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

Lijun Su, Lei Li, Hong Li, Junkun Tang, Yongming Zhang*, Wei Yu*, Chixing Zhou

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, No. 800 Dongchuan Road, Shanghai 200240, PR China

A B S T R A C T

Polysiloxane modified perfluorosulfonic acid (PFSA) composite membranes are prepared by using (3-mercaptopropyl) methyldimethoxysilane (MPMDMS) as a precursor of silicon alkoxide in supercritical carbon dioxide (Sc-CO$_2$) system. In the Sc-CO$_2$ system with the presence of water, Sc-CO$_2$ 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$_2$ system may be the suitable candidate electrolytes for direct methanol fuel cell applications.

© 2009 Elsevier B.V. All rights reserved.

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$_2$ 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$_2$ particles. To solve this

problem, some functionalized acid groups, such as –SO$_3$H, were introduced onto SiO$_2$ 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$_2$ precursor/alcohol solution. The condensation polymerization reaction was mainly catalyzed by the –SO$_3$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$_2$ 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$_2$) as a solvent and swelling reagent has attracted much attention [18–20]. Compared with the common impregnation method using organic impregnation solvents, Sc-CO$_2$ 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$_2$ system, and the solubility of solutes in the Sc-CO$_2$ can be easily controlled by adjusting the pressure. Then, it is possible to cause organic SiO$_2$ precursor to homogeneously polymerize into the PFSA membranes, not

* Corresponding authors. Tel.: +86 21 34202613; fax: +86 21 54742567.
E-mail addresses: ymzsjtu@yahoo.com.cn, ymzhang@sjtu.edu.cn (Y. Zhang), wyu@sjtu.edu.cn (W. Yu).

only polymerizing in the ion cluster regions using the common impregnation methods. Moreover, Sc-CO$_2$ can be easily removed from the products completely at the end of the process. Using Sc-CO$_2$ 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$_2$ impregnation method to reduce the methanol crossover of membranes for DMFC. Kim et al. [18] synthesized palladium/Nafion® composite membranes by using the Sc-CO$_2$ impregnation method. The composite membranes showed lower methanol permeability than that of Nafion® 117. Gribov et al. [24] prepared zeolite–Nafion® nanocomposite membranes assisted by Sc-CO$_2$. The zeolite–Nafion® composite membranes possessed of much higher selectivity (ratio of proton conductivity to methanol permeability) than that of Nafion® 115. Nevertheless, the proton conductivity decreased too much due to lower conductivity of zeolite.

In this study, the functional SiO$_2$ precursor—(3-mercaptopropyl) methyldimethoxysilane (MPMDMS) was impregnated into the pre-swelled PFSA membrane by using Sc-CO$_2$ 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$_3$H, because the group –SH in the poly(MPMDMS) can be oxidized to –SO$_3$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$^+$ type) by using 6 M NaOH and 2 M H$_2$SO$_4$ 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^{-1}, which was measured by titration method.

The modified membranes were prepared by using Sc-CO$_2$ 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$_2$ 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^{-1} 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$_2$O$_2$ aqueous solution at 60 °C for 60 min to oxidize thiol (–SH) groups of poly(MPMDMS) to sulfonic acid groups (–SO$_3$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$_2$SO$_4$ 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^{-1}, 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):

$$W_{H_2O} = \frac{M_w - M_d}{M_d} \times 100\% \tag{1}$$

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 (σ) was calculated as follows:
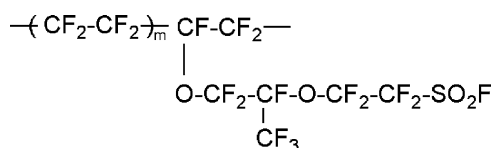
$$\sigma = \frac{L}{R \cdot A} \tag{2}$$

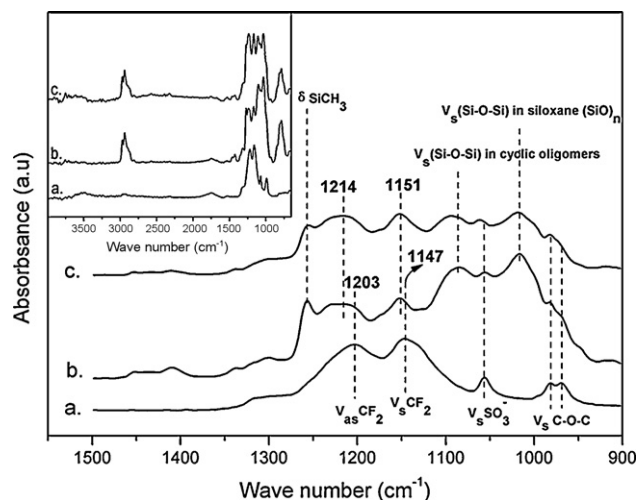**Fig. 1.** The structure formula of perfluorosulfonic acid precursor, *m* is about 5–7.

