



# Preparation of polysiloxane modified perfluorosulfonic acid composite membranes assisted by supercritical carbon dioxide for direct methanol fuel cell

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## ABSTRACT

Polysiloxane modified perfluorosulfonic acid (PFSA) composite membranes are prepared by using (3-mercaptopropyl) methyltrimethoxysilane (MPMDMS) as a precursor of silicon alkoxide in supercritical carbon dioxide (Sc-CO<sub>2</sub>) system. In the Sc-CO<sub>2</sub> system with the presence of water, Sc-CO<sub>2</sub> is not only used as a solvent and swelling agent, but also functioned as an acid catalyst for the condensation polymerization of MPMDMS. Characteristics of the modified composite membranes are investigated by using attenuated total reflection-infrared spectra, scanning electron microscopy and transmission electron microscopy. The modified membrane with 13.9 wt.% poly(MPMDMS) is the best one among all the modified membranes, whose methanol permeability is extremely lower and selectivity (ratio of proton conductivity to methanol permeability) is about 5.49 times higher than that of pristine membrane and 5.88 times than that of Nafion® 117, respectively. This modified PFSA membrane still can maintain its higher selectivity value than that of Nafion® 117 in the temperature range of 25–65 °C. Therefore, the modified membranes prepared in Sc-CO<sub>2</sub> system may be the suitable candidate electrolytes for direct methanol fuel cell applications.

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## 1. Introduction

Direct methanol fuel cell (DMFC) has attracted much attention for its promising application in portable power sources, due to its simply system and high energy density [1–3]. Perfluorosulfonic acid (PFSA) membrane, such as Nafion®, is of interest as a proton conducting electrolyte membrane in DMFC application because of its high proton conductivity, excellent chemical, mechanical and thermal stability. However, one of the main obstacles that currently prevent the wide application of PFSA membrane in DMFC is its high methanol permeability. So a lot of researchers developed PFSA composite membranes to reduce methanol permeability, such as PFSA/polymer (e.g. polyvinylidene fluoride [4], polypyrrole [5], polyaniline [6]) composite and PFSA/inorganic particle (zeolite [7], titanium dioxide [8]) nanocomposite membranes. One effective approach to reduce methanol permeability is to incorporate SiO<sub>2</sub> particles into Nafion® membranes [9–11], which could change the methanol transportation path and hinder the methanol permeation through the membrane. But proton conductivity of these composite membranes decreased too much because of the introduction of non-conductive inorganic SiO<sub>2</sub> particles. To solve this

problem, some functionalized acid groups, such as –SO<sub>3</sub>H, were introduced onto SiO<sub>2</sub> particles to improve the proton conductivity [12–16]. Then, proton conductivity of these modified membranes would not be reduced evidently during the reduction of methanol permeability. The common impregnation method was that the PFSA membranes were firstly pre-swelled by polar swelling reagents (e.g. water/alcohol solution) and further immersed in the functional organic SiO<sub>2</sub> precursor/alcohol solution. The condensation polymerization reaction was mainly catalyzed by the –SO<sub>3</sub>H groups inside the swollen PFSA polymers. However, this method caused not only environmental pollution but also a waste of organic solvents. Moreover, the condensation polymerization of the functional organic SiO<sub>2</sub> precursor was mainly restricted in the ion cluster regions, which resulted in the formation of polysiloxane particles with size of about 5 nm prevailed [17].

Recently, the new impregnation method using supercritical carbon dioxide (Sc-CO<sub>2</sub>) as a solvent and swelling reagent has attracted much attention [18–20]. Compared with the common impregnation method using organic impregnation solvents, Sc-CO<sub>2</sub> has several advantages for preparing productions. It is one of nontoxic, inexpensive and environmentally solvents, and possesses low viscosity and high diffusivity like gases. High penetration of impregnation substances can be obtained in the Sc-CO<sub>2</sub> system, and the solubility of solutes in the Sc-CO<sub>2</sub> can be easily controlled by adjusting the pressure. Then, it is possible to cause organic SiO<sub>2</sub> precursor to homogeneously polymerize into the PFSA membranes, not

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only polymerizing in the ion cluster regions using the common impregnation methods. Moreover, Sc-CO<sub>2</sub> can be easily removed from the products completely at the end of the process. Using Sc-CO<sub>2</sub> as a swelling agent, it would avoid thermal stresses and plasticizing effect on polymers during impregnation [21]. Therefore, this new impregnation method is considered to be highly effective for producing superior products and nano-materials [22,23]. However, to the best of our knowledge, so far there are few papers reported using the Sc-CO<sub>2</sub> impregnation method to reduce the methanol crossover of membranes for DMFC. Kim et al. [18] synthesized palladium/Nafion<sup>®</sup> composite membranes by using the Sc-CO<sub>2</sub> impregnation method. The composite membranes showed lower methanol permeability than that of Nafion<sup>®</sup> 117. Gribov et al. [24] prepared zeolite–Nafion<sup>®</sup> nanocomposite membranes assisted by Sc-CO<sub>2</sub>. The zeolite–Nafion<sup>®</sup> composite membranes possessed of much higher selectivity (ratio of proton conductivity to methanol permeability) than that of Nafion<sup>®</sup> 115. Nevertheless, the proton conductivity decreased too much due to lower conductivity of zeolite.

In this study, the functional SiO<sub>2</sub> precursor—(3-mercaptopropyl) methyltrimethoxysilane (MPMDMS) was impregnated into the pre-swelled PFSA membrane by using Sc-CO<sub>2</sub> as a solvent and swelling agent, and the *in situ* sol–gel reaction occurred in the PFSA membrane. The MPMDMS was used as the source of functional group –SO<sub>3</sub>H, because the group –SH in the poly(MPMDMS) can be oxidized to –SO<sub>3</sub>H. Characters and structures of the modified MPMDMS/PFSA membranes were investigated by using attenuated total reflection-infrared spectra (ATR-IR), scanning electron microscopy (SEM) and transmission electron microscope (TEM). The proton conductivity and methanol permeability were also measured in order to evaluate the performance of modified membranes.

