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Blend membranes based on sulfonated poly(ether ether ketone) and polysulfone bearing benzimidazole side groups for proton exchange membrane fuel cells

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Abstract

A novel acid–base blend membrane based on sulfonated poly(ether ether ketone) (SPEEK) and polysulfone bearing benzimidazole side groups has been synthesized, characterized, and evaluated in proton exchange membrane fuel cell (PEMFC). The benzimidazole group tethered to the polysulfone backbone acts as a medium through the basic nitrogen for transfer of protons between the sulfonic acid groups of SPEEK, supporting a Grotthuss-type mechanism in addition to the vehicle-type mechanism present among SPEEK. The blend membrane exhibits better performance in PEMFC at 90 and 100 °C compared to the pure SPEEK and Nafion 115 membranes. The polymers bearing pendant benzimidazole groups offer a promising strategy to develop new membranes that can operate at higher temperatures and low relative humidity.

Keywords: Fuel cell; Proton exchange membrane; Blend membrane; Sulfonated poly(ether ether ketone)

1. Introduction

Nafion, a commercial product of Du Pont, is currently used as the polymer electrolyte in proton exchange membrane fuel cells (PEMFC). Its high proton conductivity combined with good chemical and mechanical properties has made it an attractive membrane for PEMFC for more than 50 years. However, the proton conduction in Nafion occurs only under wet conditions (vehicle-type mechanism), which limits the operating temperatures to <100 °C and necessitates complex external humidification systems. In addition, the low operating temperature leads to a poisoning of the expensive Pt catalyst by trace amounts of CO impurity present in the fuel [1], necessitating expensive fuel cleanup processes to bring down the CO impurity level to a few ppm. Design and development of alternative polymeric membranes that can operate at higher temperatures and low relative humidity (RH) can suppress or eliminate these problems and enhance the commercialization prospects of the PEMFC technology for automotive applications.

Complexes of polybenzimidazole (PBI) and phosphoric acid, introduced by Wainright *et al.*, are known to be good candidates for high temperature PEMFC [2]. In this system, an acid–base complex occurs between the nonprotonated, basic nitrogen of the PBI repeat unit and the absorbed phosphoric acid [3]. The protons hop between the nitrogen of benzimidazole and phosphoric acid by forming benzimidazolium cation and dihydrogenphosphate anion [4,5], facilitating proton conduction by a Grotthuss-type mechanism, unlike the vehicle-type mechanism in Nafion. Similar complexed systems have also been pursued by replacing water by heterocycles as proton solvents [6–11]. For example, high proton conductivity could be achieved by replacing water by imidazole in Nafion [6],

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but its performance in fuel cell is poor due to the poisoning effect of imidazole on the platinum catalyst [8,10]. Some nitrogen containing heterocycles (e.g. imidazole) attached to small, fixed chains have also been studied, but no fuel cell data are available [3,12–15]. In addition, efforts have been made to tether heterocycles like imidazole, 1*H*-1,2,3-triazole, and benzimidazole to alkyl polymer chains [16–20], but they are not ideal for high temperature PEMFC due to the low proton conductivity and poor stabilities of the alkyl backbones.

Tethering of *N*-heterocycles to an aromatic polymer network is a promising strategy to achieve high proton conductivity at high temperatures, involving a Grotthuss-type mechanism without requiring water, while preserving good chemical and mechanical stabilities at higher temperatures. Although imidazole is a good proton solvent, it is difficult to achieve good proton conductivity after tethering imidazole to a polymer since it has a higher pK_a value of 7.0. On the other hand, benzimidazole with a lower pK_a value of 5.5 has a possibility of offering higher proton conductivity after tethering to a polymer network. However, tethering of benzimidazole to an aromatic polymer backbone has not been pursued before to our knowledge. Moreover, carboxylic acid groups attached to some aromatic polymers like polysulfone [21] can be easily transformed to benzimidazole units through condensation reactions. With this perspective, we report here a novel strategy in which the benzimidazole group is attached to an aromatic polymer like poly(sulfone), which exhibits good stability and local mobility. The aromatic polymer with the tethered benzimidazole groups (basic polymer) is then blended with an acid polymer like sulfonated poly(ether ether ketone) (SPEEK) to obtain high proton conductivity through acid–base interactions. The synthesis, characterization, and evaluation in PEMFC of such blend membranes are presented here.

