidazole side groups exhibit good performance in DMFC with enhanced proton conduction while lowering methanol crossover [24,25]. The basic benzimidazole or 2-amino-benzimidazole side groups in such blend membranes help proton transfer due to their ability to act as proton acceptors and donors [26]. Also, the similarities in the structural features of polysulfone and SPEEK offer good compatibility and mechanical strength.

N,N'-Bis-(1*H*-benzimidazol-2-yl)-isophthalamide (BBImIP), which contains two 2-amino-benzimidazole groups bonded to a phenyl ring, has been found to have potential for many applications [27]. However, it has not been explored for use in DMFC. With two 2-amino-benzimidazole groups, which could greatly increase the proton transfer sites, and three phenyl rings, which are compatible with the aromatic polymers, BBImIP is appealing as an additive to aromatic polymers like sulfonated polysulfone (SPSf) or SPEEK for use in DMFC. With this perspective, we present here, for the first time, the blending of BBImIP with SPSf or SPEEK and an

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investigation of its effect on the ion-exchange capacity, proton conductivity, cell performance in DMFC and methanol crossover.

2. Experimental

2.1. Materials synthesis

Methanesulfonic acid, isophthalic acid, and 2-amino-benzimidazole were purchased from Acros Organics and phosphorus pentoxide was purchased from Fisher Scientific. Polysulfone (Udel-1700) and poly(ether ether ketone) (PEEK450 PF) were provided by Udel and Victrex. BBImIP was synthesized by using phosphorus pentoxide-methanesulfonic acid (PPMA) as a dehydration agent, as shown in Fig. 1. Phosphorus pentoxide (2.5 g, 0.016 mol) was dissolved in methanesulfonic acid (25 mL, 0.385 mol) at 60 °C while purging with nitrogen gas in a three-necked flask to prepare PPMA. Isophthalic acid (0.456 g, 2.8 mmol) and 2-amino-benzimidazole (0.731 g, 5.5 mmol) were then added to PPMA and the mixture was stirred at 100 °C for 5 h. After the reaction was complete, the mixture was poured into de-ionized water to precipitate the product from the PPMA solution. The precipitate was then filtered and the solid was neutralized with 20% NaOH solution (500 mL) overnight, followed by filtering and washing with de-ionized water before drying the product in a vacuum oven at 100 °C for overnight. The yield was found to be 90%. The product exhibited IR bands (recorded with KBr pellets) at 3400 (N–H) and 1650 (C=N) cm^{-1} , and ^1H NMR (in $\text{DMSO}-d_6$) peaks with chemical shift δ values of 8.93 (1H), 8.30 (2H), 7.69 (1H), 7.50 (4H), and 7.21 (4H).

Sulfonated polysulfone was prepared by sulfonating the commercial polysulfone (Udel 1700) at room temperature by a method reported elsewhere [28–30]. Sulfonated poly(ether ether ketone) was synthesized by using concentrated sulfuric acid as solvent and sulfonating agent [31].

2.2. Membrane preparation

Plain SPSf or SPEEK membrane and their blend membranes with BBImIP were prepared by a casting method, employing a *N,N'*-dimethylacetamide (DMAC) solution. All membranes were dried at 90 °C overnight, followed by holding in a vacuum oven at 130 °C for 6 h. The membranes were washed thoroughly with boiled de-ionized water several times to remove the residual solvent. The thickness of the membrane was controlled by changing the amount of SPSf or SPEEK and BBImIP in the solution, and all the membranes in this study had a thickness of $50 \pm 5 \mu\text{m}$ with an active area for DMFC evaluation of 5 cm^2 .

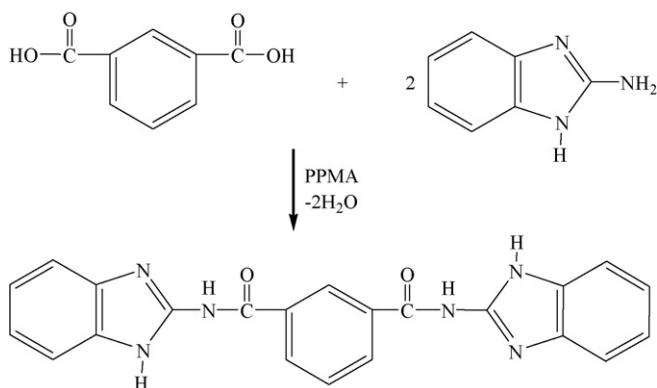


Fig. 1. Synthesis of *N,N'*-bis-(1*H*-benzimidazol-2-yl)-isophthalamide by PPMA.

