Short Communication

Surface-modified Nafion membranes with mesoporous SiO$_2$ layers via a facile dip-coating approach for direct methanol fuel cells

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ABSTRACT

In this study, Nafion® 117 membrane is surface-modified with mesoporous silica layers through in situ surfactant-templated sol–gel reaction. The reaction makes use of tetraethyl orthosilicate (TEOS) under acidic condition via dip-coating technique on both sides. Scanning electron microscopy (SEM), Fourier transformation infrared (FTIR), and thermogravimetric analysis (TGA) are employed to characterize the resultant membranes. Proton conductivity and methanol permeability of the membranes are also studied. It is determined that the aging time, along with the number of the silicon dioxide (SiO$_2$) layer, influence both proton conductivity and methanol permeability. Specifically, double-side modified membrane with 5 min interval of the second layer (S (5)) exhibits optimal properties on the combined criterion of conductivity and permeability. However, the application of mesoporous silica layer in modifying commercial Nafion membranes through dip-coating is proven to be a facile route in improving the said criteria simultaneously.

1. Introduction

Growing concern over the environmental impact of exhaust emissions has led to widespread attempts to reduce long-term dependence on oil and other fossil fuels. In turn, this rippled towards the emergence of clear energy efforts and continued development of fuel cells that can provide both ultra-low emissions and high efficiencies. Among the different types of fuel cells, the direct methanol fuel cell (DMFC) is one of the most promising power sources for vehicular and portable applications. DMFC is a polymer electrolyte fuel cell (PEFC).

In the development of DMFC, the proton conducting membrane is a key issue. It offers vessels for hydrogen ions while separating the gases on the different electrode surfaces during the electrochemical reaction. It likewise poses great influence on the performance and the efficiency of fuel cells. So far, Nafion® membranes have been commonly used as polymer electrolytes in DMFCs, owing to their good chemical stability, strong thermal resistance, and relative ideal conductivity. However, the use of the Nafion membranes as polymer electrolytes is affected by certain drawbacks. For example, its poor methanol barriers cause overpotential losses

at the negative electrode of the fuel cell. Also, the membranes cannot sustain a long-term operation when temperatures are elevated. Definitely, it will limit the commercial applications of Nafion membranes [1].

Due to these problems, modification of Nafion has attracted research attention in recent years. Much of the aims of the studies has been to diminish methanol crossover and increase the efficiency of DMFCs. Numerous efforts have been done on the preparation of Nafion/silica-based composite membranes [2]. Kim et al. [3] employed the plasma enhanced chemical vapor deposition technique to deposit nano-scaled films of silica on Nafion membrane. It was found that the composite membrane is a viable candidate for DMFC. Tang et al. [4] developed a self-assembly process to synthesize Nafion–SiO$_2$ nanoparticles. These were used to modify the Nafion/silica nanocomposite membrane. The novel membrane exhibited significantly high durability under the tests. The said result was explained as the excellent interface between the Nafion polymeric matrix and the self-assembled Nafion–SiO$_2$ nanoparticles. On the other hand, research on the preparation of composite membranes by sol–gel route has been reported [5–12]. Dimitrova et al. [8] recast the mixture of Nafion ionomer and silica solution. In their study, the composite membrane showed higher conductivity than pristine Nafion. Meanwhile, infiltration of Nafion with sol–gel solutions has also generated some promising results [13–16]. To illustrate, Miyake et al. [5,6] reported that hybrid mem-

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branes with silica content of 10–20 wt% decreased methanol uptake from the liquid phase. However, the proton conductivities of the membranes were revealed to be lower than or equal to that of pristine Nafion membranes.

In this study, a series of Nafion/SiO$_2$ composite membranes were prepared via dip-coating surfactant-templated mesostructured silica on both sides of the Nafion® 117. The aim is to improve the performance of commercial Nafion membranes by making full use of mesoporous silica thin films. Finally, the methanol permeability and proton conductivity are considered as a combined criterion for all the specimens.

2. Experimental

2.1. Membrane preparation

The Pluronic® P123 surfactant (PEO$_{20}$PPO$_{70}$PEO$_{20}$, where PEO is poly(ethylene oxide) and PPO is poly(propylene oxide)) was purchased from BASF. Tetraethyl orthosilicate (TEOS) (Beijing, China) and ethanol from the Beijing Chemical Factory were utilized as prepared. Methanol was distilled prior to use. The commercial Nafion® 117 (denoted as N117 in the paper) has 1100 equiv. weight (M_W per sulfonic acid group of Nafion 117) and 175 μm thickness. It was pretreated before use according to previously published literature [17]. The mesoporous SiO$_2$ films on each side of Nafion membrane were prepared by dip-coating silicate/surfactant sols on the membrane. The triblock copolymer surfactant P123 was used to template the pore structure of SiO$_2$ layer. Typically, the sols were prepared by mixing TEOS, P123, HCl, H$_2$O, and ethanol in a molar ratio at approximately 1:0.0097:0.0087:5:20. This process was adapted from the one suggested by Wang et al. [18], with slight modifications.