2. Experimental

2.1. Materials synthesis

The polysulfone bearing benzimidazole side group (PSf–BIm) was synthesized starting from carboxylated polysulfone (CPSf). The details of the synthesis of CPSf having different degrees of carboxylation per repeat unit are available elsewhere [21]. We used in our synthesis CPSf with a degree of carboxylation of 1.03, 1.58, and 1.90, and the PSf–BIm prepared with them are hereafter designated as, respectively, PSf–BIm-103, PSf–BIm-158 and PSf–BIm-190. For PSf–BIm-103, 0.5 g of CPSf and 0.1296 g of 1, 2-diaminobenzene were dissolved in 20 mL of dimethylformamide (DMF) in a three-necked flask, followed by an addition of 1.0 g of lithium chloride and 2.86 mL of triphenylphosphite (TPP) into the flask. The solution was stirred at 100 °C for 3 h and then at 150 °C for 10 h under nitrogen atmosphere and poured into 1000 mL of methanol to precipitate the polymer. The precipitate was collected by filtration and dried in a vacuum oven at 110 °C overnight. The details of preparation of SPEEK are available elsewhere [22], and SPEEK with an ion exchange capacity (IEC) of 1.63 Meq/g and a degree of sulfonation (DS) of 54% was used in this study. The SPEEK/PSf–BIm (3:1 weight ratio) blend membrane was prepared by a casting method employing a dimethylacetamide (DMAc) solution.

2.2. FT-IR and proton conductivity measurement

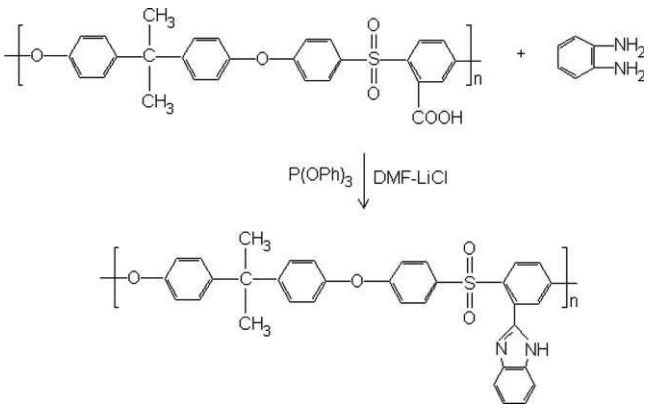
The structure of the synthesized PSf–BIm was characterized with infrared spectroscopy using a Nicolet FT-IR instrument in the range of 4000–400 cm^{-1}. Proton conductivity values of the membranes were obtained from the impedance data, which were collected with a computer interfaced HP 4192 A LF Impedance 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) fabrication and fuel cell evaluation

The fuel cell electrodes consist of gas-diffusion and catalyst layers, and the details of their preparations are described elsewhere [23]. The Pt metal loadings for the anode and cathode were both 0.4 mg/cm^2. The fuel cell performances were evaluated with a commercial fuel cell test system (Compucell GT, Electrochem. Inc.) using a single-cell fixture having an active area of 5 cm^2 and by feeding humidified hydrogen (80 °C) and oxygen (80 °C) into the anode and cathode, respectively, at a flow rate of 50 and 100 mL/min with back pressures of 10 and 12 psi.

