



A facile route to enhance the properties of polymer electrolyte-based organic–inorganic hybrid proton exchange membranes



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ABSTRACT

A series of novel sulfonated polyimide (SPI)–mesoporous organosilicate (MSiSQ) hybrid proton exchange membranes (PEMs) with enhanced properties were prepared by *in situ* sol–gel process. The MSiSQ was synthesized from 3-isocyanatopropyltriethoxysilane (IPTES) and 8-hydroxyquinoline-5-sulfonic acid (SQ). The microstructure and properties of the hybrid membranes were characterized. The microstructure of the membranes can be regulated by the hydrogen bonds formed by the nitrogen atoms of MSiSQ phase and the hydrogen atoms of sulfonic acid groups in SPI. The uniform distribution of sulfonate ion clusters was observed in the hybrid membranes. The hybrid membranes exhibited superior performance as compared with that of pure SPI membrane such as the proton conductivity, methanol permeability, mechanical properties and thermal stabilities. The SPI-40-MSiSQ membrane showed a maximum proton conductivity of 0.566 S cm^{-1} at $80 \text{ }^\circ\text{C}$ and 100% relative humidity, an optimal selectivity of $12.8 \times 10^6 \text{ S s cm}^{-3}$ and an improved fuel cell performance as compared with pure SPI membranes. These excellent properties could be attributed to the formation of the continuous microstructure and well-connected proton transport channels due to the strong hydrogen bonding interaction and the mesoporous structure in the hybrid membranes.

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1. Introduction

The proton exchange membranes (PEMs) are the key components of direct methanol fuel cells (DMFCs) which are expected to be desirable utility in automotive and portable electronic applications due to their high efficiency and energy density per volume and weight. To date, the perfluorosulfonic acid PEMs represented by commercialized Nafion are still most widely used regardless of their drawbacks such as high cost, serious methanol crossover and loss of conductivity at higher temperature than $80 \text{ }^\circ\text{C}$. Even so, the problems such as high production price, complicated production process and high environmental pollution have still hindered the large-scale commercialization of Nafion. To overcome these drawbacks, many efforts have been devoted to develop alternative membranes as a substitute for Nafion such as aromatic polymers [1,2]. In the most of proton conducting aromatic polymers, sulfonated polyimides (SPIs) have attracted considerable attention as potential PEM materials for their low cost and high performance such as thermal and chemical stability, high proton conductivity, low methanol permeability, etc [3,4].

However, compared with Nafion and many other aromatic proton conducting polymers, the high sulfonation degree of SPI membranes might also result in the excessive swelling and the amide bond could

be attacked in the actual application by the polar water molecules or oxygen-containing free radicals which could lead to the degradation of SPI membranes and thus reduce their performance as PEMs in DMFCs. So the properties of the membranes obtained from the plain sulfonated polymer electrolytes should be modified to improve their stability with high ion-exchange capacity (IEC), which might be realized through blending them with inorganic fillers [5].

As we all know, the introduction of inorganic fillers directly could restrain the swelling, enhance the thermal stability and mechanical properties of the hybrid membranes, but there are still formidable challenges in these hybrid membranes to face such as the concentration dilution problem of the sulfonic acid groups, the low IEC value and the decreasing flexibility due to their intrinsically brittle and fragile nature [6–9]. In order to solve the above-mentioned problems, scientists tried to find out methods to modify the inorganic fillers first and then incorporate them in the polymers. For example, sulfonated silica particles have been introduced into PEM membranes to improve the performance of membranes [10–16].

As compared with other inorganic fillers, the mesoporous materials were widely used to improve the properties of PEM membranes owing to their high specific surface areas, high thermal and chemical stability as well as good uniform distribution ability of pore-forming channels leading to high water retention [16–21]. An optimal approach to introduce the mesoporous silica into polymer matrix is the sol–gel technology, which could avoid the aggregation of filler particles caused by the

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weak interaction between the fillers and polymer matrix. Pereira et al. had prepared Nafion/mesoporous silica composite PEMs using the *in situ* sol–gel method in the presence of the template P123 [16]. The sol–gel method improved the dispersion of mesoporous silica and induced a uniform distribution of mesoporous silica in the polymer matrix, which could improve the water retention and provide the proton transfer channels for proton transport at the same time. Lee et al. have reported an effective method to reduce the dilution effect of inorganic fillers on the sulfonic acid groups in the polymeric matrix by incorporating the organic sulfonic acid groups modified mesoporous silica [17]. The obtained Nafion composite membrane with 5 wt.% dopant amount of sulfonated mesoporous silica exhibited higher water uptake and proton conductivity as compared to non-sulfonated mesoporous silica/Nafion membrane, and the H₂/O₂ fuel cell power density of composite membrane was twice as high as that of Nafion at 60 °C. Won et al. prepared the sulfonated mesoporous silica (0.5 wt.%)/sulfonated poly(phenylsulfone) (SPPSU) composite membrane using the modified SBA-15 and 3-mercaptopropyltrimethoxysilane as the sulfonating agent [21]. It was found that although the proton conductivity of the composite membrane was lower than that of pure SPPSU at 100% RH, the water uptake and proton conductivity of composite membrane were higher than that of pure SPPSU under low relative humidity, indicating that the mesoporous structure played an important role in water retention in composite membrane.

