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Preparation and properties of novel cross-linked sulfonated poly(arylene ether ketone) for direct methanol fuel cell application

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ABSTRACT

A series of cross-linkable sulfonated poly(arylene ether ketone)s bearing carboxylic acid groups (C-SPAEKs) have been prepared for direct methanol fuel cells (DMFCs). The chemical structure of the cross-linkable copolymers was analyzed by ^{1}H NMR and ^{13}C NMR spectra. Cross-linked membranes were obtained by thermal curing cross-linkable copolymers. The cross-linked network structure caused significant enhancement in the mechanical properties and large reduction in water uptake (WU), swelling ratio and methanol permeability of the membranes. The water uptake and methanol permeability of C-SPAEK-50 membrane was 506.9% (80 °C) and 14.83×10^{-7} cm^2/s, but after cross-linking they reduced to 75.2% and 1.74×10^{-7} cm^2/s, while maintaining proton conductivity of 0.197 S/cm, which was higher than 0.146 S/cm of Nafion 117.

1. Introduction

Today, there is a growing interest in developing proton exchange membranes (PEMs) with highly conductive, low methanol crossover and low cost for DMFCs in order to reduce Ohmic losses and enhance their efficiencies during operation [1–5]. Up to now, perfluorosulfonic acid polymers such as Nafion® have been the reference membranes for DMFCs because of their excellent chemical resistance and mechanical stability as well as their high proton conductivity. However, there are some specific limitations for Nafion® including very high cost, high methanol permeability and loss of the preferable properties at a higher temperature (>80 °C) [6,7]. This stimulated many efforts in the development of alternative PEMs.

In recent years, many kinds of sulfonated aromatic polymers, such as poly(arylene ether)s [8,9], poly(ether sulfone)s [10,11], poly(arylene ether ketone)s [12], poly(phenylene sulfide)s [13], poly(p-phenylene)s [14], polybenzimidazoles [15,16], and polyimides [17,18] have been widely investigated as candidate PEM materials. Although these polymers have their own advantages, such as good proton conductivity, thermal stability and low cost, most of them have a crucial water-swelling problem. Usually, sulfonated aromatic polymers require a high ion exchange capacity (IEC) to achieve sufficient proton conductivity. However, higher IEC usually leads to high water uptake and swelling ratio which will result in the loss of the mechanical strength. Moreover, high methanol permeability of the membranes is accompanied by high water uptake.

Cross-linking of polymer membrane was deemed to be an important prerequisite to alleviate and to overcome the high water uptake and swelling problem. In a recent review, Kerres has introduced two types of cross-linked membranes, summarizing with detailed property comparison [2,19]. However, these reviews posited that ionic acid–base ionomer membranes and covalently cross-linked membranes suffer from reduction of IEC of the membranes after elimination of sulfonic acid groups, which were involved in the cross-linking reaction, thus giving decreasing the proton conductivity of the membrane. Liu et al. recently reported PEMs cross-linked by an esterification reaction between –COOH and –OH [20]. The cross-linked membranes showed an obvious improvement in the dimensional stability, but the introduction of poly(vinyl alcohol) (cross-linker) may dilute the sulfonic acid groups, which resulted in the reduction of proton conductivity. Very few reports have presented covalently cross-linking ionomer membranes without elimination of sulfonic acid groups. Chikashige et al. introduced a trifunctional monomer for branching or cross-linking into the polymer main chain [21]. Zhong et al. and Heo et al. prepared photochemically cross-linkable aromatic membranes containing a double bond (C=C) for photo-cross-linking into the side chain and main chain of the polymers [22,23].

In this study, we synthesized a series of highly sulfonated poly(arylene ether ketone)s bearing pendant carboxylic acid

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groups. In these copolymers, the carboxylic acid groups can undergo Friedel-Craft acylation with the nucleophilic phenyl rings in the main chain to form cross-linked bonds at 160 °C and the sulfonic acid group act as a benign solid catalyst [24–26]. Thus, cross-linked membranes can be obtained by thermal-cross-linked method. Then the properties of the cross-linked membranes were investigated and compared with noncross-linked membranes in detail.

2. Experimental

2.1. Materials

4,4′-Difluorobenzophenone (DFBP) was purchased from Longjing Chemical plant, China. 4,4′-Bis(4-hydroxyphenyl) valeric acid (DPA) was purchased from Aldrich Chemical Co, while sodium 5,5′-carbonyl-bis(2-fluorobenzenesulfonate) (SDFBP) was synthesized as previously reported [27]. Nafion 117 membrane was purchased from Du Pont and treated with a 5 wt% H_2O_2 aqueous solution for 1 h and boiled with 1 M H_2SO_4 aqueous solution for 1 h and washed several times with deionized water. Other reagents were obtained commercially and used as received.