2.3. Proton conductivity measurement

Proton conductivity values of the membranes were obtained from the impedance data, which were collected with a computer interfaced HP 4192 ALF Impedance Analyzer in the frequency range of 5 Hz to 13 MHz with an applied voltage of 10 mV. The proton conductivity values of dry membranes were obtained from the impedance data collected with a home-made two-electrode setup and stainless steel as blocking electrodes in the transverse direction (*i.e.* through-plane). The proton conductivity values under humidity conditions were obtained from the impedance data collected with an open window framed two platinum electrode cell in the lateral direction (*i.e.* in-plane) by keeping the membrane in a humidity chamber oven with water vapor at 100% relative humidity (RH), and the details of the setup are available elsewhere [32]. The membranes were held in a humidity chamber oven with water vapor at 100% RH.

2.4. Ion-exchange capacity (IEC) and degree of sulfonation (DS) measurements

The ion-exchange capacity was determined by suspending 0.2 g of SPSf or SPSf/BBImIP blend membranes in 2.0 M NaCl solution (30 mL) for 24 h to liberate the H^+ ions and then titrating with standardized 0.1 M NaOH solution using phenolphthalein as an indicator.

2.5. Membrane-electrode assembly (MEA) fabrication

The electrodes (consisting of gas-diffusion and catalyst layers) for testing in DMFC were prepared as reported elsewhere [31]. The anode and cathode catalysts consisted of, respectively, commercial 40 wt.% Pt–Ru (1:1) on Vulcan carbon (E-TEK) and commercial 20 wt.% Pt on Vulcan carbon (Alfa Aesar). The electrodes prepared 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 cathodes (Pt) and anode (Pt–Ru) were 1.0 and 0.6 mg cm^{-2} , respectively, and 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 a membrane at 140 °C for 3 min. The electrochemical performances in DMFC of the MEAs thus fabricated 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 2.0 mL min^{-1} by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of 200 mL min^{-1} with a back pressure of 20 psi.

2.6. Methanol crossover evaluation

Methanol crossover was evaluated by a voltammetric method [33] in which methanol solution was fed at a flow rate of 2.0 mL min^{-1} into the anode side of MEA while the cathode side was kept in an inert humidified 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.

3. Results and discussion

In order to study effect of BBImIP on proton transfer in the SPSf/BBImIP blend membranes, proton conductivity was measured under anhydrous conditions. Fig. 2 compares the proton conductivities of the SPSf/BBImIP blend membranes with various contents of

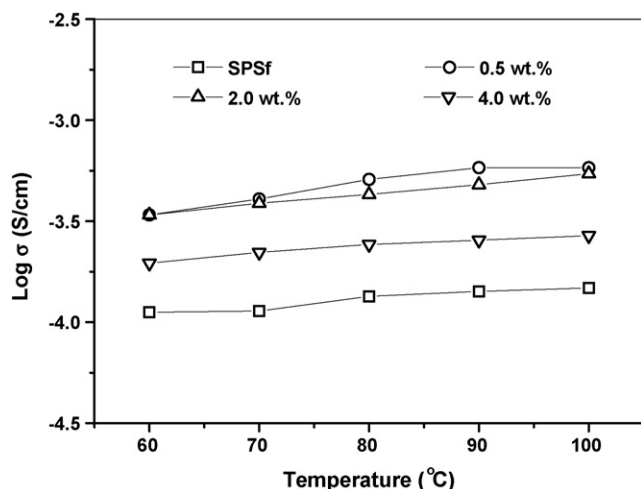


Fig. 2. Variations of the proton conductivities of the plain SPSf and SPSf/BBImIP blend membranes under anhydrous conditions with temperature. The wt.% values refer to the BBImIP content.

BBImIP and plain SPSf membrane. Proton conduction under anhydrous conditions can be considered to be due to the hopping of proton between the sulfonic acid groups of SPSf and the nitrogen atoms of BBImIP. The 2-amino-benzimidazole (ABIm) in BBImIP contains six nitrogen atoms, which could act as proton acceptors and donors and help proton hopping under anhydrous conditions. As seen in Fig. 2, all the blend membranes show higher conductivities than plain SPSf at a given temperature due to the presence of BBImIP and the hopping of protons through it. However, the proton conductivity is highest at 0.5–2 wt.% BBImIP ($[-SO_3H]/[ABIm]$ ratio = 33.9 to 8.3), and it decreases as the content of BBImIP increases to 4.0 wt.% ($[-SO_3H]/[ABIm]$ ratio = 4.1), suggesting that the proton conductivity is maximized at an optimum content of BBImIP in this kind of blend membranes. At higher BBImIP content, the increasing possibility of crosslinking between sulfonic acid and 2-amino-benzimidazole groups results in a lowering of proton conductivity.