Here, we reported a series of novel SPI-mesoporous organosilicate (MSiSQ) hybrid PEMs with different dopant amounts were obtained through *in situ* sol–gel method in the presence of template agent. MSiSQ was obtained from a new siloxane precursor with sulfonic acid groups and quinoline groups prepared through the reaction between 8-hydroxyquinoline-5-sulfonic acid (SQ) and 3-isocyanatopropyltriethoxysilane (IPTES). Our design is based on the following considerations. Firstly, the introduction of organosiloxane containing sulfonic acid groups can enhance the compatibility between the organosilicate phase and the sulfonated polymer matrix and reduce the dilution effect of inorganic materials on the sulfonic acid groups in PEMs. Secondly, the generated mesoporous structure can enhance the water retention ability of hybrid membrane. Thirdly, the hydrogen bonds between the nitrogen atoms in quinoline of MSiSQ and the hydrogen atoms in sulfonic acid groups of SPI can well regulate the microstructure of the hybrid membrane, which is beneficial to the proton conduction. Finally, the introduction of organosilicate phase can also reduce the methanol permeability and improve the mechanical performance and chemical stability of the hybrid membranes. The influences of MSiSQ on the membrane micromorphology and properties such as the thermal stability, mechanical properties, methanol-resistance, hydrophilicity and electrical performances were studied in detail.

2. Experimental

2.1. Materials

4,4'-Binaphthyl-1,10,8,8'-tetracarboxylic dianhydride (BNTDA) and 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS) were prepared according to the reported procedures [22,23]. 8-Hydroxyquinoline-5-sulfonic acid was purchased from Shanghai Chemical Reagent Plant. 3-Isocyanatopropyltriethoxysilane (IPTES) was purchased from TCI. 4,

4'-Diaminodiphenyl ether (ODA) was purified by sublimation in vacuum. Other reagents were of analytical grade and used as received.

2.2. Synthesis of sulfonated polyimide

Sulfonated polyimide (SPI) was synthesized according to the method reported in the literature [22]. The chemical structure of SPI is given in Scheme 1, and the molar ratio of BNTDA, ODADS and ODA is 1:0.6:0.4. The synthetic procedure was as follows: 1.62 g (4.5 mmol) of ODADS, 45 mL of *m*-cresol, and 1.08 g (10.8 mmol) of triethylamine were added into a three-necked flask equipped with a mechanical stirrer under nitrogen atmosphere. After ODADS was completely dissolved, 2.95 g (7.5 mmol) of BNTDA, 0.60 g (3 mmol) of ODA and 1.82 g (15 mmol) of benzoic acid were added. The mixture was stirred at room temperature for 20 min, and then heated at 80 °C for 2 h and 180 °C for 10 h. After cooling to 100 °C, 30 mL of *m*-cresol was added to dilute the viscous solution. Then the reaction solution was poured into acetone with stirring. The fiberlike precipitate was filtrated off, washed with acetone, extracted with methanol for 24 h, and then dried in vacuum for 4 h at 100 °C.

2.3. Synthesis of sulfonated organosiloxane (SiSQ)

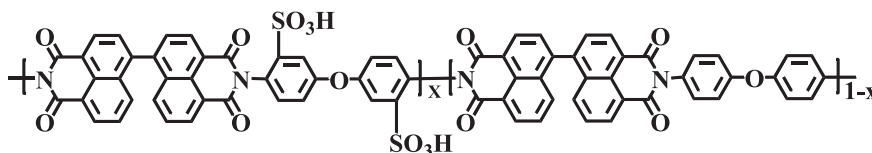
SiSQ was synthesized as shown in Scheme 2. The synthetic procedure is described below: 2.25 g (10 mmol) of 8-hydroxyquinoline-5-sulfonic acid, 1.16 mL (10 mmol) of triethylamine and 250 mL of chloroform were added into a three-necked flask equipped with magnetic stirrer under a nitrogen atmosphere. After 8-hydroxyquinoline-5-sulfonic acid was completely dissolved, 2.47 g (10 mmol) of IPTES was added. The mixture was stirred at room temperature for 5 min, and then heated at 70 °C for 8 h, after cooling to room temperature, the chloroform was removed by vacuum distillation, and then the yellow and oleaginous product was obtained.

2.4. Synthesis of template-containing organosiloxane sol

1.90 g of template agent CTAB was dissolved in 13 mL of deionized water by the ultrasonic method. After the solution became transparent, 13 mL of DMSO, 4.7 g of SiSQ and 1.16 g of concentrated hydrochloric acid were added. The final molar ratio of SiSQ:DMSO:H₂O:HCl:CTAB is typically to be 1:2.1:8.25:1:0.06. Then the mixture was stirred at room temperature for 24 h, a solution of CTAB-containing pre-hydrolyzed organosiloxane sol with a solid-content of 10.5 wt.% was obtained.

2.5. In situ preparation of SPI/mesoporous organosiloxane (MSiSQ) composite membranes

SPI was added into DMSO, and the mixture was heated to 80 °C for 4 h with stirring till all the SPI dissolved. Then the solution was cooled to room temperature, and a certain amount of template-containing organosiloxane sol was added and the mixture was stirred for another 15 h. By adjusting the adding amount of the organosiloxane sol to the SPI solution, different SPI–MSiSQ mixture solutions with 5 wt.%, 10 wt.%, 20 wt.% and 40 wt.% of MSiSQ in DMSO were obtained. The different hybrid membranes were prepared by casting the corresponding mixed solutions onto glass dishes and dried at 70 °C for 8 h, then heated at 120 °C for 12 h.



Scheme 1. Chemical structure of SPI.

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