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Cross-linked poly(ether ether ketone) membranes with pendant sulfonic acid groups for fuel cell applications

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ABSTRACT

A series of cross-linkable poly(ether ether ketone)s (PEEKs) with pendant sulfonic acid groups were synthesized and used to prepare polymer electrolyte membranes for fuel cells. These transparent and flexible membranes are insoluble in common organic solvents and demonstrated little swelling in hot water. Thermal and mechanical stability of the membranes were evaluated using a thermogravimetric analyzer and strain–stress test, respectively. The methanol permeability of the cross-linked PEEKs with pendant sulfonic acid group membranes is much lower than that of Nafion 117 membrane, by more than 10 times. The conductivity of the cross-linked PEEK membrane with a 5% degree of cross-linking is comparable to that of Nafion 117 at 50 °C (0.053 S cm^{-1}) and even better above 80 °C. This kind of membrane is expected to be a good alternative to Nafion 117 in polymer electrolyte fuel cell applications.

1. Introduction

Polymer electrolyte membrane fuel cells have been extensively studied as electrochemical devices for convenient and efficient power sources. The proton exchange membrane is a core component in the system that should not only exhibit low resistance to the diffusion of protons from one electrode to the other, but also provide a barrier to keep the fuel and oxidant separate. To achieve a high fuel cell efficiency, the following membrane properties are desirable [1,2]: (1) high proton conductivity; (2) adequate mechanical strength and stability; (3) low fuel or gas permeability; (4) chemical and electrochemical stability; (5) low swelling; (6) low cost. Currently, perfluorosulfonic acid polymer membranes such as Nafion are the only commercially available proton exchange membranes for fuel cells because of high proton conductivity and outstanding chemical and thermal stability at temperatures below 80 °C [3]. Perfluorosulfonic acid polymer membranes, however, are quite expensive and exhibit high methanol permeability, which drastically reduces direct-methanol fuel cell (DMFC) performance and limits their extensive application. In hydrogen fuel cells, perfluorosulfonic acid polymer membranes show low conductivity and thus low performance efficiency at high temperatures above 80 °C by de-sorption of water molecules. In view of those problems involved with the Nafion membrane, many efforts have been focused on development of low cost alternatives for large-scale application. Many candidate polymers are based on polyaromatic or polyheterocyclic repeat units, such as: polysulfones (PSU) [4,5]; poly(ether ketone)s (PEK) [6,7]; poly(ether sulfone)s (PES) [8]; and polybenzimidazole (PBI) [9,10], as they have excellent chemical resistance, high thermo-oxidative stability, and low cost. Among these polymers, sulfonated poly(ether ether ketone) (SPEEK) was shown to be of considerable promise, as it allows membrane casting from organic solutions and thus offers a more convenient and less expensive preparation process.

Most sulfonated PEEKs were synthesized by post-sulfonation of commercial polymers or direct copolymerization of sulfonated monomers. The post-sulfonation method is a simple procedure because of the availability of commercial PEEK, but it is difficult to control the Degree of Sulfonation (DS) and distribution of the sulfonic acid groups along the main chain. In addition, the rigorous reaction conditions of high temperature and concentrated sulfuric acid may lead to degradation of the PEEK backbone or cross-linking of the polymer chains [11]. In the case of direct copolymerization of sulfonated monomers and non-sulfonated monomers [12], DS and chain structure were well defined; however, high molecular weight PEEK is difficult to achieve.

In the sulfonated polymer membranes, proton conductivity was strongly dependent on the degree of sulfonation. SPEEK with high degrees of sulfonation usually exhibited high proton conductivity. However, the mechanical properties of SPEEK tend to deteriorate progressively upon sulfonation *via* extreme swelling in water, making long-term stability of the sulfonated membrane questionable. Cross-linking [13–18] is a simple and efficient way to enhance