Table 1 compares values of ion-exchange capacity and proton conductivity measured under 100% RH at 65 and 80 °C for various contents of BBImIP (or $[-SO_3H]/[ABIm]$ ratios) in the SPSf/BBImIP blend membranes. It can be seen that the IEC values of the blend membranes are lower than that of plain SPSf, indicating the occurrence of acid–base interactions in the blend membranes and the consequent reduction in the amount of H^+ ions dissociating from sulfonic acid groups. Moreover, the IEC value decreases as the content of BBImIP increases due to an increase in the degree of acid–base interaction. The proton conductivities of the blend membranes are also lower than the plain SPSf membrane. In the SPSf/BBImIP blend membranes, all the 2-amino-benzimidazole groups may be protonated due to the excess sulfonic acid groups present (see the $[-SO_3H]/[ABIm]$ ratio in Table 1). The proto-

Table 1

Ion-exchange capacity and proton conductivity (σ) of plain SPSf and SPSf/BBImIP blend membranes with various $[-SO_3H]/[ABIm]$ (ABIm = 2-amino-benzimidazole) molar ratios

Membrane	$[-SO_3H]/[ABIm]$ ratio	IEC (mequiv. g ⁻¹)	σ at 100% RH (S cm ⁻¹)	
			65 °C	80 °C
Plain SPSf	–	0.86	3.1×10^{-2}	3.4×10^{-2}
SPSf + 0.5 wt.% of BBImIP	33.9	0.76	2.3×10^{-2}	2.6×10^{-2}
SPSf + 2.0 wt.% of BBImIP	8.3	0.57	2.7×10^{-2}	2.9×10^{-2}
SPSf + 4.0 wt.% of BBImIP	4.1	0.43	1.3×10^{-2}	1.7×10^{-2}

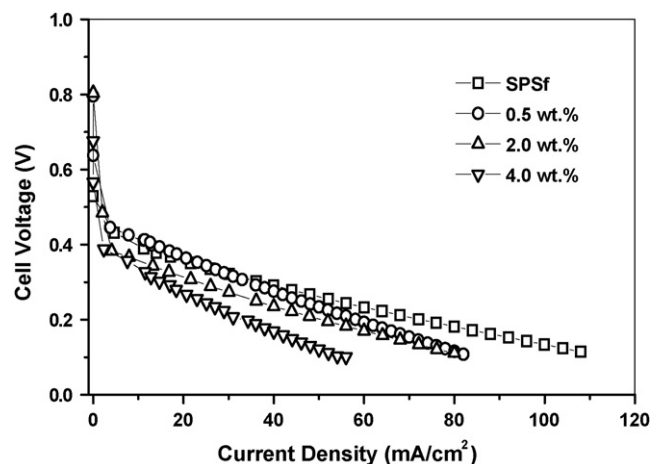


Fig. 3. Comparison of the polarization curves of the plain SPSf and SPSf/BBImIP blend membranes in DMFC. The wt.% values refer to the BBImIP content. Methanol concentration, 1 M and cell temperature, 65 °C.

nated 2-amino-benzimidazole groups can help proton transfer by hopping. Therefore, it can be anticipated that proton conduction may occur by both vehicle-type and hopping mechanisms under humidified conditions. The vehicle-type mechanism could occur in the hydrophilic regions formed by the clustering of the sulfonic acid groups, while the hopping mechanism could occur in the regions where the 2-amino-benzimidazole of BBImIP may insert into the hydrophilic regions formed by the sulfonic acid group cluster due to acid–base interaction. Thus, the vehicle-type mechanism may be predominant in both the plain SPSf membrane and the SPSf/BBImIP blend membranes under humidified conditions, resulting in a lower proton conductivity values for the blend membranes compared to the plain SPSf since proton transfer through 2-amino-benzimidazole by the hopping mechanism could be more sluggish than that by the vehicle-type mechanism. Also, the proton conductivity values measured under hydrous condition were much higher than those measured under anhydrous condition, suggesting that the vehicle-type mechanism is predominant in the blend membranes under 100% humidified condition.