3. Results and discussion

Condensation reaction between 1,2-diaminobenzene and carboxylic acid is a universal method to synthesize benzimidazole unit. Carboxylated polysulfone was first synthesized as reported by Guiver *et al.* [21]. The degree of carboxylation (DC) per repeat unit could be varied from 0.2 to 1.9, which provides the flexibility to convert the carboxylic acid groups to benzimidazole side groups over a wide range. Scheme 1 shows the synthesis of polysulfone bearing benzimidazole side group by a reaction between carboxylated polysulfone and 1,2-diaminobenzene using triphenylphosphite (TPP) as a dehydration agent. To avoid the formation of the amide structure by cross-linking, the reaction was first carried out at a lower temperature of 100 °C for 3 h to form a single C–N bond between the carboxylic acid group and one amino group of 1,2-diaminobenzene, followed by heating at 150 °C for 10 h to form the C=N bond between the carboxylic carbon atom and the other amino group of 1,2-diaminobenzene. Lithium chloride was used to enhance the dissolution of the product in DMF.



Scheme 1. Synthesis scheme of polysulfone bearing benzimidazole side group.

Fig. 1 shows the FT-IR spectra of carboxylated polysulfone (CPSf), PSf–BIm-103, PSf–BIm-158, and PSf–BIm-190. The main absorption bands of PSf–BIm indicating the presence of benzimidazole are closely similar to those of PBI or poly(2,5-benzimidazole) (ABPBI) [24]. The bands around 3400 cm^{-1} in PSf–BIm are attributed to the isolated N–H stretching. The strong absorption at 1740 cm^{-1} due to the C=O asymmetric stretching in CPSf almost disappeared in PSf–BIm, indicating the conversion of almost all of the carboxylic acid groups into benzimidazole groups. The product after 3 h at 100 °C was also collected and characterized by FT-IR. The observation of C=O asymmetric stretching and the isolated N–H stretching confirms the reaction of only one amino group of 1,2-diaminobenzene and the absence of the formation of the imidazole ring of benzimidazole at 100 °C. More importantly, the C=N stretching at 1630 cm^{-1}, which distinguishes PSf–BIm from CPSf, increase as the DC in the starting CPSf increases. These spectral data confirm the formation of benzimidazole side groups on polysulfone.

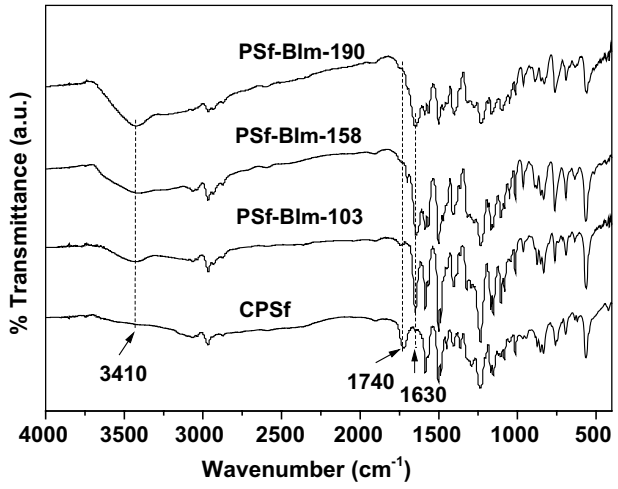


Fig. 1. FT-IR spectra of carboxylated polysulfone and polysulfone bearing benzimidazole side group.

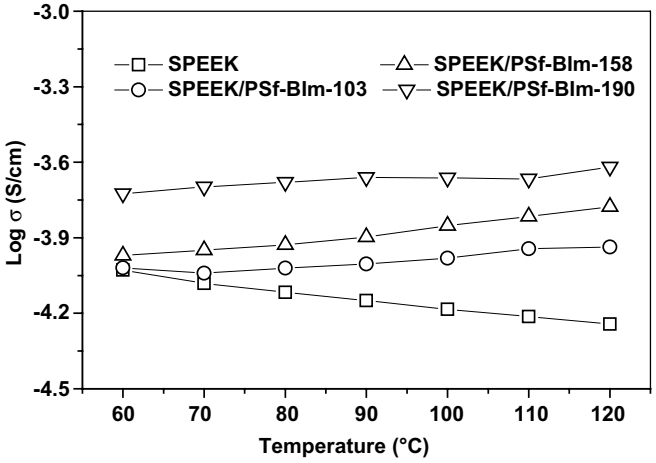


Fig. 2. Variations of the proton conductivities of the SPEEK and SPEEK/PSf–BIm blend (3:1 weight ratio) membranes with temperature under anhydrous condition.