2.2. Synthesis of cross-linkable copolymers (C-SPAEKs)

A typical synthesis procedure of C-SPAEK-50, where 50 denotes the molar ratio of SDFBP to the total moles of DFBP and SDFBP, is described as follows. 12.5 mmol SDFBP, 12.5 mmol DFBP, 25 mmol DPA and 50 mmol potassium carbonate were added into a 250 mL three-neck flask equipped with a mechanical stirrer, a Dean-Stark trap, and a nitrogen gas inlet. Then, 35 mL dimethyl sulfoxide (DMSO) and 17 mL toluene were charged into the reaction flask under a nitrogen atmosphere. The reaction mixture was heated to 140 °C. After dehydration and removal of toluene, the temperature was increased to 180 °C. When the increase of the solution viscosity became obvious, the mixture was cooled to room temperature and poured into 500 mL HCl (0.01 M) solution. The copolymers were washed with hot deionized water for several times, and then dried in vacuum at 80 °C for 24 h.

2.3. Membrane preparation and cross-linking treatment

Membranes were prepared by dissolving C-SPAEKs in dimethylformide (DMF) with 10% (w/v) composition under constant stirring. Resulting solution was cast onto the glass plates followed by heating at 45 °C for 12 h, 60 °C for 2 h, and 100 °C for 6 h to remove the solvent. For the cross-linked membranes, the acid-form C-SPAEKs were dissolved in DMF with 10% (w/v) composition. DMF was slowly removed in the same manner described above. The cross-linking bonds were formed by a Friedel-Craft reaction by heating to 160 °C and holding for 10 h under vacuum. All the membranes were then acidified with 1.0 M HCl solution for 24 h and washed with pure deionized water.

2.4. Characterization of copolymers

FTIR measurements were performed with a Nicolet Impact 410 Fourier transform infrared spectrometer. ^{1}H NMR and ^{13}C NMR experiments were carried out on a 500 MHz Bruker 510 spectrometer with deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane as an internal reference. The intrinsic viscosities of the copolymers were measured in DMF at 25 °C with a copolymer concentration of 5.0 g/L.

2.5. Thermal and mechanical strength analysis

The thermal degradation processes of the membranes were investigated using a Pyris 1 TGA (Perkin-Elmer) under a nitrogen atmosphere from 100 to 700 °C with a heating rate of 10 °C/min under N_2 flow. The mechanical properties of the membranes were measured by Shimazdu AG-I 1 kN at the test speed of 2 mm/min. The size of the films was 15 mm × 4 mm. For each measurement, at least three samples were used and their average value was calculated.

2.6. Water uptake and swelling ratio

The membranes were dried at 120 °C for 24 h until constant weights and lengths were obtained. Then the films were immersed in deionized water at desired temperatures for 24 h. The films were taken out, wiped with tissue quickly, and the weights or lengths of the wet membranes were measured. The water uptake (WU) was calculated by the following equation:

$$\text{WU (\%)} = \frac{W_s - W_d}{W_d} \times 100 \tag{1}$$

where W_s and W_d are the weights of wet and dry samples, respectively. The swelling ratio was calculated from:

$$\text{swelling ratio (\%)} = \frac{l_w - l_d}{l_d} \times 100 \tag{2}$$

where l_w and l_d are the lengths of the wet and dry membranes, respectively.

2.7. Ion exchange capacity (IEC)

Weight based IEC (IEC_w) was determined by titration method. Membrane samples in acid-form were immersed in 1 M NaCl solution for 48 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). Then the H^+ ions were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC_w was calculated from the following formula:

$$IEC_w = \frac{\text{consumed NaOH (mL)} \times \text{molarity NaOH}}{\text{weight of dry membrane}} (\text{meq./g}) \tag{3}$$

Membrane density was measured from a known membrane dimension and weight after drying at 75 °C for 2 h. A volume based IEC (IEC_v) was then obtained by multiplying the membrane density to IEC_w. This calculation resulted in IEC_v (dry) based on dry membrane density. An IEC_v (wet) was then also calculated based on water uptake measurements using the following equation:

$$IEC_v(\text{wet}) = \frac{IEC_v\ (\text{dry})}{(1 + 0.01\text{WU}\delta_m/\delta_w)} (\text{meq./cm}^3) \tag{4}$$

2.8. Proton conductivity

The proton conductivity (σ) of each membrane was measured using an electrode system that contained a four-probe cell connected to an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurement. Repeated measurements were