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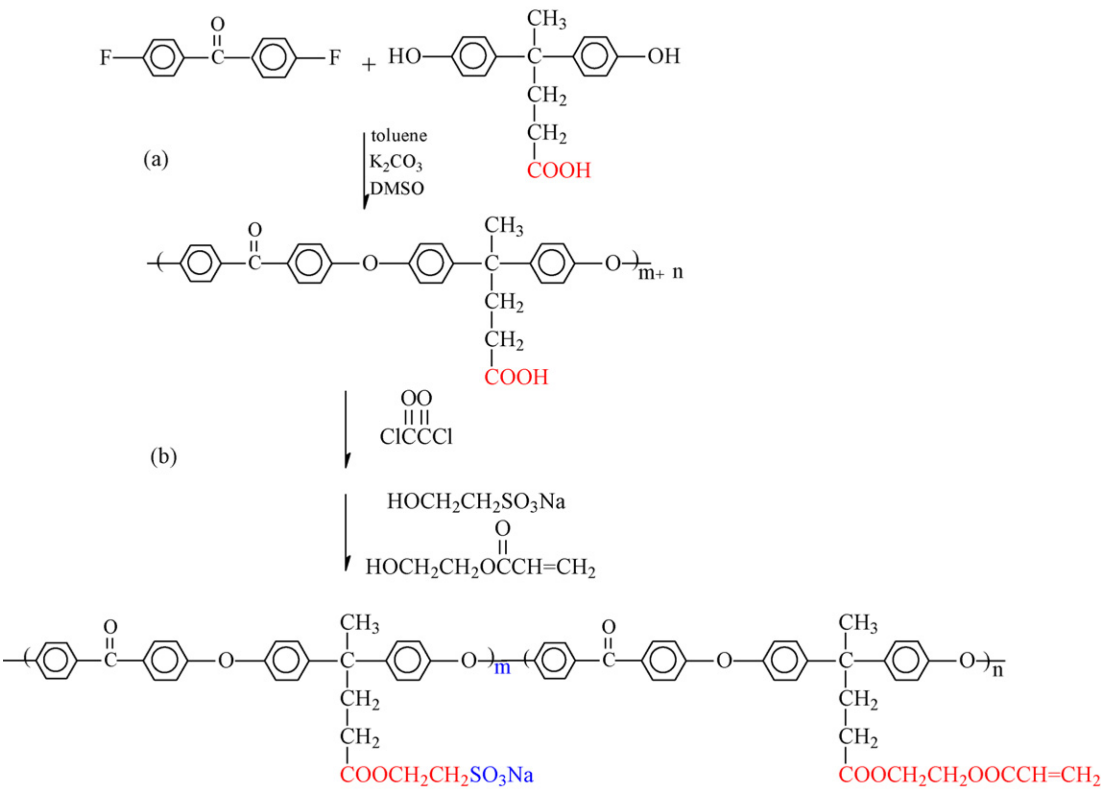

Scheme 1. Synthetic pathway: (a) functionalized poly(ether ether ketone) with carboxylic groups; (b) cross-linkable poly(ether ether ketone) with pendent sulfonation groups.

mechanical strength and also limits methanol diffusion and water uptake.

Recently, several polymer membranes with pendant sulfonic acid group were reported [19–21] with excellent mechanical properties, good thermal and oxidative stability, and acceptable dimensional stability in hot water. Miyatake et al. [22,23] also suggested that the polymers with sulfonated groups attached to the pendant side groups are very stable under heat, hydrolysis, and oxidation. Wang et al. [24] reported that polymers with pendant sulfonic acid groups are more stable to hydrolysis than those with sulfonic acid groups directly attached the main chain.

In this study, a series of cross-linked sulfonated PEEK proton exchange membranes were prepared. Grafting of sulfuric acid groups onto the PEEK main chain provided the opportunity of controlling the ion exchange capacity and sulfonation sites, thereby providing the opportunity to tune the properties of the polymer by controlling the degree of substitution. The cross-linked membranes were expected to possess high proton conductivity and low methanol diffusion with high chemical, thermal, and mechanical stability.

2. Experimental

2.1. Materials

4,4-Bis(4-hydroxyphenyl)-valeric acid, 4,4′-difluorobenzophenone, potassium carbonate (K_2CO_3), dimethyl sulfoxide (DMSO), toluene, isethionic acid sodium salt, 2-hydroxyethyl acrylate, dimethylformamide (DMF), hydrochloric acid (HCl), methanol, oxalyl chloride, tetrahydrofuran (THF), and benzoyl peroxide (BPO) were purchased from Aldrich (Aldrich, USA) and used directly.

2.2. Synthesis of poly(ether ether ketone) (PEEK)

The synthesis of PEEK was performed according to a procedure described by Thomas et al. [25]. As shown in Scheme 1a, dry DMSO (50.0 g), toluene (30.0 g), 4,4-bis(4-hydroxyphenyl)-valeric acid (0.01 mol), and K_2CO_3 (0.02 mol) were added to a 250 mL 3-necked round bottom flask, equipped with a Dean-stark trap and nitrogen inlet. The reaction mixture was first stirred for approximately 2 h at room temperature, then raised up to 145 °C for 4 h with continuous stirring. Subsequently, the reaction mixture was cooled to room temperature and 4,4′-difluorobenzophenone (0.01 mol) was added to the mixture. The reaction mixture temperature was slowly raised to 148 °C for 4 h to remove water by azeotropic distillation. The temperature was then raised to 160 °C until the product precipitated from the solution (4–6 h). The mixture was cooled to room temperature and the precipitate dissolved in 50 mL of THF/concentrated HCl mixture (40/10). The crude polycondensate was obtained by pouring the solution into 1000 mL water. The crude product was washed with deionized water and dried in a vacuum oven. The dry, crude product was dissolved in 50 mL of THF and precipitated again in 800 mL methanol; the pure product was dried for 2 d at 80 °C under vacuum to obtain a 94% yield.

^{1}H NMR (ppm, DMSO-d_6) 1, 7.03; 2, 7.72; 3, 6.945; 4, 7.24; 5, 1.58; 6, 2.02; 7, 2.45; 8, 12, respectively.

2.3. Synthesis of PEEK with pendant sulfonic acid groups

A series of cross-linkable, sulfonated poly(ether ether ketones) (CSPEEKs) with different DS were synthesized as shown in Scheme 1b. The compositions of all the CSPEEKs are presented in Table 1. For CSPEEK4, 4.64 g (0.01 mol) PEEK was dissolved in 40 mL of dry THF, after 1.5 mL of oxalyl chloride was added. The