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Acid–base blend membranes consisting of sulfonated poly(ether ether ketone) and 5-amino-benzotriazole tethered polysulfone for DMFC

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ABSTRACT

Low cost, acid–base blend membranes have been synthesized by blending sulfonated poly(ether ether ketone) (SPEEK) (an acid polymer) and various amounts of polysulfone tethered with 5-amino-benzotriazole (a basic polymer). The blend membranes have been characterized by ion-exchange capacity (IEC), liquid uptake, proton conductivity, methanol crossover, and fuel cell performance measurements. The blend membranes exhibit superior performance in direct methanol fuel cells (DMFC) compared to plain SPEEK and Nafion 115 membranes due to enhanced proton conductivity and much suppressed methanol crossover while preserving good swelling stability. The maximum power density of the blend membrane is two times higher than that of Nafion 115 membrane at 80 °C with 1 M methanol feed. Additionally, the effects of the size, pK_a, and the number of nitrogen atoms of the tethered heterocycle groups on the properties of the blend membranes have also been investigated by comparing the properties of the blend membranes consisting of SPEEK and different basic polymers.

1. Introduction

Direct methanol fuel cells (DMFC) are attractive power sources for portable electronic devices as they do not need recharging with an electrical outlet [1,2]. The use of liquid methanol as a fuel also makes DMFC appealing as the difficulties encountered with the production, storage, and transportation of gaseous hydrogen fuel can be avoided [3]. However, the commercialization of the DMFC technology is hampered by the high methanol permeability through the currently used Nafion membranes as well as the sluggish methanol oxidation and oxygen reduction reactions.

Several aromatic polymers with attached sulfonic acid groups such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated polysulfone (SPSf), and sulfonated polyimide (SPI) have been widely investigated as candidates to substitute for the Nafion membrane in DMFC due to their lower cost, high thermal stability, good mechanical properties, and excellent resistance to hydrolysis and oxidation [4–9]. More importantly, the more rigid aromatic polymer backbones in these polymers could lower methanol crossover due to the smaller ionic cluster size compared to that in Nafion membrane, which has a flexible polytetrafluoroethylene (PTFE) backbone. However, the lower acidity of the sulfonic acid groups in aromatic polymers (p$K_a \sim -1$) compared to that of Nafion (p$K_a \sim -6$) results in comparatively lower proton conductivity [10]. In order to maximize the proton conductivity, a high degree of sulfonation (DS) is desired, which often causes an increase in membrane swelling and degradation in mechanical stability.

Covalent and ionic cross-linking is found to be an effective way to control the dimensional stability and suppress methanol crossover of aromatic polymer membranes with high DS without unduly sacrificing the proton conductivity [11]. Covalently cross-linked sulfonated aromatic polymers with high DS such as SPEEK and SPSf have been found to exhibit much better swelling stability and lower methanol permeability compared to the uncross-linked sulfonated polymers. However, covalently cross-linked polymers have a tendency to become brittle in the dry state, which is a critical problem for fuel cell application. The brittleness is possibly caused by the inflexibility of the covalent networks [12–15]. Because of this reason, more attention is being directed towards the development of ionomer networks containing ionically cross-linked blend systems such as SPPO (poly(2,6-dimethyl-1,4-phenylene oxide))/PBI (polybenzimidazole respectively), SPEEK/PBI, and SPSf/aminated PSf, which are more flexible [16–19]. Our group reported recently [20–23] that blend membranes based on acid–base interactions between the sulfonic acid groups of SPEEK and the *N*-heterocycle groups (benzimidazole (BIm), amino-benzimidazole (ABIm), nitro-benzimidazole (NBIm), and 1*H*-perimidine (PImd)) tethered to PSf show improved DMFC performance compared to plain SPEEK membranes due to both suppressed methanol crossover and enhanced proton conductivity. This blend membrane concept is based on industrially available, inexpensive polymer precursors like PEEK

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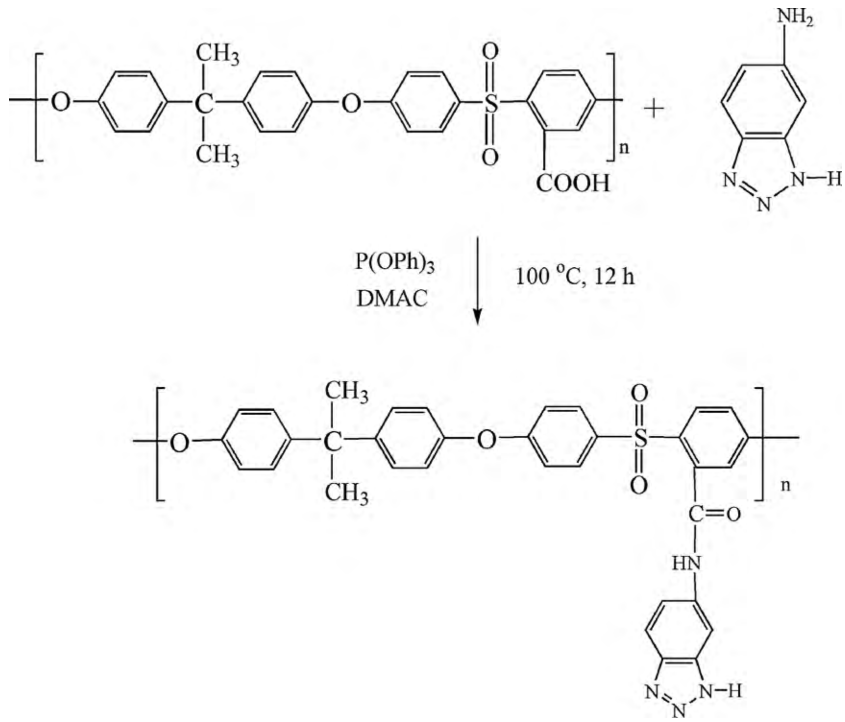