Fig. 2. ATR-IR spectra of (a) pristine PFSA membrane, (b) modified PFSA membrane with 13.9 wt.% poly(MPMDMS), (c) modified PFSNa membrane with 12.8 wt.% poly(MPMDMS) in dried state.

where L and A are the distance between the two electrodes and cross-sectional area of the sample, respectively, R is the resistance of membrane.

2.5. Methanol permeability measurements

The methanol permeation of each membrane was conducted using a home-made diffusion cell, which consisted of two compartments. One compartment (A) was filled with 2 M methanol aqueous solution, the other compartment (B) was filled with deionized water. The testing membrane samples were clamped between the two compartments. The concentration of permeated methanol in compartment (B) was measured by using gas chromatography with a thermal conductivity detector (GC9790-II, Fuli, China). In our experiments, the measured temperature was controlled from room temperature to 65 °C. Methanol permeability (P) was calculated from the slope of the linear plot of methanol concentration versus permeation time, according to Eq. (3).

$$C_B(t) = \frac{S \cdot P}{V_B \cdot L} C_A t \qquad (3)$$

where C_B and C_A are the concentrations of methanol in compartment B and A, respectively, V_B is the liquid volume in compartment B, S and L are the area and thickness of the membranes.

3. Results and discussion

The representative ATR-IR spectra between 4000 and 650 cm^{-1} of the pristine PFSA and modified MPMDMS/PFSA membranes are shown in Fig. 2. The characteristic infrared bands and their assignations [27–30] for the pristine PFSA membrane are presented in Table 1. In contrast to the ATR-IR spectrum of pristine PFSA membrane, the characteristic bands of poly(MPMDMS) in the modified membranes (PS-4) were observed at about 769 cm^{-1}, 1257 cm^{-1}

Table 1
ATR-IR characteristic peaks and their assignments for the pristine PFSA membranes.

Absorbance peaks	Pristine membrane (cm^{-1})
CF$_2$ asymmetric stretching	1201
CF$_2$ symmetric stretching	1146
SO$_3^-$ symmetric stretching	1057
C–O–C stretching	981 and 970
C–S stretching	804

and 2920 cm^{-1}, assigning to the chemical bonding absorption of V_s(Si–C), δ(SiCH$_3$) and V_s(CH$_2$), respectively. In this study, the PFSNa membrane (Na$^+$ type) also went through the impregnation procedure and a remarkable phenomenon was found that the condensation polymerization reaction of MPMDMS also occurred to produce poly(MPMDMS) without the catalysis of –SO$_3$H groups in the PFSA membranes. As can be seen in Fig. 2, there emerge strongly characteristic absorption bands of poly(MPMDMS) in the PFSNa membrane even at the shorter impregnation time (within 10 min) by using the Sc-CO$_2$ method. Toews et al. [31] pointed out that the pH value of water in equilibrium with Sc-CO$_2$ at 40 °C and 20 MPa was 2.80 and the pH value would be even lowered at higher pressure and lower temperature. So the presence of water in Sc-CO$_2$ would provide an acid atmosphere to catalyze the condensation polymerization of MPMDMS. Further more, compared with the pristine PFSA membrane, another significantly feature for the modified membrane (PS-4) is the distinct blue shift from 1203 cm^{-1} to 1214 cm^{-1} for V_{as}(CF$_2$) and 1147 cm^{-1} to 1151 cm^{-1} for V_s(CF$_2$), which indicated that the poly(MPMDMS) has been incorporated into the backbone domain of the PFSA polymers by using the Sc-CO$_2$ system and interacted with the C–F bonds of PFSA polymers.