Fig. 3 compares the polarization curves of the SPSf/BBImIP blend membranes with various contents of BBImIP at 65 °C, recorded with 1 M methanol solution as the fuel. The fuel cell performances of blend membranes are lower than that of plain SPSf membrane due to their lower proton conductivities under humidified conditions as seen in Table 1. Also, as the content of BBImIP increases, the fuel cell performance decreases. For the SPSf/BBImIP blend membrane with 2.0 wt.% BBImIP, the slope in the linear part of the polarization curve, which is reflective of the bulk resistance of the membrane, is smaller than those of the other two blend membranes due to the higher proton conductivity. In addition, all the SPSf/BBImIP blend membranes show higher open circuit voltages (OCVs) than the plain SPSf membrane, which could be related to the lower methanol crossover through the blend membranes and a reduced poisoning of the cathode catalyst by methanol [34].

Fig. 4 compares the methanol crossover current densities of the SPSf/BBImIP blend membranes with various contents of BBImIP. It is well known that SPSf membrane usually exhibits lower methanol crossover than Nafion® membrane due to its narrow water/methanol pathway [30]. It can be seen that the SPSf/BBImIP blend membranes exhibit even much lower methanol crossover than the plain SPSf, indicating the effectiveness of BBImIP in blocking methanol crossover by inserting into the hydrophilic regions formed by the sulfonic acid groups. While the protonated 2-amino-benzimidazole could help proton transfer by a hopping, it could

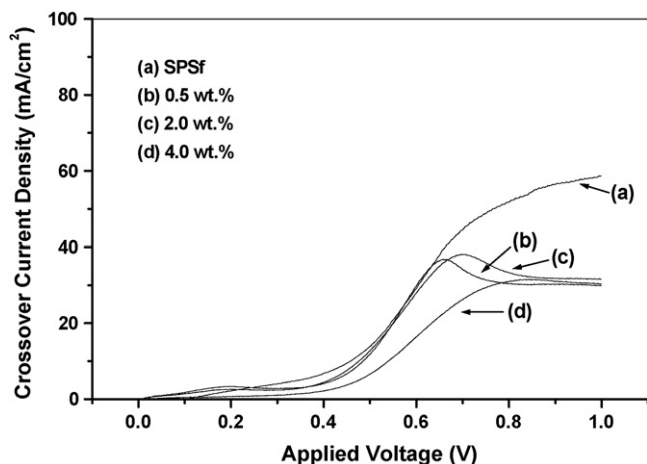


Fig. 4. Comparison of the variations of the methanol crossover current density for the plain SPSf and SPSf/BBImIP blend membranes in DMFC. The wt.% values refer to the BBImIP content. Methanol concentration, 1 M and cell temperature, 65 °C.

block methanol permeability through the hydrophilic region. The lower methanol crossover in the SPSf/BBImIP blend membrane could help to lower the Pt catalyst loading at the cathode in addition to lowering the methanol fuel waste.

To study the effect of BBImIP in other sulfonated polymer systems, fuel cell performances and methanol crossover values of the SPEEK/BBImIP blend membranes were also measured and compared with those of plain SPEEK membrane. For SPEEK membranes, the degree of sulfonation has a profound effect on the IEC, proton conductivity, and water uptake. Although the proton conductivity of SPEEK increases with increasing degree of sulfonation, SPEEK membranes with degree of sulfonation higher than 55% exhibit high water uptake and methanol permeability, which could degrade the mechanical stability and increase the methanol crossover during fuel cell operation. Generally, SPEEK membranes with degree of sulfonation between 40 and 55% show reasonable proton conductivity, low solubility, and good mechanical stability [21,31]. With this perspective, we chose SPEEK with a degree of sulfonation of 42% and IEC of 1.31 mequiv. g⁻¹ for studying the effect of BBImIP.

Fig. 5 compares the polarization curves of the SPEEK/BBImIP blend membranes with various contents of BBImIP (1.0, 2.0, and

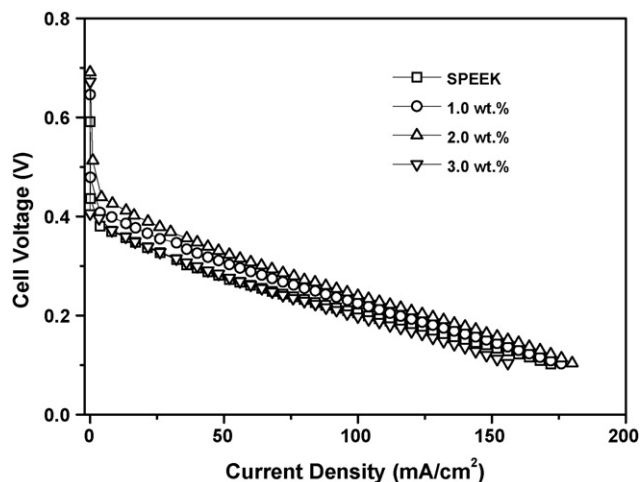


Fig. 5. Comparison of the polarization curves of the plain SPEEK and SPEEK/BBImIP blend membranes in DMFC. The wt.% values refer to the BBImIP content. Methanol concentration, 1 M and cell temperature, 65 °C.

