



Nanocrystalline cellulose reinforced sulfonated fluorenyl-containing polyaryletherketones for proton exchange membranes

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ABSTRACT

Sulfonated fluorenyl-containing polyaryletherketones (SFPAEKs) were synthesized through a postsulfonation approach under a mild reaction condition. The composite proton exchange membranes based on SFPAEKs and various amounts of the modified nanocrystalline cellulose (NCC) were prepared by solution casting method. The existence of the multiple hydroxyl and sulfonic acid groups on the chemically modified nanocrystalline cellulose was supposed to benefit the formation of hydrogen-bond network and proton-conducting channels, which would improve the proton conducting ability of the composite membranes. Furthermore, the properties, such as mechanical properties, thermal stability, water uptake, swelling ratio and so on, were thoroughly investigated. In comparison to the pristine SFPAEK, the composite membranes containing a “performance enhanced” NCC component presented the higher proton conductivity and better mechanical properties. It was found that the proton conductivity of the composite membrane with 4 wt% of NCC could reach 0.234 S cm^{-1} at $100 \text{ }^\circ\text{C}$, and this value was higher than that of most of the reported membranes. The results showed that the modified nanocrystalline cellulose reinforced SFPAEK composite membrane would be promising for the application as middle-temperature proton exchange membranes in fuel cells.

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1. Introduction

Fuel cell industry has made considerable progress and moved into a new market development phase after a long period of technical development [1,2]. Proton exchange membrane fuel cells (PEMFCs) are the devices for transforming chemical energy directly into electricity for portable applications, such as notebook computers and mobile phones [3,4]. Because of their outstanding features, such as high energy density, high efficiency and environmental friendliness, PEMFCs are considered to be a kind of promising clean power source [5]. Extensive efforts are being made to develop proton exchange membranes (PEMs). PEMs, as a selective medium for proton transportation from the anode to the cathode, are regarded as the key component of the proton exchange membrane fuel cells (PEMFCs) [6,7]. Known as a representative of the PEMs, Dupont's Nafion is typically used as the polymer electrolytes in PEMFCs because of its excellent chemical and mechanical stabilities as well as high proton conductivity. However, some drawbacks, such as

high cost, low operation temperature ($\leq 80 \text{ }^\circ\text{C}$), high fuel crossover and environmental recycling uncertainties, have limited Nafion's widespread commercial applications [8]. Therefore, it is necessary to develop some new PEMs with low cost and excellent performance aiming to replace Nafion.

Polyaryletherketones (PAEKs) are a class of high-performance polymers known for their well combination of chemical, physical, and mechanical properties [9–11]. Majority of PAEKs-type PEMs were synthesized via a post-sulfonation of polymeric precursors or a copolymerization of sulfonated monomers [12]. It was reported that the post-sulfonation approach was relatively simple, and the difficulties were the structure design of the high-molecular-weight precursors and the optimization of the sulfonation reaction conditions to avoid the chain degradation or side reactions [13]. In order to prepare exclusively sulfonated polymers presenting well-defined chemical structure and good performance, new polymeric precursors containing fluorenyl-containing units were developed [14]. Theoretically, four sites on each fluorenyl group can be substituted by $-\text{SO}_3\text{H}$ groups if the sulfonation reactions are well controlled.

Normally, high proton conductivity could be obtained if there are enough sulfonic acid groups on the molecular chains of sulfonated polyaryletherketones (SPAEEKs) [15]. However, plenty of sulfonic acid groups will result in the excessive water absorption of the SPAEK

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membranes and the loss of the mechanical strength and dimensional stability under the circumstances of high temperature and high humidity. To well balance the proton conductivity and dimensional stability, an effective strategy of the incorporation of nano-sized materials, such as sulfonated nanoparticles, carbon nanotubes (CNTs) and nanofibers into the SPAEK-type PEMs were applied to further modify their overall performance [16].

As one of the most abundant materials in nature, cellulose can be extracted from different plants including ramie, cotton and jute [17,18]. Nanocrystalline cellulose (NCC) is typically a rigid nanocrystalline domain with 1–100 nm in diameter and tens to hundreds of nanometers in length [19]. NCC possesses several advantages, such as excellent mechanical property, non-toxicity, renewable nature, high crystallinity and high surface area [20]. And it can be served as a good additive being capable of improving the mechanical performance of polymers with quite low NCC concentrations [21,22]. The abundant hydroxyl groups on cellulose molecules facilitate their further chemical modifications, and sulfonic acid-containing NCC has been successfully produced by treating microcrystalline cellulose (MCC) powders in sulfonic acid [19].

In the present study, a new family of sulfonated fluorenyl-containing polyaryletherketones (SFPAEKs) was successfully prepared through a mild postsulfonation reaction. As a “performance-enhanced” component, sulfonic acid functionalized NCC was introduced into the SFPAEK matrix to obtain some composite membranes with high proton conductivity, high strength and good dimensional stability. The properties of the NCC reinforced SFPAEKs composites related to PEM applications have been thoroughly evaluated.

