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Novel nanocomposite membranes based on sulfonated mesoporous silica nanoparticles modified sulfonated polyimides for direct methanol fuel cells

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ABSTRACT

Novel nanocomposite proton exchange membranes were prepared by using sulfonated mesoporous silica nanoparticles (SMSNs) as inorganic fillers through direct blending with sulfonated polyimides (SPIs). The microstructure and properties of the resulting hybrid membranes were studied. The SMSNs with a diameter of 50–300 nm exhibited the ordered mesopores of about 2.3 nm. The introduction of sulfonated mesoporous silica improved the thermal stability, water uptake and methanol permeability of the resulting nanocomposite membranes as compared with SPI. The hybrid membrane with 3 wt% SMSNs showed the highest water-uptake value of 54.2% and lowest methanol permeability value of 5.23×10^{-6} cm^2 s^{-1}. When the content of SMSNs was higher than 3 wt%, both the values decreased slightly because of the aggregation of SMSNs. All of the membranes showed the excellent proton conductivity as compared with Nafion 117. When 7 wt% SMSNs were incorporated into the SPI, the membrane sample presented the highest proton conductivity at different testing temperatures, indicating that the addition of SMSNs can also improve the proton conductivity of composite membranes.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) as a new electric power source have the important applications for automobiles and residential heat and power supply among all kinds of fuel cells because of high efficiency and clean exhaust gas. Direct methanol fuel cells (DMFCs) have been extensively studied in PEFCs. DMFCs have high efficiency and are energy-saving and portable. The polymer electrolyte membrane (PEM) is the most important part in a PEFC. The performance of PEFCs is dependent on the electrocatalysts [1,2] and properties of PEM to a large extent. Nafion series are the most common commercially used sulfonated perfluoropolymers due to their excellent thermal properties and high proton conductivity. However, Nafion membranes still have some drawbacks, such as low conductivity at low humidity and high temperatures, high methanol permeability as well as high cost. These defects impede their wider practical applications [3–6]. So it is highly desirable to improve the properties of PEM by modifying Nafion membranes or developing novel structure of PEM.

The studies for improving the properties of PEM include: (1) to modify the surface of PEM [7], (2) to prepare crosslinking or block polymers [8], (3) to prepare new kinds of PEM [9] and (4) to prepare organic–inorganic hybrid membranes by introducing inorganic components into the polymers [10]. In particular, the fabrication of organic–inorganic hybrid membranes is a promising and widely used method. Inclusion of inorganic materials mainly improves the thermal stability and water retention properties. Most Nafion-based hybrid membranes have been prepared by the introduction of ceramic oxoclusters [11–13]. The inorganic materials can improve not only the properties of Nafion, but also of other PEM materials, such as sulfonated poly(ether ether ketone), sulfonated polysulfones, sulfonated polyimides, and so on. The direct blending method is a feasible and common used route for preparing the organic–inorganic hybrid membranes. Many studies indicated that the introduction of hydrophilic inorganic particles, such as silica [14,15], clay [16], titanium dioxide [17], zeolite [18] and carbon nanotube [19], could improve the water uptake of the membranes and thus the proton conductivity could be kept at the high level at higher temperature. Also, the addition of solid acids [20,21] and heteropolyacids [22] could also improve the proton conductivity of the hybrid membranes.

It is known that the mesoporous silica is an inorganic poriferous material which owns large surface area and periodic mesoporous structure along with the high chemical and thermal stability [23]. Besides, the pores of mesoporous silica could be modified by using amine, thiol and sulfonic acid groups, etc. Thus, mesoporous silica could be used in various fields such as catalyst, sensor, proton exchange materials and selective separation [24–27]. Also, mesoporous silica is a usual inorganic material that can be introduced

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into the polymers to prepare proton exchange membranes. Because of the existence of mesoporous structure, the mesoporous silica may hold more water and this is helpful for improving proton conducting abilities. Also, the dispersion of the inorganic silica can block the transport channel of methanol when the membranes are applied in DMFCs. For example, Tominaga et al. prepared hexagonally ordered mesoporous silica as inorganic materials, and they added it to Nafion to prepare composite membranes [28]. The composite membranes showed 1.5 time higher proton conductivities at 80 °C than Nafion and they also displayed good thermal properties. Lin and co-workers [29] introduced sulfonated mesoporous silica into Nafion and the resulting composite membranes showed an increase of proton conductivities when sulfonated mesoporous silica content increased. Also, the methanol permeability of the composite membrane with 3 wt% sulfonated mesoporous silica was 30% lower than that of Nafion. Recently, the novel mesoporous silica containing sulfonic acid groups has been prepared, and this kind of mesoporous silica could be used as solid proton conductive electrolytes [30]. Although the mesoporous silica has many excellent properties, there are few studies on introducing sulfonated mesoporous silica nanoparticles into sulfonated polyimides to fabricate organic–inorganic hybrid proton exchange membranes for DMFCs.

In this paper, a series of sulfonated mesoporous silica nanoparticles (SMSNs)/sulfonated polyimide (SPI) nanocomposite proton exchange membranes were prepared by using blending method. The 50–300 nm of SMSNs with the ordered mesopores of about 2.3 nm were prepared from γ-thiopropyltrimethoxysilane and tetraethyl orthosilicate under basic condition in the presence of template agents. The mesoporous structure of SMSNs improved the water uptake of SPI membranes, and resulted in the higher proton conductivities. The introduction of SMSNs also improved the thermal properties, mechanical properties and methanol permeability of the pure SPI. The structure, morphology and properties of these nanocomposite membranes were studied in detail.

