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A novel proton-conductive membrane with reduced methanol permeability prepared from bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO)

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Abstract

A series of proton-conducting membranes were developed for direct methanol fuel cell (DMFC) applications via sulfonation of bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) base membranes. Besides the low manufacture cost, the membranes exhibited an excellent control on methanol crossover and swelling, and a sound balance with high proton conductivities. These can be attributed to the inherent properties of membrane structures: (i) benzyl substitution with bromine, which imparted the membrane stronger hydrophobicity, (ii) cross-linking between BPPO chains, which enhances the dimensional stability and renders the membrane a dense texture, (iii) proper content of sulfonic acid groups, which guarantees the proton conductivity. An optimal membrane was obtained after investigating the effects of the bromination degree and sulfonation process on the performances of corresponding membranes, *i.e.*, the membrane possesses the methanol permeability of 2.64×10^{-8} cm^2/s and characteristic factor Φ value of 30 times higher than that of Nafion® 117. The sulfonation process should be controlled within a proper period of time and in mild sulfonation conditions so as to achieve a proton conductivity higher than 0.07 S/cm for potential applications in DMFC.
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Keywords: Proton-conductive membrane; Methanol crossover; DMFC; Bromomethylation; PPO

1. Introduction

Direct methanol fuel cell (DMFC) is attractive as a promising power source for several applications including automotive and portable power sources in view of some advantages, such as high efficiency, low emissions, potentially renewable fuel source as well as fast and convenient refueling [1]. This kind of fuel cell (DMFC) is based on solid polymer electrolyte in the form of proton-conductive membrane and has an additional advantage of no liquid electrolyte [2,3]. The current popular proton-conductive membrane is Nafion® of poly(perfluorosulfonic acid) structure, a DuPont product that was developed in the late 1960s and primarily used as a permselective separator in chlor-alkali electrolyzers [4]. Nafion® has high proton conductivity, excellent chemical stability and good mechanical property for fuel cells running below 90 °C. However, its high methanol crossover usually causes depolarization losses at the cathode and conversion losses in terms of lost fuel. Furthermore, its cost is too high to be used in commercial development [2]. Therefore, new membranes which have significantly reduced methanol permeability, lower price and high conductivity are required for the practical realization of DMFC. Recently, intense scientific interest has been devoted to proton-conducting membranes for DMFC, especially with respect to methanol crossover. Approaches to minimize methanol permeability of the proton-conductive membranes by means of various modifications of Nafion® polymers [5–8], or development of new polymers [9–11], have appeared in the literature. For example, polyoxyphenylene (POP)-like polymers were proved to be an essential ingredient in methanol crossover minimization strategies [12].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a versatile and well-known thermally stable engineering plastic, which was subjected to many modifications by bromination, carboxylation

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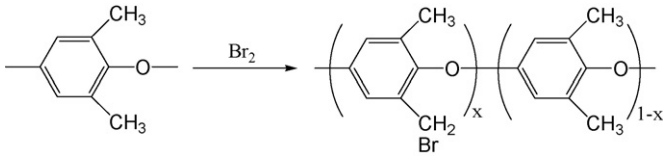
and methyl esterified carboxylation, sulfonation and acylation for some special properties [13]. Furthermore, thermal properties of these modified polymers do not change much as compared to parent PPO [14]. With the extraordinary electrochemical properties, sulfonated PPO (SPPO) has been considered as a new polymeric electrolyte material for proton-conductive membrane. Unfortunately, SPPO is also a strong hydrophilic material and may swell strongly in hot water. To improve the mechanical properties of SPPO membranes, our group has initiated a new cation exchange membrane by simultaneous sulfonation and bromination in the aryl position (the aromatic ring) [15]. Although the mechanical strength of the new membranes was enhanced to a certain extent, the conductivity was inevitably reduced and the water uptake (swelling) still could not meet the need for fuel cells. On the other hand, bromomethylated PPO (BPPO) has excellent membrane forming and mechanical properties as well as good resistance to a number of chemical agents [16]. However, little studies on sulfonation of bromomethylated PPO was reported. The possible reason is that BPPO after homogeneous sulfonation cannot be dissolved in conventional solvents and thus it is hard to prepare membranes by conventional casting method.