Fig. 3 shows the representative images of the pristine and modified membranes (PS-4). As can be seen, both of the pristine and modified membranes possessed of compact structure without any pores on the surfaces. A notable feature for Fig. 3b is that a very thin layer of poly(MPMDMS) overlaid on the surface of PFSA membrane and induced a slightly coarse surface of the modified membrane. Fig. 4 shows the representative TEM images for the pristine and
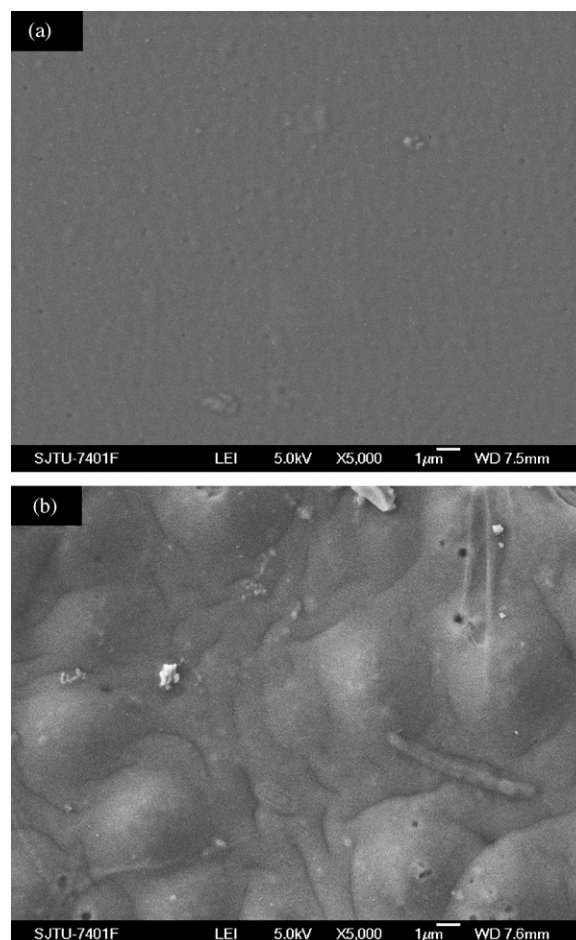

Fig. 3. Representative SEM images for the surfaces of (a) pristine and (b) modified PFSA membranes with 13.9 wt.% poly(MPMDMS).
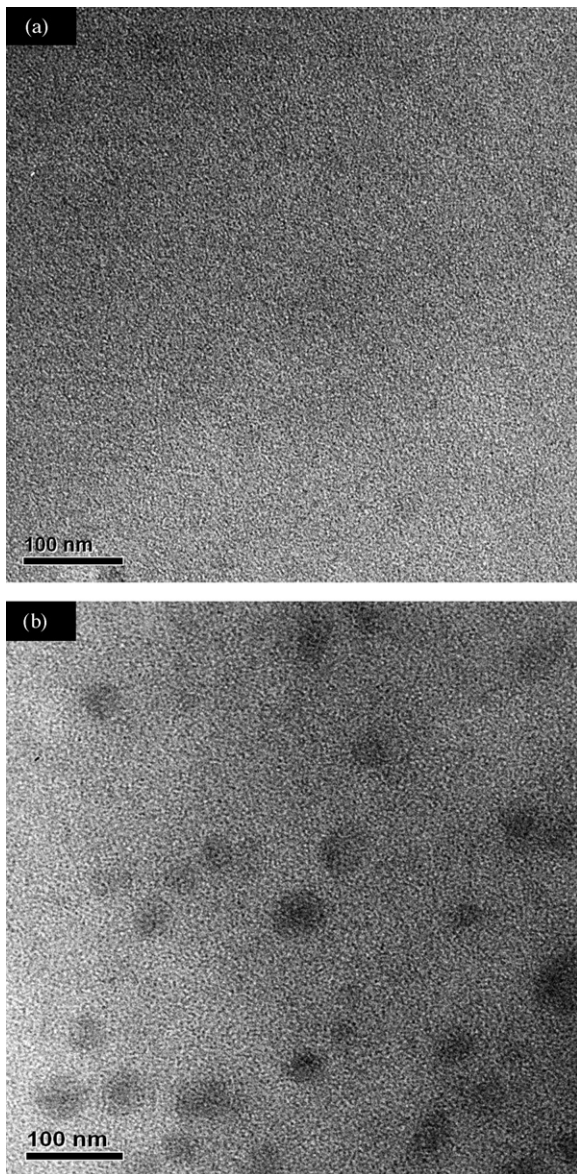
Fig. 4. Representative TEM images of the (a) pristine and (b) modified PFSA membranes with 13.9 wt.% poly(MPMDMS).