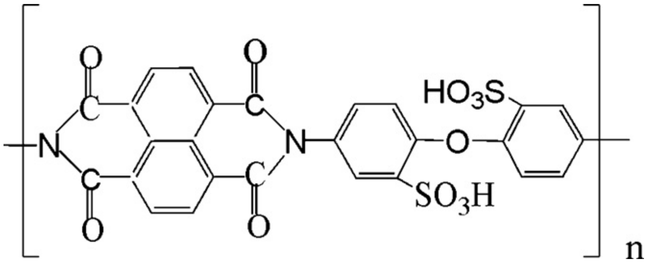
2. Experimental

2.1. Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) and 4,4′-diaminodiphenyl ether (ODA) were purchased from Tokyo Kasel Co., and were purified by vacuo sublimation prior to use. 4,4′-Diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) was synthesized using ODA as raw material by the method mentioned elsewhere [31]. Benzoic acid, concentrated hydrochloric acid, concentrated sulfuric acid (98%), acetone, ethanol, sodium hydroxide, hexadecyltrimethyl ammonium bromide (CTAB), γ-thiopropyltrimethoxysilane (KH-590), hydrogen peroxide (33%) and fuming sulfuric acid (SO_3, 60%) were used as received. Dimethyl sulfoxide (DMSO), *m*-cresol and tetraethyl orthosilicate (TEOS) were distilled prior to use. Et_3N was distilled and dried with 4 A molecular sieves prior to use.

2.2. Synthesis of sulfonated polyimide (SPI)

To a 250 mL dried three-neck flask were added 5.4 g (15 mmol) of ODADS, 50 mL of *m*-cresol, and 3.6 g (36 mmol) of triethylamine successively under nitrogen flow with stirring. After ODADS was completely dissolved, 4.02 g (15 mmol) of NTDA and 2.6 g (21.3 mmol) of benzoic acid were added. The mixture was stirred at room temperature for a few minutes, and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to 100 °C, an additional 50 mL of *m*-cresol was added to dilute the viscous solution, which was then poured into 800 mL of acetone. The fiberlike precipitate was filtered off, washed with acetone, and dried in vacuo. Scheme 1 shows the structure of SPI. The directory of IR and NMR signals of SPI is listed in Supporting Information.



Scheme 1. Chemical structure of SPI.

2.3. Synthesis of sulfonated mesoporous silica nanoparticles (SMSNs)

5.3 mL of 2 M NaOH and 1.53 g of CTAB were dissolved in 720 mL of water, the resulting solution was heated to 80 °C, then the mixture of 7.5 mL TEOS and 0.64 mL KH-590 was added to the solution under stirring and the reaction was kept at this temperature for 2 h. After the reaction, white precipitate was obtained by centrifugation. The precipitate was washed with deionized water one time. Template extraction was performed with 30 mL conc. HCl in 240 mL of ethanol. Usually, one gram of sample was treated two to three times with 100 mL of the extraction solution by sonication for 30 min. Subsequent washing was performed as described above. After the extraction of template, the precipitate was added into concentrated hydrogen peroxide (33%) for 24 h in order to oxidate the mercapto groups of KH-590 moieties to sulfonic groups. The final obtained samples were separated by centrifugation, washed with deionized water three times and dried at 60 °C under vacuum.

2.4. Preparation of SPI/SMSNs nanocomposite membranes

A certain amount of SMSNs was added into DMSO and the mixture was sonicated for 30 min. Meanwhile the SPI was dissolved in DMSO thoroughly to form a uniform solution with 10 wt% solid content. Then the SMSNs in DMSO were added into the SPI solution, sonicated for 30 min, then cast onto the glass dishes, dried at 80 °C for 8 h. After this, the samples were heated at 150 °C for 2 h and 180 °C for 8 h. When the films were cooled to room temperature, they were boiled in deionized water to be peeled off. Through this method, a series of SPI/SMSNs nanocomposite membranes were obtained (thicknesses between 90 and 120 μm). The contents of SMSNs in nanocomposites were 1%, 3%, 7% and 10%, respectively. These membranes were defined as SPI–SMSN-1, SPI–SMSN-3, SPI–SMSN-7 and SPI–SMSN-10.

2.5. Characterization and property measurements

2.5.1. Instrumental characterization

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet AVATAR360 spectrometer. Small-angle X-ray scattering measurements were made using a Siemens D-5005 system with Cu Kα. Thermogravimetric analysis (TGA) was conducted utilizing a Perkin-Elmer TGA-2 thermogravimetric analyzer by heating the samples from ambient temperature to 800 °C with a heating rate of 10 °C min^{-1} under nitrogen. The morphologies of fractured surfaces of the composite membranes were studied using SEM (XL-30 ESEM FEG, FEI Company). Nitrogen (N_2) adsorption/desorption isotherms were measured by using a Nova l000 analyzer with nitrogen. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and pore sizes by the Barrett–Joyner–Halenda (BJH)