



Self-crosslinked organic-inorganic nanocomposite membranes with good methanol barrier for direct methanol fuel cell applications

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ARTICLE INFO

Keywords:

Crosslinking
Direct methanol fuel cell
Nanocomposite
Methanol barrier
Selectivity

ABSTRACT

The organic-inorganic latex particles with sulfonic acid groups and core-shell structure are successfully obtained and then are heated to fabricate the self-crosslinked organic-inorganic nanocomposite membranes. Fourier transform infrared (FTIR) spectra confirm the chemical structure of membranes. The effects of inorganic component on the performances of nanocomposite membranes are investigated extensively. TGA analyses show that the membrane materials possess excellent thermal stability and 5% weight loss temperature increase with increasing SiO₂ content. Solvent absorption measurement suggests the membranes are less permeable to methanol than water. The obtained membranes show conductivity values above 10⁻² S cm⁻¹. More importantly, all the membrane materials exhibit more excellent methanol barrier and higher selectivity compared with Nafion® 117, demonstrating that those membranes could be a potential candidate as proton exchange membranes for future direct methanol fuel cells.

1. Introduction

In nowadays, the research and development of direct methanol fuel cell (DMFC) has received widespread attention because of its own advantages, including ease of fabricate, eco-friendly, high energy efficiency, long service life, simple operation condition, small size and light weight [1–4]. As a key component of DMFC, proton exchange membrane (PEM) affects the performance and service life of fuel cell directly [5,6]. The perfluorosulfonic acid membranes, like Nafion® developed by DuPont, are most widely used PEMs. These membranes show excellent proton conductivity, outstanding thermal, mechanical and chemical stability [7]. Nevertheless, their expensive cost, excessive methanol crossover, unstable properties at high temperature and environmental impact have hindered their commercialization [8,9]. Therefore, much attempt has been done to modify perfluorosulfonic acid membranes and develop the new PEM materials [10–19]. During the various modification methods, the crosslinking and composite techniques seem to be extremely promising due to their respective advantages. The former can enhance mechanical strength and stability of membranes, and suppress methanol diffusion and swelling of membranes simultaneously [14–16]. The latter can not only combine the appealing advantages of each component, but also reduce their disadvantages [17–20].

In this work, to prepare the cost-effective, environmentally friendly PEM materials with significant selectivity and methanol barrier, inorganic SiO₂ nanoparticles were encapsulated by low cost organic polymer material with sulfonic acid groups. Then the organic-inorganic latex particles were heat-treated to fabricate the self-crosslinked organic-inorganic nanocomposite membranes. The formed membranes were expected to possess excellent performance. On the one hand, it has been demonstrated that adding inorganic nanoparticles (for instance, titanium oxide, silica, alumina, zirconia or clay) into polymer matrix could decrease the methanol crossover and improve the mechanical properties of PEMs [21–26]. On the other hand, the crosslinking in the membranes make the connection more closely within the polymers and hence could increase stability and control effectively swelling and methanol diffusion of PEMs. We evaluate the potential of self-crosslinked organic-inorganic nanocomposite membranes for DMFC application by measuring the stability, solvent absorption, methanol diffusion coefficient, proton conductivity and selectivity, etc. Furthermore, the influence of SiO₂ content on the performances of membranes was also investigated.

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2. Experimental

2.1. Materials

Butyl acrylate (BA) and ammonium persulfate (APS) in the reagent-grade form were supplied by Tianjin Fuchen Chemical Reagents Factory. 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and tetraethoxysilane (TEOS) were used as received from Aldrich and Tianjin Guangfu Fine Chemical Research Institute, respectively. Methyl methacrylate (MMA) and methacrylic acid (MAA) were provided by Xilong Chemical Co., Ltd. and Shanghai Chemical Reagent Co. (China), respectively. The water used in this experiment was distilled followed by deionization.

2.2. Preparation of the organic-inorganic latex particles

The organic-inorganic latex particles with sulfonic acid groups and core-shell structure were prepared through emulsifier-free emulsion polymerization technique. First, a 250 ml four-neck flask was charged with 80 ml of deionized water, 0.1 g of sodium bicarbonate and 0.7 g of AMPS. Then various amounts of colloidal nanosilica prepared via Stöber method were charged into the flask. After stirring the mixture for half an hour at 50 °C, one quarter of monomer mixture of 5.0 ml of MMA, 5.0 ml of BA and 0.5 ml of MAA was dropped into the reaction flask and the mixture was elevated to 75 °C. Subsequently, one fifth of APS aqueous solution (0.2 g of APS was solved in 10 ml water) was added dropwise into the above flask to induce monomer polymerization at 80 °C and the residual initiator and monomers were added dropwise into the above flask in 1.5 h and the reaction was continued for 3 h. The resultant latex particles showed high monomer conversion (> 91.45%) and narrow size distribution (polydispersity index < 0.1).

