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Crosslinking effect in nanocrystalline cellulose reinforced sulfonated poly (aryl ether ketone) proton exchange membranes

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ABSTRACT

Two novel series of poly(aryl ether ketone)s (PAEK) bearing pendant carboxylic acid groups have been synthesized, and subsequently sulfonated to obtain sulfonated poly(aryl ether ketone)s with carboxylic acid groups (SPAEK-COOH-*x*). The expected structures of the sulfonated copolymers were confirmed by FTIR. Modified nanocrystalline cellulose (NCC) was prepared and introduced into the SPAEK-COOH-*x* as the "performance-enhancing" filler and crosslinking agent. The nanocomposite proton exchange membranes were prepared via a solution-casting procedure. The composite membranes containing NCC presented the higher proton conductivity and better mechanical properties. After further crosslinking, the covalent crosslinked composite membranes showed even better mechanical properties while the proton conductivity and thermal stability were maintained. The hydrophilic/hydrophobic domains were observed from the TEM morphology investigation of COOH-10/NCC-*y* and C/COOH-10/NCC-*y* membranes. A balance of mechanical stabilities, proton conductivity, and thermal property could be designed by the incorporation of NCC and the crosslinking between NCC and SPAEK-COOH-10 to meet the requirements for the applications in the fuel cells.

1. Introduction

Fuel cell is a kind of electrochemical cell which is different from the traditional internal combustion engine. It has high conversion efficiency, low emission, high working current and high power and many other advantages. Proton exchange membrane fuel cells (PEMFCs) have received extensive attention on account of their simple system features, such as light weight, environmentally friendly and high energy conversion efficiency [1]. Proton exchange membrane (PEM) is a key component in PEMFCs for providing proton transfer and preventing fuel penetration between anode and cathode [2]. So far, perfluorosulfonic acid (PFSA) polymers such as Nafions (DuPont) are the most common commercially available materials in fuel cell applications due to their high proton conductivity and chemical stability. But it also has well-known limitations, such as high cost, fuel crossover and restricted operation temperature, have limited their applications in PEMFCs [3].

As a kind of special engineering plastics, poly (aryl ether ketone) (PAEK) has excellent thermal oxidative stability properties, mechanical properties and good chemical stability for advanced materials. And the sulfonated PAEK (SPAEK) not only inherited the good mechanical properties and thermal stabilities of PAEK, but also present good proton conductivity because of the introduced sulfonic acid group. Therefore, SPAEK is promising in the application prospect of PEMs. A large number of SPAEK-type PEMs have been obtained via a post-sulfonation of polymeric precursors or a copolymerization of sulfonated monomers [4,5].

Crosslinking has been an effective method for the formation of compact membrane structure which is considered as a promising strategy to control the excessive swelling and methanol permeability of the PEMs [6]. The crosslinked polymeric membranes had outstanding properties including high proton conductivity, excellent mechanical properties and good dimensional stability [7]. Presently, organic-inorganic nanosize crosslinked composite membranes have attracted much attention for PEM due to their excellent performance. Several inorganic nanoparticle, such as SiO_2 [8,9], polyhedral oligomeric silsesquioxane (POSS) [10], and graphene [11], have been successfully introduced into sulfonated polymer matrices as "performance-enhancing" components. Chun [8] introduced silica nanoparticles into poly

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(aryl ether ketone) and prepared organic-inorganic composite membranes by esterification reaction. All composite membranes show better water uptake and proton conductivity than the unmodified membrane. Yen [12] incorporated POSS moieties into sulfonated poly(ether ether ketone) (SPEEK) to form a new crosslinked proton exchange membrane (PEM). A PEM formed by incorporating 17.5% of the crosslinker (containing POSS macromer and sulfonic acid groups) into SPEEK exhibits excellent comprehensive performance. He [11] prepared polydopamine-modified graphene oxide (DGO) nanocomposite membrane by the presentation of the acid-base pairs. The DGO sheets are interconnected and homogeneously dispersed in SPEEK matrix, which provides unique rearrangement of the nanophase-separated structure and chain packing of nanocomposite membrane through interfacial electrostatic attractions. The nanocomposite membrane exhibits much higher proton conductivity than the polymer control membrane. From this point of view, the incorporation of inorganic materials into sulfonated polymers by crosslinking reaction has become a principal method of fuel cell technology to improving the comprehensive performance of proton exchange membrane.

Recently, several inorganic particles or organic polymers, such as SiO_2 [13], POSS [14], and graphene [15] have been successfully introduced into sulfonated polymer matrices as “performance-enhancing” components. For example, POSS has a cubic octameric molecule with an inner inorganic silicon and oxygen framework, which is externally surrounded by organic function groups. It has a nanometer sized cage nanostructure that can be further functionalized with various functional groups. Geng [16] introduced octaAmino POSS-Ph8 to poly(ether ether ketone) and observed that the tensile strength of composite membranes was 55% higher than that of original membranes under the same test conditions.

As the most abundant renewable polymer in the world, biodegradable cellulose presents large quantity of hydroxyl groups [17]. Nanocrystalline cellulose (NCC) is typically a rigid crystalline with 1–100 nm in diameter and tens to hundreds of nanometers in length. Extensive studies have shown that NCC has excellent performance in tensile strength and Young's modulus, and should be an extremely good reinforcing filler for various composite materials for improving the mechanical performance of polymers with quite low NCC concentrations [18,19]. NCC is commonly produced from the hydrolysis of microcrystalline cellulose (MCC) with a strong acid such as sulfuric acid [20]. In the sulfuric acids, MCC break down into NCC and sulfonic acid groups will be modified onto the NCC surface. NCC is apt to be modified because of the rich active hydroxyl groups on their surface.