modified PFSA membranes (PS-4). The dark regions are areas of high silicon concentration [12]. From Fig. 4b, it can be found that there are a lot of approximately roundish dark regions with size of about 40–70 nm homogeneously dispersed in the membrane after the impregnation by using Sc-CO$_2$ method. The noticeable advantage of preparing modified membranes by using Sc-CO$_2$ method is its possibility to obtain ordered and larger silicone particles. For the PFSA membrane, such as Nafion®, there exist ion clusters with size of about 5 nm formed by the side chains' –SO$_3$H groups of PFSA polymers. With the assistance of Sc-CO$_2$ which is a low surface tension reagent and has a certain interaction with C–F bonds of fluoropolymers [32,33], MPMDMSs would be brought into the fluorocarbon regions of PFSA membranes and condensation polymerization occurred in these regions with the assistance of water/Sc-CO$_2$ (catalyst) system. As shown in Fig. 4b, the poly(MPMDMS) particles with size of about 40–70 nm were not restricted to the ionic clusters of the PFSA membrane and the regions of high density poly(MPMDMS) actually coexisted with the PFSA backbone phases at least at their periphery. All the morpholo-

gies suggested that the transportation properties of methanol and proton through the PFSA membrane might be changed.

The proton conductivity of our PFSA membranes and Nafion® 117 was measured in the plane direction at room temperature and 100% R.H. The measurement results as well as water uptakes are listed in Table 2. Each sample was measured at least five times within a standard deviation of about ±5%. As can be seen in Table 2, proton conductivity of the membranes has the same trend as water uptake with increasing the poly(MPMDMS) content. Such an observation is consistent with the research that has shown an increased conductivity with increased water content in Nafion® membrane [34,35]. Moreover, proton conductivity of the pristine PFSA membrane was higher than that of Nafion® 117 membrane, maybe resulted from the different preparation methods and IEC values. As we know, Nafion® 117 membrane with 0.91 meq g^{-1} was prepared by the melt-extrusion method. However, our PFSA membranes with 0.924 meq g^{-1} were prepared by the solution-casting method. After the pristine membrane was modified with poly(MPMDMS), proton conductivity increased initially with increasing the content of poly(MPMDMS) from 0 wt.% to 5.0 wt.% because of the introduction of –SO$_3$H functional group to facilitate the proton transportation. However, the proton conductivity decreased when more poly(MPMDMS)s were introduced above 5.0 wt.%, maybe caused by the slight phase separation [13] or the impregnation of more poly(MPMDMS)s with lower conductivity.

Methanol uptake and methanol permeability of the pristine and modified PFSA membranes are also listed in Table 2. Compared with the water uptake, methanol has a more preferential solubility into all membranes over water, in particular for the pristine and Nafion® 117 membranes. However, after the impregnation of poly(MPMDMS), methanol uptake of the modified membranes decreased evidently. Therefore, the modified membrane might be endowed lower methanol permeation during the DMFC operation [36]. From Table 2, it can be found that the methanol permeability of the pristine membrane was similar with Nafion® 117. However, as expected, after the introduction of poly(MPMDMS) into the PFSA membrane, methanol permeability decreased and became much lower with more poly(MPMDMS)s impregnated. For PS-4 with 13.9 wt.% impregnation, the methanol permeability was reduced to 2.14×10^{-7} cm^2 s^{-1}, decreasing about 87.0% than that of pristine membrane. The permeation of methanol occurred not only through the ion clusters but across the hydrophobic polymer backbones [10,37,38]. By using this Sc-CO$_2$ impregnation method, the impregnated poly(MPMDMS)s had not only been incorporated with of ion clusters but coexisted with hydrophobic polymer backbones, which would change the methanol transportation path and hinder methanol permeation. With more impregnated poly(MPMDMS)s, higher resistance would be formed to hinder the methanol permeation inside the PFSA membrane. Moreover, the overlaid thin layer of poly(MPMDMS) on the PFSA membrane surface might be another reason to reduce the methanol permeation.

Accordingly, Table 2 shows the selectivity (ratio of proton conductivity to methanol permeability) [39] of the pristine and modified PFSA membranes at room temperature. As can be seen, all the modified PFSA membranes had higher selectivity values than the unmodified and Nafion® 117 membranes. The maximum selectivity value was reached for the modified membrane PS-4, which was about 5.49 times higher than that of pristine membrane and 5.88 times higher than that of Nafion® 117. Further more, Table 3 lists the transport properties of some new membranes reported from the literature references [40–42] and the modified membrane PS-4. It can be seen that our modified membrane (PS-4) had a good performance along with them.