2.3. Preparation of self-crosslinked organic-inorganic nanocomposite membranes

Self-crosslinked organic-inorganic nanocomposite membranes were fabricated by solution casting and heat treatment technology. First, the organic-inorganic nanocomposite latex nanoparticles were poured onto a glass surface and heated up 60 °C above 10 h and 120 °C about 2 h for drying under vacuum. Second, the membrane was removed and cooled to room temperature. Finally, the product was stripped off the glass support by immersion in deionized water, and then stored in deionized water for further analysis.

2.4. Measurements

The particle size and polydispersity of latex nanoparticles were determined by a BI-90Plus ZetaPALS DLS detector (15 mW laser, incident beam = 660 nm).

FTIR spectra of the samples were obtained by a NICOLET-AV360 Fourier transform infrared spectrometer. The experiments were run with air as the background. KBr disc were pressed and tested for each sample in the frequency range of 4000–400 cm⁻¹.

Thermal analysis was performed with Pyris 1TGA (Perkin Elmer) analyzer to estimate the thermal stability of membranes. First, the specimens were preheated to 120 °C and kept it for 20 min to eliminate moisture. Afterward, the temperature of specimens were dropped to 100 °C, and then reheated to 650 °C with a heating rate of 10 °C per minute under nitrogen atmosphere.

The water uptake of each membrane was conducted by determining the weight differences between the fully hydrated membranes and the dried one. Namely, the weight of dried membrane was measured after heating at 100 °C for 24 h under vacuum. The dried membranes were immersed in distilled water for 24 h at a set temperature. Afterward, the membranes were taken out and removed the water on the surfaces by the filter paper, and their weights were immediately determined. Their

water uptakes were obtained by the expression as following:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

Where W_{wet} and W_{dry} are the weight of the wet and dry membrane, respectively.

The methanol uptake was investigated via the method similar with water uptake, 2M methanol solution replaced water to soak the membranes in the sealed beaker at 25 °C. Their methanol uptakes were obtained from the relationship:

$$\text{Methanol uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

The methanol diffusion coefficient was determined with a glass diffusion cell which consists of two identical reservoirs separated by a vertical membrane sample, which was immersed in deionized water for at least 24 h before testing. The methanol solution (2 M) and water were added into each reservoir, respectively. The solutions in each reservoir were stirred uninterruptedly during measurement. The change of the methanol concentration in the water reservoir was monitored by a SHTMADU GC-8A gas chromatograph and the methanol diffusion coefficient was obtained from the equation:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0)$$

Where A (cm²) and L (cm) are the effective area and the thickness of membrane samples, respectively. C_A and C_B (mol L⁻¹) are the methanol concentration in feed and in diffusion reservoirs, respectively. DK (cm² s⁻¹) is the methanol diffusion coefficient. V_B (cm³) is the volume of diffusion reservoir.

The membranes' conductivity was measured with AC impedance method. Impedance spectra were measured by an SI 1260 + SI1287 impedance analyzer in the frequency of 10 to 10⁶ Hz. Membrane samples were cut into strips and equilibrated in distilled deionized water for at least 24 h prior to testing. Subsequently, the hydrated membrane was set in a distilled deionized water bath to control temperature followed by being stucked in the middle of two stainless steel electrodes. The proton conductivity (σ) was calculated according to equation:

$$\sigma = \frac{d}{Rtw}$$

Where d is the distance between the electrodes. R is the membrane resistance, t and w are the thickness and width of the membranes, respectively.

3. Results and discussion

3.1. Structure analysis of organic-inorganic nanocomposite latex particles

The organic-inorganic nanocomposite membranes with different SiO₂ content were characterized by FTIR spectra and the results were given in Fig. 1. It is noted that all the samples exhibited the broad band at 3450 cm⁻¹ which was originated from the stretching vibration of OH groups resulted from SO₃H groups and absorbed water. In addition, this band increased with the increasing of the SiO₂ content. Furthermore, the FTIR spectra displayed the characteristic stretching and distortion vibration of CH₂ at 2970 and 2880 cm⁻¹, as well as 1470 and 1405 cm⁻¹, respectively. In Fig. 1, the peaks at about 1650 cm⁻¹ and 1079 cm⁻¹ were also attributed to the bending vibration of amide groups and the asymmetric stretching vibration of SO₃ originated from AMPS. In addition, the characteristic peaks of the C=O and -COO- groups were also observed at around 1750 cm⁻¹. For all the samples, the peak at about 478 cm⁻¹ was attributed to the Si-O-Si asymmetry flexible vibration, and the intensity of this peak increased with the increment of SiO₂ content. Above results clearly demonstrated

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