Sulfonic Acid Modified Hollow Silica Spheres and Its Application in Proton Exchange Membranes

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Abstract: In order to improve the proton conductivity of hollow silica spheres (HSS)/perfluorosulfonic acid ion-exchange (PFSA) composite membranes as proton exchange membrane, sulfonic acid groups were grafted onto the surfaces of HSS via post grafting methods. TEM images and FT-IR spectra of the obtained sulfonic acid groups modified hollow silica spheres (SAMHSS) illustrated that the sulfonic acid groups were successfully grafted onto the surfaces of HSS. Water uptake and swelling degree of SAMHSS/PFSA composite membranes were found much higher than those of HSS/PFSA membranes due to the introduction of hydrophilic sulfonic acid groups. In a range from 50 °C to 130 °C, the highest conductivity of composite membranes was obtained when 5 wt% SAMHSS was loaded. The maximum conductivity reached 7.5×10−2 S·cm−1 at 100 °C and 100% relative humidity, even the temperature increased to 130 °C, the conductivity of composite membranes with 5 wt% SAMHSS could reach 3.7×10−2 S·cm−1 at 100% relative humidity, while the conductivity of the recast PFSA was only 2.2×10−3 S·cm−1.

Key words: composite; hollow silica spheres; proton exchange membrane; sulfonation; conductivity

1 Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is one of the best candidates for clean power sources in both mobile and stationary applications. The proton exchange membrane (PEM) is the most crucial component in PEMFC system. At present, the predominant proton exchange membranes are PFSA membranes which show high proton conductivity, chemical stability and excellent mechanical properties. Another kind of PEMFC operating at higher temperature (100-200 °C) is reported, which exhibits several additional advantages at elevated temperature, such as improved carbon monoxide tolerance of the anodic catalyst, reduction of the needs of expensive Pt catalyst in electrodes, higher energy efficiency, simplified heat management[1] and so on. However, the proton conductivity of PFSA membrane decreases quickly as temperature increasing because of the water in membrane evaporating fast at higher temperature. So, it is of great importance to keep high water retention in PFSA membranes at high temperature both practically and theoretically.

Organic–inorganic composite materials for fuel cell membrane have been studied widely due to the potential enhancement of the water retention properties and proton conductivity at high temperature[2]. For example, silica/PFSA composite membranes have been prepared in various ways and tried in high temperature PEMFCs[3]. Nevertheless, the excess incorporation of these nonconductive inorganic compounds in PEM normally results in a decrease of proton conductivity. To minimize the loss of proton conductivity caused by inorganic compound, conductive groups (such as sulfonic acid group and phosphoric group) are often grafted onto the surface of silica particles. Su[4] modified PFSA membrane with sulfonated silica nanoparticles, the composite membranes exhibited improved stability, reduced methanol crossover and higher proton conductivity compared with native PFSA membrane. Gomes[1] prepared a new kind of functionalized particles by attaching sulfonated aromatic bishydroxy compounds onto the surface of fumed silica particles. Kim[5] prepared sulfonic-functionalized heteropolyacid-SiO2 nanoparticles/PFSA membrane, the obtained composite membrane was thermally stable up to 290 °C and the operating temperature of the composite membrane increased from 80 to 200 °C. Marschall et al[6] found
that highly ordered mesoporous silica functionalized with grafted sulfonic acid groups showed promising proton conductivities for an application in fuel cell membranes operating at temperatures around 140 °C. Munakata et al. [7] found that the conductivity of inorganic-organic composite electrolyte membrane was enhanced by addition of sulfonic groups.

Maniwa et al. [8] found that water in confined space such as in single-walled carbon nanotube exhibits a liquid-gas like phase transition around 315-330 K, this temperature is higher than 300 K of bulk water at 27 torr. Hollow silica spheres possess a confined space, so it is assumed that the water in hollow silica spheres should display a higher liquid-gas like phase transition temperature than that of bulk water. This would improve the proton conductivity of proton exchange membranes at higher temperature if it can be added into the proton exchange membrane. Furthermore, hollow silica spheres having mesoporous shells, large surface areas, lower density and high amounts of hydroxyl group which can adsorb more water and are also advantageous to enhance the proton conductivity of proton exchange membrane at higher temperature. In addition to, according to the results of our previous work in this area, the proton conductivity of the hollow silica spheres/PFSA composite membranes was found to be improved to some extent compared to that of the recast pure PFSA membrane, additionally, the results also indicated that the proton conductivity of composite membranes with smaller size hollow silica spheres was better than that of those with bigger ones [9]. So, in order to further improve the proton conductivity of hollow silica spheres/PFSA composite membranes distinctively, sulfonic acid modified hollow silica spheres (SAMHSS) were prepared and the effect of SAMHSS loading on the properties of the recast PFSA membrane were investigated for a purpose of improving the conductivity of the membranes at higher temperature preferably.

2 Experimental

2.1 Materials

Styrene (St) was purchased from Shanghai Chemical Reagent Co. and distilled in a vacuum before use. Perfluorosulfonic acid ion-exchange resin (PFSA) was purchased from Shandong Dongyue Shenzhen New Material Co., Ltd. Both 2,2'-Azobis(2-amidinopropane)dihydrochloride (AIBA) and mercaptopropyltrimethoxysilane (MPTMS) were purchased from Sigma-Aldrich. Tetraethylorthosilicate (TEOS), dimethylformamide (DMF), ethanol (99.7 wt%, AR. grade), polyvinylpyrrolidone (PVP, $M_w=40 000$) aqueous ammonia solution (28 wt%) and hydrogen peroxide (30 wt%) were supplied by Shanghai Chemical Reagent Co.

2.2 Preparation of sulfonic acid modified hollow silica spheres

At first, positively charged polystyrene (PS) particles were prepared as template for the target sulfonic acid modified hollow silica spheres according to the references reported methods [9]. Then the obtained PS emulsion was diazylized in ethanol using a cellulose membrane in order to remove the undesired water. After dialysis, 40 mL ethanol was added into 5.0 g PS emulsion and 5 mL aqueous ammonia solution was dropped into the mixture with stirring at 100 rpm for 5 min. Afterwards, 1.0 g TEOS was added quickly into the mixture and kept the reaction at 50 °C for 1 h with the same stirring rate. Finally, 1.0 g MPTMS was dropped into the solution and reacted for additional 2 h. The reaction solution was deoxygenated by bubbling N$_2$ for the whole reaction process. The obtained thiol modified hollow silica spheres (TMHSS) suspension were separated from the reaction medium by centrifuging at 8 000 rpm, washed several times with ethanol and finally TMHSS paste was obtained.

The paste of TMHSS was added into 30 wt% hydrogen peroxide solution and the mixture was stirred at 40-60 °C under N$_2$ protection for 12 h. The obtained sulfonic acid groups modified hollow silica spheres (SAMHSS) were centrifuged at 8 000 rpm, washed several times with deionized water, then redispersed in deionized water until use. The schematic diagram of preparation of SAMHSS was shown in Fig. 1.

![Fig. 1 The schematic diagram of preparation of SAMHSS](image)

2.3 Preparation of PFSA solution

A certain amount of PFSA resin was added into DMF solution. The solution was deoxygenated by bubbling N$_2$ at room temperature for about 1 h, and then was heated to 160 °C for 72 h.

2.4 Preparation of SAMHSS/PFSA composite membranes

The composite membranes were prepared using the following procedure. Firstly, 5 wt% PFSA solution was mixed with SAMHSS and stirred in an ultrasonic bath for 30 min. Subsequently the solution was cast.