Fig. 2 compares the proton conductivities of SPEEK and the blend membranes obtained with SPEEK and PSf–BIm (3:1 weight ratio) 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–BIm blend membranes increase with increasing temperature due to the presence of benzimidazole tethered onto polysulfone. The pendant benzimidazole could act as a 'bridge' to promote proton conduction between sulfonic acid groups under low relative humidity conditions. Also, the proton conductivity increases as the DC of polysulfone to which benzimidazole is tethered increases, confirming the role played by benzimidazole on proton conduction.

Fig. 3 shows a plausible proton transfer mechanism for the pendant benzimidazole, which is analogous to the Grotthuss-type mechanism proposed for the complexes of the PBI system [5,25]. The sulfonic acid group of SPEEK can protonate the nitrogen site of benzimidazole, facilitating the hopping of the proton bound to the other nitrogen of the benzimidazole unit to another basic site of the benzimidazole unit or to the oxygen of another sulfonate anion group. The interaction between the sulfonic acid group and the nitrogen of the pendant benzimidazole group was confirmed by FTIR. A shift of the strong band at 1016 cm^{-1}, which is attributed to the symmetric stretching of the sulfonate S–O group of SPEEK, occurs with increasing PSf–BIm content in the polymer blends. Proton conduction in

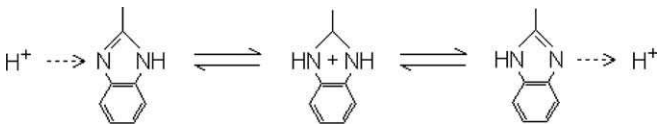


Fig. 3. Plausible proton transfer mechanism involving the pendant benzimidazole group.

the blend membrane may occur by a mixed mechanism (a partial vehicle-type mechanism in the domain of sulfonic acid groups and a partial Grotthuss-type mechanism in the domain of benzimidazole groups). The presence of benzimidazole group thus promotes proton conduction under anhydrous condition at higher temperatures. Another advantage of pendant benzimidazole group is the ease of swaying, which could promote long-range proton motion in the polymer system.

Fig. 4 compares the performances of the SPEEK/PSf–BIm-190 (3:1 weight ratio) blend membrane in single cell PEMFC at different temperatures with those of Nafion. In the case of the SPEEK/PSf–BIm-190 blend membrane, the polarization loss decreases as the temperature increases from 80 to 90 °C as one would expect due to the increasing proton conductivity as seen in Fig. 2, which is in contrast to the increase in polarization loss found with the Nafion membrane due to the decrease in water content. Fig. 5 compares the performances of Nafion 115, SPEEK, and SPEEK/PSf–BIm-190 membranes in single cell PEMFC at 90 and 100 °C. The thickness of SPEEK and SPEEK/PSf–BIm-190 membranes were kept the same and the electrodes were also fabricated in the same manner for all the three MEAs to have a good comparison of the intrinsic properties of the three membranes. Clearly, the SPEEK/PSf–BIm-190 blend membrane exhibits better performance with lower polarization loss than both the Nafion and SPEEK membranes at 90 or 100 °C. The data demonstrate that the benzimidazole group present in PSf–BIm promotes proton conduction at higher temperatures. The decline in performance on going from 90 to 100 °C is due to the use of Nafion in our electrodes (cathode and anode). Additionally, the decline in performance on going from 90 to 100 °C is drastic in the cases of SPEEK and Nafion membranes compared to that in the case of the SPEEK/PSf–BIm-190 blend membrane. This is due to a significant decrease in the proton conductivity at 100 °C with the SPEEK and Nafion membranes, arising from a loss of the proton conducting solvent, water.