Fig. 1. Synthesis scheme of polysulfone bearing 5-amino-benzotriazole side groups.

and PSf, which are compatible with each other due to their similar aromatic backbones.

To improve further the performance of the acid–base blend membrane systems, we present here the synthesis of a novel polymer, polysulfone bearing 5-amino-benzotriazole (PSf-BTraz), via a condensation reaction between carboxylated polysulfone (CPSf) and 5-amino-benzotriazole (BTraz). The blend membranes consisting of SPEEK and PSf-BTraz (with various PSf-BTraz contents) are prepared and investigated. The BTraz group is larger in size compared to BIm group, and the four nitrogen sites comprising BTraz could facilitate proton transfer more easily through a Grotthuss-type mechanism [24]. The ion-exchange capacity (IEC), proton conductivity, liquid uptake, electrochemical performance in DMFC, and methanol crossover of the SPEEK/PSf-BTraz blend membranes with various PSf-BTraz contents are compared with those of plain SPEEK and Nafion membranes.

Also, to further understand the effects of the size, pK_a, and the number of nitrogen atoms of the heterocycles tethered to PSf on the properties of the acid–base blend membranes, blend membranes consisting of SPEEK and different basic polymers with the same [$-SO_3H$]/[heterocycle] ratio are prepared and characterized. The microstructure, proton conductivity, and electrochemical performance as well as the methanol crossover of those membranes are compared.

2. Experimental

2.1. Materials synthesis

The PSf-BTraz polymer was synthesized by a condensation reaction between CPSf and BTraz (Acros) as shown in Fig. 1. CPSf with a degree of carboxylation of 1.03, 1.58, and 1.90 were synthesized following the procedure reported elsewhere [25]. The PSf-BTraz samples prepared with these CPSf are hereafter designated as, respectively, PSf-BTraz-103, PSf-BTraz-158, and PSf-BTraz-190. Triphenyl phosphite (TPP) and *N*,*N*-dimethylacetamide (DMAc, Acros) were used, respectively, as dehydration agent and solvent in the reaction. For the preparation of PSf-BTraz-158, 0.5 g of CPSf-158 and 0.207 g of BTraz were dissolved in 30 mL of DMAc in a 100 mL three-neck round-bottom flask, the solution was heated to 100 °C under nitrogen atmosphere, and 2.87 mL of TPP was then added. After holding the temperature for 12 h, the resulting solution was cooled down and poured into 400 mL of methanol, where a white power was precipitated. The precipitated product polymer was washed with methanol and de-ionized water and dried in a vacuum oven at 100 °C overnight. The other PSf-BTraz derivatives were made in a similar manner. The structures of the resulting polymers were characterized by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum BX FTIR instrument).

The SPEEK was synthesized by a sulfonation reaction using concentrated sulfuric acid as both a solvent and a sulfonating agent, and the detailed procedure has been reported elsewhere [23]. The degree of sulfonation was controlled by changing the reaction time. In this study, SPEEK with an IEC of 1.42 meq/g was used. The polysulfones tethered with different heterocycles (BIm, ABIm, NBIm, PImd) were synthesized using CPSf-158 as a precursor and following the procedure reported before [20–23].

2.2. Membrane preparation

Plain SPEEK membrane and blend membranes consisting of SPEEK and PSf-BTraz were prepared by casting onto a glass plate from DMAc solutions containing the polymers (~10% w/w). The resulting membranes were dried at 90 °C overnight and at 130 °C for another 6 h, followed by washing thoroughly with boiled de-ionized water several times. All the membranes were controlled to have a thickness of 60 ± 5 μm with an active area of 5 cm^2 for DMFC evaluation. Although blend membranes consisting of SPEEK and PSf-BTraz-103, PSf-BTraz-158, and PSf-BTraz-190 were prepared, mainly the data of the SPEEK/PSf-BTraz-158 membranes are presented here.

The blend membranes consisting of SPEEK and polysulfone tethered with various heterocycles were prepared by a similar procedure described above. The [$-SO_3H$]/[heterocycle] ratio in the