Herein, proton conductivity of the pristine and modified PFSA membranes PS-4, as well as Nafion® 117, as a function of temperature is shown in Fig. 5. As expected, proton conductivity of all

Table 2
Performances for the pristine and modified PFSA membranes at room temperature within standard deviation of about ±5%.

	Samples					
	Pristine	PS-1	PS-2	PS-3	PS-4	Nafion® 117
Content of poly(MPMDMS) (wt.%)	0	2.4	5.0	9.3	13.9	0
Thickness of wet membranes (μm)	72	71	72	73	72	201
Water uptake (wt.%)	36.3	38.0	38.7	36.6	32.2	35.8
Methanol uptake (wt.%)	100.1	90.5	81.0	72.9	54.7	91.2
Proton conductivity (mS cm^{-1})	105.3	107.7	116.5	106.6	88.6	98.7
Methanol permeability (10^{-7} cm^2 s^{-1})	16.5	13.1	10.3	7.36	2.14	16.4
Selectivity (10^4 S s cm^{-3})	6.38	8.22	11.3	14.5	41.4	6.02

Table 3
Transport properties of our membrane and some new membranes described in the literature at room temperature.

Membrane	Proton conductivity (mS cm^{-1})	Methanol permeability (10^{-7} cm^2 s^{-1})	Selectivity		Reference
			10^4 S s cm^{-3}	Relative to Nafion®	
SPEEK-20[a]	≈1.28	0.36	≈ 3.56	1.27	[40]
SPEEK-56[a]	10.61	5.93	1.79	1.68	[41]
SPEEK-66[a]	19.96	6.04	3.30	3.10	[41]
PSA-SPAE[b]	13[c]	0.56	23.2	4.79	[42]
Sc-naf-coll[d]	3.8	0.084	45	19	[24]
PS-4	88.6	2.14	41.4	6.88	

[a] SPEEK-X: sulfonated polyether ether ketone with degree of sulfonation X%.
[b] Side-chain-type sulfonated poly(arylene ether)s bearing sulfoalkyl pendant groups.
[c] Measured at 30 °C.
[d] Nafion® 115 membrane immersing in pre-silicalite sol after treated in Sc-CO$_2$.

membranes increased with increasing temperature. However, proton conductivity of the modified membrane PS-4 increased faster than that of the pristine and Nafion® 117 membranes. When the temperature was above 65 °C, proton conductivity of PS-4 was close to that of Nafion® 117. The apparent activation energy of PS-4 (11.3 kJ mol^{-1}) was higher than that of both pristine (9.2 kJ mol^{-1}) and Nafion® 117 (9.8 kJ mol^{-1}) membranes. This phenomenon may be caused by the introduction of poly(MPMDMS)s with relatively weak acid group –SO$_3$H. Since –SO$_3$H in the PFSA membranes was a strong acid, both pristine and Nafion® 117 membranes can be fully ionized at room temperature, so an increase in temperature would have no effect on the ionic density of membranes. However, –SO$_3$H in poly(MPMDMS)s was a relatively weak acid, the modified PFSA membrane cannot be fully ionized at room temperature. The dissociation constant of –SO$_3$H in poly(MPMDMS)s varied with temperature, then ionic density in the modified membranes also

varied. Thus, the activation energy of the modified membranes was higher than that of PFSA membranes [43].

The relation between methanol permeability and temperature is shown in Fig. 6. The apparent activation energy of our pristine PFSA membrane was close to Nafion® 117, 20.9 kJ mol^{-1} for the pristine membrane and 19.6 kJ mol^{-1} for Nafion® 117, respectively. For the modified membrane PS-4, the apparent activation energy was about 38.3 kJ mol^{-1}, much higher than that of both pristine and Nafion® 117 membranes. This seemed to indicate that the nano-fillers might have altered the membrane microstructure to a significant extent and the methanol permeation path might have been changed, thus resulting in higher resistance to the methanol permeation after the impregnation by using this Sc-CO$_2$ method.

