

Fabrication and characterization of PFSI/ePTFE composite proton exchange membranes of polymer electrolyte fuel cells

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Abstract

PFSI/ePTFE composite proton exchange membranes were fabricated by impregnating perfluorosulfonic acid resin (PFSI resin, Nafion) into chemically modified expanded PTFE (ePTFE) matrix. Chemical modification of sodium–naphthalene treatment and *N*-methylol acrylamide (NMA) grafting decreased the contact angle of the as-received ePTFE from $125 \pm 0.5^\circ$ to $67 \pm 0.5^\circ$, effectively converting the as-received hydrophobic ePTFE to a hydrophilic ePTFE matrix. The composite membrane fabricated with the hydrophilic ePTFE have higher impregnated PFSI loading, much lower porosity and better PTFE/PFSI interface contact, as compared to the composite membranes with the as-received ePTFE. This leads to much lower gas permeability and significantly improves the durability under an accelerated dry/wet cycle test. The fuel cell made from the PFSI/ePTFE composite membranes with hydrophilic ePTFE showed superior performance as compared to that with the composite membrane made from the as-received ePTFE and Nafion 211 membrane.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are considered the most promising power sources for transportation and portable applications such as automobiles, un-interrupted power suppliers, mobile phones and laptop computers due to their high-energy conversion efficiency, very low greenhouse gas emission, quiet and continuous operation mode [1–3]. However, cost reduction of various cell components and enhancement of the cell performance and stability are critical to the commercial viability of the PEMFC technologies [4–5]. One of the key components that has significant effect on the overall cost and performance of a PEMFC is the perfluorosulfonic acid proton exchange membranes (PFSI PEMs) [6]. It has been reported that cost reduction and performance improvement could be achieved by replacing PFSI membrane with a PTFE-based composite membrane [7–16]. PTFE-based composite membrane is traditionally fabricated by impregnating PFSI ionomers into inert

porous poly(tetrafluoroethylene) membranes (expanded PTFE, or ePTFE for short) [17,18]. Due to the high strength of the ePTFE matrix, the thickness of the composite membranes can be reduced significantly, resulting in the significant reduction in the loading of the expensive PFSI resin and higher area conductance.

However, preparation of dense PFSI/ePTFE composite PEMs without voids or pinholes is not an easy task because it is very difficult to impregnate the hydrophilic PFSI solution into the porous ePTFE matrix due to its hydrophobic nature [19,20]. The existence of voids or pinholes would lead to the gas crossover, a potential hazard for the performance stability of PEMFCs.

It has been reported that the hydrophobic and adhesion properties of the PTFE polymer can be modified by sodium naphthalene treatment, ion beam irradiation, or chemical grafting [21–24]. The improvement in the hydrophilicity will enhance the PFSI impregnation process and decrease the porosity, whereas the improvement of the adhesion will give a better interface contact between the ePTFE and the PFSI, resulting in better durability under the fuel cell operation conditions.

Here we report the fabrication of the PFSI/ePTFE composite membranes with chemically modified ePTFE matrix through sodium naphthalene treatment and chemical grafting. Such

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fabricated PSFA/ePTFE composite membranes show significantly reduced contact angle, much lower porosity, low gas crossover or permeability and high stability and cell performance as compared to that made from the as-received ePTFE matrix.

2. Experimental

2.1. Chemical modification of ePTFE matrix

Sodium–naphthalene complex solution was prepared by dissolving 128 g naphthalene (Hongyan Reagent Comp., China) and 11.5 g of sodium (Hongyan Reagent Comp., China) in 1000 mL tetrahydrofuran (THF, Shanghai Reagent Comp., China) at 80 °C under N₂ atmosphere. The mixture was stirred continuously until the color of the solution changed from colorless to black. The solution was then allowed to cool down to room temperature and ready for use. The ePTFE membranes with 85% porosity (Shanghai Dagong Comp.) were washed with ethanol for 5 min. Then the membranes were immersed in sodium–naphthalene complex solution for 5 s, followed by washing with ethanol and deionized water for 5 min each step to remove residual solvent and sodium.

Additional chemical modification of the ePTFE matrix was performed by immersing the sodium–naphthalene-treated ePTFE into a 15 wt.% *N*-methylol acrylamide (NMA, EMA) solution for 30 min. This was followed by washing with deionized water for 5 min to remove residual NMA ionomers.