Consequently, in this study, the efforts were made to prepare proton-conductive membranes for the potential application in DMFC by heterogeneous sulfonation of BPPO base membranes. The detailed discussion on the various sulfonation processes of BPPO membranes was carried out and some characteristics of the prepared membranes related to DMFC applications, such as proton conductivity, water uptake, methanol uptake and permeation were investigated. Hopefully, an inexpensive proton-conductive membrane with high proton conductivity and extremely low methanol permeability was obtained for DMFC applications.

2. Experimental descriptions

2.1. Materials and bromination of PPO

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of intrinsic viscosity equal to 0.57 dl/g in chloroform at 25 °C was supplied by Institute of Chemical Engineering of Beijing (China). Chlorosulfonic acid, concentrated sulfuric acid, chlorobenzene, bromine and other chemicals used in the experiments were of analytical grade. The bromomethylation of PPO was achieved at 135 °C according to a method reported in a previous article [16], and the extent of bromination was controlled by the amount of bromine being added. Scheme 1 shows the corresponding chemical reactions. The degree of bromine substitution on the methyl group was determined by ^{1}H NMR (Unity plus 400) and listed in Table 1.



Scheme 1. Bromomethylation of PPO (*x*, the bromination degree).

2.2. Membrane preparation

The base membranes were prepared by solvent casting techniques. The bromomethylated PPO (BPPO) was dissolved in chlorobenzene (1 g/3.5 ml) to get the casting solution, which was cast on a glass plate and dried at room temperature for 24 h in a vacuum oven. The base membranes were peeled off the plate and then dried at 50 °C for 24 h in an air oven to remove residual solvent, then heated at 150 °C for 2 h for cross-linking.

The sulfonation of the base membranes was conducted by the mixture of chlorosulfonic acid and concentrated sulfuric acid. First, immerse the membranes in the mixed acid for some time and the mixed acid was heated in a water bath at the needed temperature. Then, take out the sulfonated membranes and immerse them in sulfuric acid with the concentration of 98%, 90%, 80%, 50%, 20% (v/v), deionized water, and 1N NaOH solution in turns. Finally, treat the membranes with 1N HCl for 12 h and then wash them with deionized water thoroughly.

Scheme 2 shows the possible cross-linking and sulfonation processes, which are put forward on the basis of the following experimental results. The detailed descriptions of the various sulfonation processes are displayed in Table 2. The prepared membranes under different bromination or sulfonation process were denoted as M-1, M-2, . . ., etc., as listed in Tables 1 and 2.

For comparison, SPPO membrane with IEC = 1.93 mequiv./g (DS = 27.4%) was formed by casting solution of SPPO in DMF (1 g/3.5 ml) on a glass plate and then drying in an oven at 60 °C.

2.3. Membrane characterizations

2.3.1. FTIR, energy-dispersing X-ray analysis (EDXA) and thermal stability

The membrane samples were dried at 50 °C under vacuum condition for 24 h before testing.

Table 1
The effect of methyl bromination degree

Membrane number	Methyl bromination degree[a] (%)	Properties of the final prepared membrane[b]		
		IEC (mequiv./g dry)	Sulfonation degree (%)	Water uptake (%)
M-1	60	1.50	28.6	12.2
M-2	80	0.97	19.3	10.3
M-3	100	0.54	11.2	5.82

[a] Calculated by NMR results.
[b] Sulfonation conditions: mixed acid containing $ClSO_3H$ and concentrated sulfuric acid of equal volume (50%, v/v), time = 1 h, temperature = 50 °C.

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