Crosslinking has been an effective method for the formation of compact membrane structure which is considered as a promising strategy to control the excessive swelling and methanol permeability of the PEMs [6]. The crosslinked polymeric membranes had outstanding properties including high proton conductivity, excellent mechanical properties and good dimensional stability [21]. To date, many crosslinking methods have been studied, such as ionic crosslinking [22] and covalent crosslinking [23,24]. It has already been demonstrated that membranes prepared from various acid-base polymer blends offered good mechanical properties and competitive fuel cell performance. Wycisk [25] prepared acid-base complex through acid-base interaction between the sulfonic acid group of Nafion and the imidazole group of PBI which functioned as a crosslinker with the resultant reduction of swelling and methanol permeability in such a system. Zhang [26] prepared covalently crosslinked ionomer membranes by the reaction with the crosslinker diiodobutane and subsequent hydrolysis of the sulfochloride groups by aqueous post-treatment. The membranes showed strongly reduced swelling.

In this study, a new family of SPAEK copolymers with carboxyl group was successfully synthesized through a mild postsulfonation reaction. As a “performance-enhanced” component, sulfonic acid functionalized NCC was introduced into the SPAEK matrix to form a hydrogen bond between the −OH of NCC and $-SO_3$ groups of SPAEK. Furthermore, the covalent crosslinking membrane was prepared via esterification reaction between the −OH of NCC and −COOH groups of SPAEK. The properties were compared before and after the esterification. And the effect of NCC and carboxyl groups content on the properties of the composite membranes was also studied. PEMs with excellent mechanical and swelling performance while maintaining a high standard of proton conductivity via crosslinking was obtained.

2. Experimental

2.1. Materials

4,4-Bis(4-hydroxyphenyl)valeric acid and 2-phenylhydroquinone were purchased from Energy Chemical and Sigma-Aldrich, individually. 1,4-Bis(4-fluorobenzoyl)benzene was obtained from Jilin University, China. K_2CO_3, sulfuric acid (95–98%) and toluene was purchased from Beijing Chemical Reagent Company, China. K_2CO_3 was dried at 120 °C for 24 h and ground into fine powder prior to use. Cellulose microcrystalline (25 μm, Powder) was obtained from Admas Company. Dimethyl sulfoxide (DMSO) and tetramethylene sulfone (TMS) were purchased from Tianjin Chemical Reagent, China. All other organic solvents were obtained from commercial sources and purified by conventional methods.

2.2. Preparation of a sulfonic acid-functionalized nanocrystalline cellulose

NCC was prepared by the following method and the same preparation conditions of NCC were reported in our previous work [27]. Firstly, dilute sulfuric acid (175 mL, 64%) was prepared by concentrated sulfuric acid (98%). MCC powder (10.0 g) was then put into a 1000 mL round-bottomed flask and dilute sulfuric acid was added slowly for 3 h at 45 °C with continuous stirring. The reaction was terminated by diluting the mixture with a large amount of deionized water. The excess acid in newly generated suspension was removed by centrifugation, and the residual acid was further removed by dialysis with deionized water until the pH of the suspension reached neutral. Finally, the chemically modified NCC bearing $-SO_3H$ and −OH groups was received by freeze-drying the suspension for 8 h.

2.3. Synthesis of the sulfonated carboxyl-containing polyaryletherketone derived from a copolymer precursor

The synthesis of the sulfonated carboxyl-containing polyaryletherketone (SPAEK-COOH-*x*) was shown in Scheme 1. The mole ratios of 4,4-bis(4-hydroxyphenyl)valeric to 2-phenylhydroquinone for the synthesis of SPAEK-COOH-10 and SPAEK-COOH-30 copolymers are 1:9 and 3:7, respectively. A series of crosslinked polymeric membranes with different NCC content were prepared. The polycondensation reaction for synthesizing SPAEK-COOH-10 was carried out as follows: 4,4-bis(4-hydroxyphenyl)valeric acid (0.4292 g, 1.5 mmol), 2-phenylhydroquinone (2.5135 g, 13.5 mmol), 1,4-bis(4-fluorobenzoyl)benzene (4.8343 g, 15 mmol), excess K_2CO_3 (3.0452 g, 22 mmol), 24 mL of TMS and 8 mL of toluene were stirred in a 100 mL three-neck round-bottom flask under nitrogen atmosphere at 140 °C–160 °C for 5 h with a Dean-Stark trap in order to remove water. The reaction mixture was then heated to 180–190 °C for 2.5 h. Then 3 mL of TMS was added and the homogeneous viscous solution was poured into 1000 mL deionized water under the condition of continuous stirring. The isolated polymer was ground into powder and alternated washed with water and alcohol in order to remove the salts and solvents, and dried in oven at 60 °C for three days. The synthesis process of SPAEK-COOH-30 was the same as that of the SPAEK-COOH-10.

Dry powdered polymer (5.0 g, SPAEK-COOH-10 or SPAEK-COOH-30) and 95–98% concentrated sulfuric acid (100 mL) were placed in a 250 mL three-neck bottle and stirred at room temperature for 24 h. The homogeneous viscous solution was poured into a mixture of ice water.