2.2. Preparation of the PFSI/ePTFE composite membranes

The Nafion solutions containing Triton-100 for ePTFE impregnation were prepared by mixing Nafion DE 520 solutions (5 wt.%, EW 1000, DuPont) and Triton X-100 (Aldrich) with a volume ratio of 95:5. A ePTFE membrane after the chemical modification was mounted on a 15 cm × 15 cm plastic frame and immersed in the Nafion/Triton X-100 solution for 5 min. Then, the impregnated membrane was dried at 120 °C for 5 min. The impregnation and drying steps were repeated for three times in order to eliminate the voids or pinholes in the composite membrane. The as-prepared membranes were soaked in distilled water for 24 h, and in isopropanol for 5 min to dissolve Triton X-100, followed by washing with distilled water. Finally, the membrane was treated with 0.5 M sulfuric acid and distilled water for 4 h respectively to obtain the H-form PFSI/ePTFE composite PEMs. The membrane was termed as HLC PEM.

For the purpose of comparison, composite PFSI/ePTFE PEMs were also fabricated with as-received ePTFE membranes by the procedures as described above. The membrane was termed as HBC PEM.

2.3. Characterization of the ePTFE matrix and the PFSI/ePTFE composite membrane

The hydrophilicity of the ePTFE matrix with and without chemical modification was characterized by the contact angle measurement. The contact angle of water on the membranes was measured in air at room temperature using the sessile drop

method (Automatic Contact Angle Meter, Kyowa Interface Science Co., Japan). By increasing or decreasing the volume of the water drop until the three-phase boundary moves on the sample surface, the advancing or receding of contact angles were measured. The water was dropped at least ten different points on each sample, and the contact angle was obtained as the average of the measurements.

Ion exchange capacity (IEC value) was determined by titration. Membrane samples were soaked in 50 mL of 1 M NaCl aqueous solution for 24 h, and then titrated with 0.01 M NaOH solution. The IEC was derived from $IEC = V_{\text{NaOH}} N_{\text{NaOH}} / W_{\text{dry}}$, where V_{NaOH} , N_{NaOH} and W_{dry} are the volumes of NaOH consumed, the concentration of NaOH and the weight of dried membranes, respectively.

Water uptake of the composite membranes was measured by immersing membranes in water. Before the test, the membrane had been dried at 100 °C for 12 h, and the weight of the membrane was test as W_1 . Subsequently, the membrane was immersed in water at 25 °C for 8 h and equilibrated at 25 °C and 50% RH for 12 h. Then the weight of the membrane was test as W_2 . The water content (ΔW) was calculated by the weight difference of the samples before and after the immersion in water:

$$\Delta W \text{ (wt.\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

For dimensional stability test, the membrane was dried at 50 °C under vacuum and was stored at 25 °C and 25% RH for 24 h. The specimens were then soaked in deionized water at 100 °C for 1 h. The dimension of the specimens was recorded before (L_1) and after (L_2) the water immersion treatment. The change in dimension (ΔL) was calculated by using the following equation:

$$\Delta L \text{ (\%)} = \frac{L_2 - L_1}{L_1} \times 100 \quad (2)$$

Mechanical strength of membranes was measured with an Electromechanical Universal Testing Machine (WDW-1C) using a Chinese Standard QB-13022-91. The samples were measured at a strain rate of 50 mm/min.

The shrinkage stresses generated by humidity change was tested by Electromechanically Universal Testing Machine with an environment chamber. The chamber was fitted on the horizontal rail of the machine load frame and had independent T/RH control. The RH control was achieved by circulating a low speed water vapor saturated gas stream with a controlled dew point. During the test, the samples were cut to spindle shape and two ends of the sample were clamped by the claws of the Electromechanical Universal Testing Machine.

Surface and cross-sections of the ePTFE matrix and the composite membranes were examined by scanning electron microscopy (SEM, JEOL JSM-5610LV). Cross-section specimens of the composite membrane were prepared by breaking the membrane under liquid nitrogen (77 K). The samples were Au-sputtered under vacuum before the SEM examination.

In-plane conductivities of the proton exchange membranes were measured by using an impedance analyzer (Autolab

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