2. Experimental

2.1. Materials

4,4-(9-Fluorenylidene)-diphenol and 1,4-hydroquinone were purchased from Sigma-Aldrich. 1,4-Bis(4-fluorobenzoyl)benzene was offered by Jilin University, China. K_2CO_3 (Beijing Chemical Reagent, China) was dried at 120 °C for 24 h and ground into fine powder before use. Cellulose microcrystalline (25 μ m, Powder) was purchased from Admas Company. Sulfuric acid (95–98%) and toluene were obtained from Beijing Chemical Reagent, China. 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 sulfonic acid-functionalized nanocrystalline cellulose

The first step was to mix deionized water and microcrystalline cellulose (MCC). The water/MCC-suspension was then put into a 1000 mL round-bottomed flask and stirred while concentrated sulfuric acid was added slowly until the acid concentration was reached 64%. After stirring for 3 h at 45 °C, the reaction was terminated by diluting the mixture with a big amount of water. The excess acid was removed by centrifugation, and the residual acid was further removed by dialysis with deionized water. 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 fluorenyl-containing polyaryletherketone derived from a copolymer precursor

The synthesis of fluorenyl-containing polyaryletherketone copolymer precursor (FPAEK) was as following. Into a 100 mL three-neck round-bottom flask, 2.4529 g (7 mmol) of 4,4-(9-fluorenylidene)-diphenol, 0.7710 g (7 mmol) of 1,4-hydroquinone, 4.5120 g (14 mmol) of 1,4-bis(4-fluorobenzoyl) benzene, 2.073 g (15 mmol) of K_2CO_3 , 24 mL of TMS and 8 mL of toluene were added. The reaction mixture was stirred for 3 h at 140 °C with a Dean–Stark trap and a condenser under nitrogen protection. The toluene was removed after azeotropic

distillation with toluene. The reaction temperature was then heated to 180–190 °C for 2.5 h. The viscous solution was poured into 1 L of deionized water slowly with stirring to precipitate the produced polymer prior to another 6 mL of TMS was added. The isolated polymer was refluxed in deionized water and ethanol several times after pulverized into powder in order to remove the salts and solvents, and dried in oven at 80 °C for three days.

Sulfuric acid (100 mL) and fully dried FPAEK powder (5.0 g) were added into a three-neck bottle and stirred at room temperature. The homogeneous viscous solution was poured into a mixture of ice water to get a white silk-like solid. The solid was washed with hot water until the washed water was neutral. The synthesis of the sulfonated FPAEK (SFPAEK) was as follows:

2.4. Preparation of composite membranes

The SFPAEK/NCC composite membranes were prepared by solution casting. NCC powder was dispersed in DMSO, and then SFPAEK was added. The mixture was stirred for another two days to form a homogeneous solution. The filtered solution was spread on a clean glass plate and dried at 30 °C for 12 h, then 60 °C for 12 h, and finally 80 °C for two days. At last, the membranes were transferred into 1 M HCl at room temperature for 24 h, and thereafter thoroughly washed with deionized water until the washed water achieved neutral. The NCC contents in quality in the composite membranes were 0%, 2%, 4%, 6%, 8%, and 10%. They were named SFPAEK/NCC-0, SFPAEK/NCC-2, SFPAEK/NCC-4, SFPAEK/NCC-6, SFPAEK/NCC-8 and SFPAEK/NCC-10, respectively. The thickness of the membranes was in the range of 90–100 μ m.

2.5. Characterization

Fourier transform infrared spectroscopy (FTIR, Nicolet iS10, USA) was used to characterize the chemical structure and composition of the NCC and membrane samples. The spectra were measured in Attenuated Total Reflectance (ATR) transmittance mode over a wave number range of 4000–550 cm^{-1} and a resolution of 32 cm^{-1} .

The morphology observations of NCC and composite membranes were performed with transmission electron microscopy (TEM) instrument. The model was JEOL JEM-1011, and the accelerating voltage was 100 kV. NCC was dispersed in deionized water. 0.05 g of SFPAEK/NCC-4 composite membrane was dissolved into 5 mL of DMSO. Afterward, one drop of the solution was dipped onto the TEM sample grid, respectively. The grids were dried at 80 °C for 12 h before TEM observation.

The crystal structure of proton exchange composite membranes and nanocrystalline cellulose was investigated with X-ray diffraction spectroscopy (XRD) instrument D/max-2500PC Rigaku (Japan) at 40 kV and 100 mA scanned from 5° to 60°. Copper target (Cu Ka, $\lambda = 1.54 \text{ \AA}$) was selected as a radiation source. The scan step was 0.02°, and the scan speed was 3°/min.

TGA (Netzch Sta 449c) was used to determine the thermal degradation of the NCC and composite membranes. Firstly, the vacuum dried sample was kept in TGA furnace at 100 °C under nitrogen atmosphere for 30 min to further remove the moisture. Then the sample was reheated to 800 °C with a rate of 10 °C/min in nitrogen atmosphere.

The mechanical properties of wet membranes were evaluated at room temperature on a SHIMADZU AG-I 1KN instrument with a strain rate of 2 mm/min. Before test, the samples were immersed in deionized water at least 24 h and the sample size was 50 mm \times 5 mm. The measurement results of each membrane were measured at least five times. The test result was the average of a plurality of parallel samples.

The water uptake and swelling ratio of the membranes were determined by measuring the variations in weight and length before and after hydration. All membrane samples were dried at 80 °C in vacuum at least 24 h, and then the lengths and weights of the samples were measured which was recorded as W_{dry} and L_{dry} , respectively. The

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