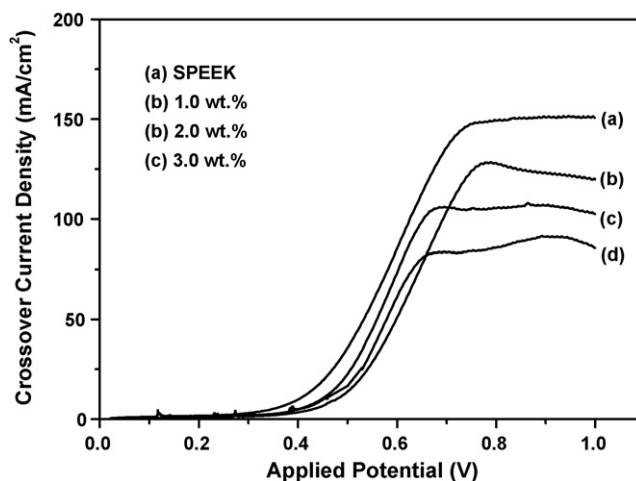


Fig. 6. Comparison of the variations of the methanol crossover current density for the plain SPEEK and SPEEK/BBImIP blend membranes in DMFC. The wt.% values refer to the BBImIP content. Methanol concentration, 1 M and cell temperature, 65 °C.

3.0 wt.%) at 65 °C, recorded with 1 M methanol solution as the fuel. As seen, the SPEEK/BBImIP blend membrane with 1.0 and 2.0 wt.% BBImIP show higher fuel cell performances than the plain SPEEK membrane. However, as the content of BBImIP increases to 3.0 wt.%, the fuel cell performance of the blend membrane decreases slightly lower than that of the plain SPEEK membrane. Also, the blend membranes show higher OCVs than the plain SPEEK membrane due to a suppression of methanol crossover. The higher fuel cell performance of the SPEEK/BBImIP blend membranes with certain compositions compared to that of plain SPEEK, which is in contrast to that found with the SPSf/BBImIP blend membranes in Fig. 3, may be related to the stronger acidity of the sulfonic acid groups in SPEEK. The sulfonated phenyl ring in SPEEK is more electron withdrawing than that in SPSf, which leads to strong acidity. The stronger acidity of the sulfonic acid groups in SPEEK could help to enhance the proton conduction by the hopping mechanism in the SPEEK/BBImIP blend membranes, resulting in improved fuel cell performance. Fig. 6 compares the methanol crossover current densities of the SPEEK/BBImIP blend membranes with various contents of BBImIP. As seen, BBImIP in the SPEEK/BBImIP blend membrane lowers methanol crossover similar to that in the SPSf/BBImIP blend membranes. In addition, the methanol crossover decreases gradually as the content of BBImIP in the SPEEK/BBImIP blend membranes increases.

4. Conclusion

N,N-Bis-(1*H*-benzimidazol-2-yl)-isophthalamide has been synthesized and explored as an additive, for the first time, in sulfonated aromatic polymer membranes like SPSf and SPEEK for use in DMFC. While the SPEEK/BBImIP blend membranes with 1.0–3.0 wt.% BBImIP exhibit performance in DMFC similar to or better than that of plain SPEEK membrane, the SPSf/BBImIP blend membranes with 0.5–4.0 wt.% BBImIP show lower performance than plain SPSf in DMFC. Nevertheless, both the blend membranes offer an important advantage of suppressed methanol crossover in DMFC compared to their plain counterparts SPEEK or SPSf. The reduced methanol crossover of the SPSf/BBImIP or SPEEK/BBImIP blend membranes in DMFC could result in better long-term performance and lower cathode catalyst loading. The study demonstrates that blend membranes based on acid–base interactions between acidic and basic aromatic polymers may offer an attractive strategy to develop high performance membranes for DMFC.