## 2. Experimental

### 2.1. Preparation of the modified membranes

The PFSA precursor was supplied by Dongyue Shenzhou New Materials Co. Ltd. (Zibo, China). The structure formula of its precursor is shown in Fig. 1. Preparation of the pristine PFSA membranes was carried out according to the following steps, as described by Luan in our group [25]: (1) converting the precursor to PFSA resin (H<sup>+</sup> type) by using 6M NaOH and 2M H<sub>2</sub>SO<sub>4</sub> aqueous solution, respectively, (2) dissolving PFSA resin into *N,N*-dimethyl formamide (DMF) by using an autoclave at 230 °C [26] and subsequently concentrating the solution to 13.6 wt.%, (3) casting the PFSA/DMF solution onto a glass plate by using a stainless steel scraper and treating it in an oven at 180 °C for 4 h, (4) peeling off the pristine PFSA membranes. Thickness of the PFSA membranes was about 58 ± 3 μm and the ion exchange capacity (IEC) was 0.924 meq g<sup>-1</sup>, which was measured by titration method.

The modified membranes were prepared by using Sc-CO<sub>2</sub> impregnation method. In a typical experiment for the impregnation process, a certain amount of MPMDMS and deionized water (ratio of 5:1 v/v) were placed into the bottom of a 110 ml stainless-steel autoclave (Zhangjiang Huali Factory, China). A desired piece of dry PFSA membrane (8 cm × 16 cm) was fixed with a stainless-steel cage at the upper part of the autoclave for the purpose of not con-

tacting with the MPMDMS solution. After that, the autoclave was heated to 40 °C and CO<sub>2</sub> was filled into the autoclave up to a desired pressure of about 20 MPa by using a syringe pump. The supercritical impregnation system was stirred by a magnetic stirrer and kept for 8 h. Then, the autoclave was cooled down to room temperature and the pressure was released at the speed of 2.0 MPa h<sup>-1</sup> through a needle valve. Finally, the modified PFSA membrane which has been impregnated with poly(MPMDMS) was taken out and rinsed with ethanol aqueous solution to remove the remnant reactants. The impregnated amount of poly(MPMDMS) in the modified membrane was controlled by the amount of MPMDMS which would be added into the autoclave.

The modified membranes were then treated with 10 wt.% H<sub>2</sub>O<sub>2</sub> aqueous solution at 60 °C for 60 min to oxidize thiol (–SH) groups of poly(MPMDMS) to sulfonic acid groups (–SO<sub>3</sub>H) as described in the literature [13]. Subsequently, the membranes were rinsed with deionized water, dried at 100 °C in a vacuum oven, and weighed to determine the impregnated content. Finally, the membranes were treated in 1 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 2 h and rinsed with deionized water for further use. The contents of poly(MPMDMS) in the modified PFSA membranes were 2.4 wt.%, 5.0 wt.%, 9.3 wt.% and 13.9 wt.%, which were donated as PS-1, PS-2, PS-3 and PS-4, respectively.

### 2.2. Characterization of the modified membranes

Before ATR-IR measurements, the membranes were dried in a vacuum oven at 100 °C for 4 h. The ATR-IR spectra were obtained by using a FT-IR spectrophotometer (Bruker, EQUINOX 55) equipped with an attenuated total reflection accessory using a ZnSe crystal, at the resolution of 4 cm<sup>-1</sup>, 64 scans. Surface morphology observation of the membranes was carried out on a JSM-7401F (JEOL Ltd, JP) SEM. Before TEM measurements, the membrane samples were embedded in epoxy resin, sectioned to yield slices with the thickness of about 60 nm by using a microtome (Leica Ultracut UCT6, Leica, Germany), and then placed on copper grids. The TEM images were taken on a JEM-2010 (JEOL, Japan) TEM.

### 2.3. Water and methanol uptake measurements

The membranes were cut into approximately 2 cm × 4 cm pieces. Weights of the wet samples were measured after being boiled in deionized water for 1 h. After that, the membranes were dried in vacuum oven at 100 °C for 8 h and subsequently reweighed. Water uptake ( $W_{H_2O}$ ) was calculated by the Eq. (1):

$$W_{H_2O} = \frac{M_w - M_d}{M_d} \times 100\% \quad (1)$$

where  $M_d$  and  $M_w$  are the weights of the dry and water-boiled membrane samples, respectively.

Methanol uptake was measured with the similar method, by weighing the membranes after being soaked in methanol solvent for about 12 h and re-weighing the membranes after being dried in vacuum oven at 100 °C for 8 h.

### 2.4. Proton conductivity measurements

The proton conductivity of the membranes in the plane direction was measured with two electrode AC impedance method by using Autolab PGSTA302 electrochemical test system (Eco Chemie, Netherlands) at 100% relative humidity (R.H.). In our experiments, the measured temperature was controlled from room temperature to 65 °C. Proton conductivity ( $\sigma$ ) was calculated as follows:

$$\sigma = \frac{L}{R \cdot A} \quad (2)$$

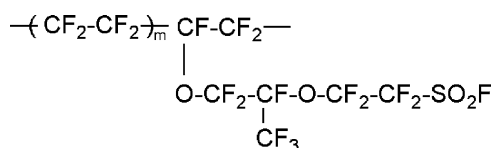


Fig. 1. The structure formula of perfluorosulfonic acid precursor,  $m$  is about 5–7.

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