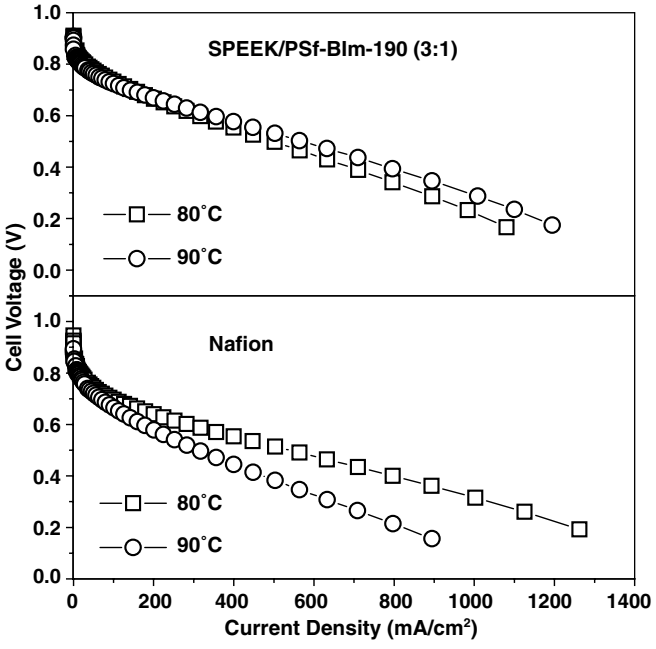


Fig. 4. Comparison of the performances of the SPEEK/PSf–BIm-190 (3:1 weight ratio) blend membranes at different temperatures in single cell PEMFC with those of Nafion membrane: squares refer to $T_{cell} = 80\ ^\circ C$ and $T_{H_2} = T_{O_2} = 80\ ^\circ C$ and circles refer to $T_{cell} = 90\ ^\circ C$ and $T_{H_2} = T_{O_2} = 80\ ^\circ C$.

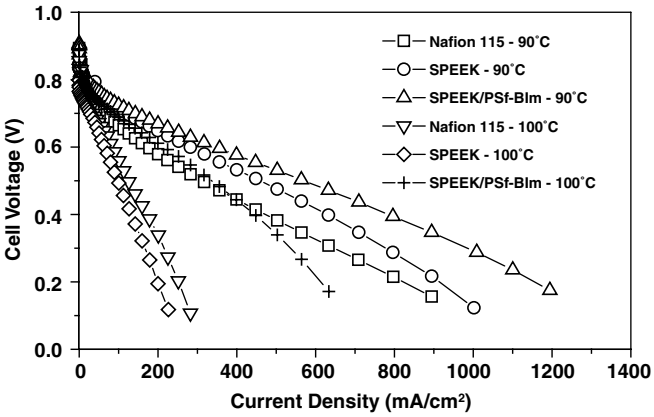


Fig. 5. Comparison of the performances of the Nafion 115, SPEEK, and SPEEK/PSf–BIm-190 (3:1 weight ratio) blend membranes in single cell PEMFC: $T_{H_2} = T_{O_2} = 80\ ^\circ C$ and $T_{cell} = 90$ or $100\ ^\circ C$.

4. Conclusions

In summary, a novel aromatic polymer (polysulfone) bearing a heterocycle (benzimidazole) side group has been synthesized. It is totally different from the well known PBI polymer, and it has the benzimidazole units attached to the main chain. Blend membranes fabricated with sulfonated poly(ether ether ketone) and poly(sulfone) bearing benzimidazole side group exhibit higher proton conductivity and better performance in PEMFC at 90 and 100 °C compared to the SPEEK or Nafion membranes. The study demonstrates that polymers bearing benzimidazole side groups may become a viable strategy to develop new membranes that could operate at higher temperatures and low relative humidity.

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