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References

- [1] J. Lin, J.K. Lee, M. Kellner, R. Wycisk, P.N. Pintauro, J. Electrochem. Soc. 153 (2006) A1325.
- [2] P.P. Kundu, V. Sharma, Y.G. Shul, Crit. Rev. Solid State Mater. Sci. 32 (2007) 51.
- [3] C.W. Lin, Y.F. Huang, A.M. Kannah, J. Power Sources 171 (2007) 340.
- [4] B.S. Pivovar, Y. Wang, E.L. Cussler, J. Membr. Sci. 154 (1999) 155.
- [5] S.Z. Ren, G.Q. Sun, C.N. Li, J. Membr. Sci. 282 (2006) 450.
- [6] V. Tricoli, J. Electrochem. Soc. 145 (1998) 3798.
- [7] C. Pu, W. Huang, K.L. Ley, E.S. Smotkin, J. Electrochem. Soc. 142 (1995) L119.
- [8] B. Bae, B.H. Chun, H.Y. Ha, I.H. Oh, D. Kim, J. Membr. Sci. 202 (2002) 245.
- [9] F. Finsterwalder, G. Hambitzer, J. Membr. Sci. 185 (2001) 105.
- [10] L.J. Hobson, H. Ozu, M. Yamaguchi, S. Hayase, J. Electrochem. Soc. 148 (2001) A1185.
- [11] L.J. Hobson, H. Oozu, M. Yamaguchi, S. Hayase, J. New Mater. Electrochem. Syst. 5 (2002) 113.
- [12] E.B. Easton, B.L. Langsdorf, J.A. Hughes, J. Sultan, Z.G. Qi, A. Kaufman, P.G. Pickup, J. Electrochem. Soc. 150 (2003) C735.
- [13] A. Sungpet, J. Membr. Sci. 226 (2003) 131.
- [14] M.A. Smit, A.L. Ocampo, M.A. Espinosa-Medina, P.J. Sebastian, J. Power Sources 124 (2003) 59.
- [15] T. Shimizu, T. Naruhashi, T. Momma, T. Osaka, Electrochemistry 70 (2002) 991.
- [16] N.Y. Jia, M.C. Lefebvre, J. Halfyard, Z.G. Qi, P.G. Pickup, Electrochem. Solid-State Lett. 3 (2000) 529.
- [17] P. Dimitrova, K.A. Friedrich, B. Vogt, U. Stimming, J. Electroanal. Chem. 532 (2002) 75.
- [18] D.H. Jung, S.Y. Cho, D.H. Peck, D.R. Shin, J. Power Sources 118 (2003) 205.
- [19] J.-C. Lin, M. Ouyang, J.M. Fenton, H.R. Kunz, J.T. Koberstein, M.B. Cutlip, J. Appl. Polym. Sci. 70 (1998) 121.
- [20] M. Walker, K.-M. Baumgartner, J. Feichtinger, M. Kaiser, E. Rauchle, J. Kerres, Surf. Coat. Technol. 116 (1999) 996.
- [21] R. Jiang, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc. 153 (2006) A1554.
- [22] Q. Guo, P.N. Pintauro, H. Tang, S. O'Connor, J. Membr. Sci. 154 (1999) 175.
- [23] Y.S. Kim, M. Sumner, W.L. Harrison, J.S. Riffle, J.E. McGrath, B.S. Pivovar, J. Electrochem. Soc. 151 (2004) A2150.
- [24] Y.-Z. Fu, A. Manthiram, M.D. Guiver, Electrochem. Commun. 8 (2006) 1386.
- [25] Y.-Z. Fu, A. Manthiram, M.D. Guiver, Electrochem. Solid-State Lett. 10 (2007) B70.
- [26] Y.-Z. Fu, A. Manthiram, M.D. Guiver, Electrochem. Commun. 9 (2007) 905.
- [27] N. Grier, J. Coat. Technol. 48 (1976) 50.
- [28] F. Lufrano, G. Squadrito, A. Patti, E. Passalacqua, J. Appl. Polym. Sci. 77 (2000) 1250.
- [29] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci, E. Passalacqua, Solid State Ionics 145 (2001) 47.
- [30] Y.-Z. Fu, A. Manthiram, J. Power Sources 157 (2006) 222.
- [31] B. Yang, A. Manthiram, Electrochem. Solid-State Lett. 6 (2003) A229.
- [32] T.A. Zawodzinski, M. Neeman, L.O. Sillerud, S. Gottesfeld, J. Phys. Chem. 95 (1991) 6040.
- [33] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 92.
- [34] X. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) L12.