The sample was designated as S (min) relative to Nafion® 117. For example, S (0) represents the sample of the second layer which was coated immediately. Meanwhile, S (5) pertains to the second layer coated 5 min after the formation of the first layer. In addition, NS means the sample with only one coated layer. Dip-coating

was carried out at a speed of 50 mm min^{-1} and a typical route is as follows. The membranes were immersed in the sol and were subsequently pulled out. For the second layer, the above process was repeated after 5 min. The prepared membranes were laid in a petri dish and aged for 4–6 h. Afterwards, they were eluted with ethanol and deionized water to remove the surfactant completely. Membrane composition and symbols are presented in Table 1. All the samples were soaked in deionized water prior to taking the different measurements.

2.2. Analysis

Thermogravimetric analysis (TGA) was performed with TGA-51H, Shimadzu at a heating rate of 2 °C min^{-1} under N$_2$ in the range of 20–140 °C. Scanning electron microscopy (SEM) images were taken using a Philips XL 30 ESEM FEG scanning electron microscope. Similarly, transmission electron microscopy (TEM) images were taken with a JEOL JEM-2010 transmission electron microscope, with an accelerating voltage of 200 kV. Samples were then scraped from the surface of modified membrane, and the result was shown in the supporting information. Fourier transform infrared spectroscopy (FTIR) spectra of the composites were recorded on a Bruker Vertex 70 FTIR spectrometer in Attenuated Total Reflection (ATR) mode from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}.

The water uptake experiment was carried out by drying the membranes in a vacuum oven at 80 °C for 4 h and weighed subsequently. Afterwards, the membranes were immersed in distilled water and isothermally oscillated at 60 °C for 2 h, and after drying with filter paper, the wet membrane was weighed. The water uptake in Table 1 was calculated using the following equation: water uptake (%) = (W_{wet} − W_{dry})/W_{dry}; where W_{wet} and W_{dry} represent the weights of the wet and dry membrane, respectively. Next, the dimension of wet membranes was measured.

Proton conductivity σ (S cm^{-1}), was measured by the alternating current (AC) impedance method using a Princeton Applied Research Model 273A Potentiostat (Model 5210 Frequency Response Detec-

Table 1
Water uptake for N117 and modified membranes

Sample name	Preparation conditions	Number of SiO$_2$ layers on one side of N117	Thickness[a] (μm)	Water uptake (%)	Dimensional change[b] (%)
N117	Nafion® 117 membrane	0	210	18.8	11.9
NS	One SiO$_2$ layer coated on N117	1	210	33.2	2.1
S (0)	The second SiO$_2$ layer was coated immediately on NS	2	220	28.5	1.6
S (5)	The second SiO$_2$ layer was coated at 5 min later on NS	2	230	36.9	1.5
S (7)	The second SiO$_2$ layer was coated at 7 min later on NS	2	220	31.6	1.5
S (10)	The second SiO$_2$ layer was coated at 10 min later on NS	2	220	27.3	1.5
S (15)	The second SiO$_2$ layer was coated at 15 min later on NS	2	220	36.8	1.5
S (20)	The second SiO$_2$ layer was coated at 20 min later on NS	2	220	30.3	1.4
S (25)	The second SiO$_2$ layer was coated at 25 min later on NS	2	220	27.6	1.4
S (30)	The second SiO$_2$ layer was coated at 30 min later on NS	2	230	36.0	1.4
S (45)	The second SiO$_2$ layer was coated at 45 min later on NS	2	230	29.6	1.4
S (5)-3	The third SiO$_2$ layer was coated at 5 min later on S (5)	3	230	29.0	1.4
S (5)-4	The fourth SiO$_2$ layer was coated at 5 min later on S (5)-3	4	220	31.2	1.3
S (5)-5	The fourth SiO$_2$ layer was coated at 5 min later on S (5)-4	5	230	25.1	1.1

[a] In hydrated state.

[b] Dimensional change in length in both hydrated and dry state, $\Delta L/L$ (%).