The selectivity values of pristine and modified membranes PS-4 as well as Nafion® 117 at different temperatures are listed in Table 4. Because of its high proton conductivity and low methanol perme-
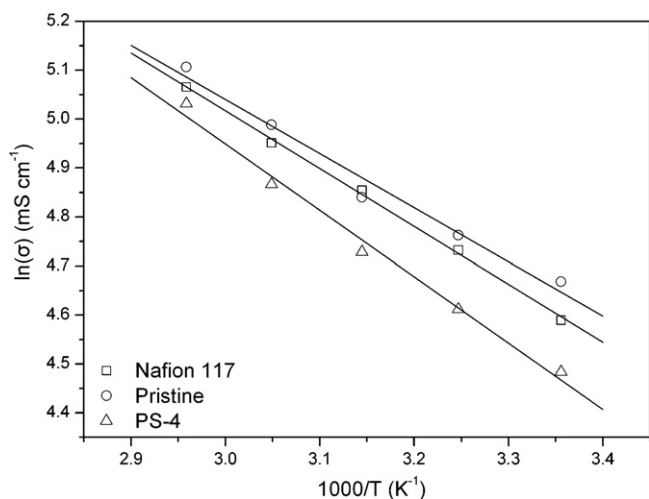
Fig. 5. Arrhenius plot of proton conductivity for pristine, modified PFSA membranes with 13.9 wt.% poly(MPMDMS) and Nafion® 117.
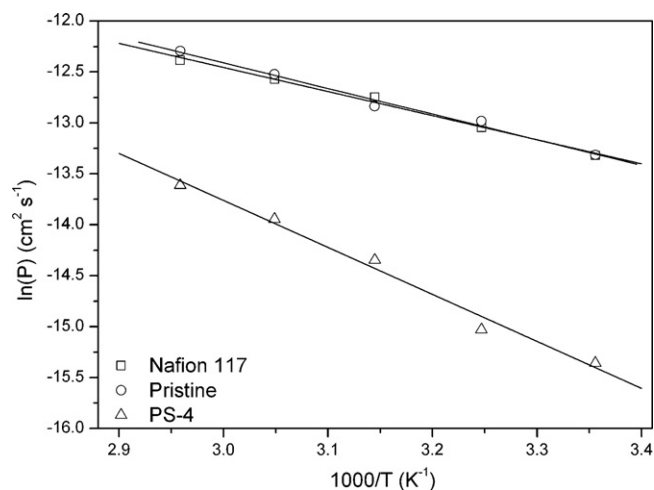
Fig. 6. Arrhenius plot of methanol permeability for pristine, modified PFSA membranes with 13.9 wt.% poly(MPMDMS) and Nafion® 117.

Table 4
Selectivity values of the pristine, modified PFSA membranes PS-4 and Nafion® 117 at different temperatures.

	Temperature (°C)				
	25	35	45	55	65
Pristine (10^4 S s cm^{-3})	6.38	5.35	4.30	4.19	3.87
Nafion® 117 (10^4 S s cm^{-3})	6.02	5.25	4.41	4.07	3.79
PS-4 (10^4 S s cm^{-3})	41.4	33.9	19.2	14.8	12.5

ability, the modified PFSA membrane PS-4 had higher selectivity values than the unmodified pristine and Nafion® 117 membranes over all the temperature range of 25–65 °C. Therefore, the modified membrane prepared by Sc-CO$_2$ method may be a promising candidate electrolyte for DMFC applications.

4. Conclusion

In this work, MPMDMS-PFSA composite membranes were successfully prepared with the assistance of Sc-CO$_2$ which is an environmental friendly, nontoxic and inexpensive solvent. It was found that the Sc-CO$_2$ with the presence of water can be functioned as an acid catalyst for the condensation polymerization of MPMDMS. The agglomerated poly(MPMDMS) particles with size of about 40–70 nm were formed not only within the ion clusters but also in the PFSA C–F backbone matrix regions. The methanol permeability of modified PFSA membrane PS-4 with 13.9 wt.% impregnation showed a remarkable decrease without evident reduction of proton conductivity in the temperature range of 25–65 °C. Therefore, the modified membrane PS-4 was endowed a superior selectivity of about 5.49 times higher than that of the pristine membrane and 5.88 times than that of Nafion® 117 at room temperature. The apparent activation energies of PS-4 membrane for both proton conduction and methanol permeation were higher than that of the pristine and Nafion® 117 membranes. At 65 °C, the selectivity of PS-4 was 2.23 and 2.30 times higher than that of the pristine and Nafion® 117 membranes, respectively. It indicated that the modified PFSA membrane prepared by Sc-CO$_2$ impregnation may be a promising candidate electrolyte for DMFC applications.

References

[1] M. Broussely, G. Archdale, J. Power Sources 136 (2004) 386–394.
[2] N.A. Hampson, M.J. Willars, B.D. McNicol, J. Power Sources 4 (1979) 191–201.
[3] R.F. Service, Science 296 (2002) 1222–1224.
[4] S.W. Choi, Y.Z. Fu, Y.R. Ahn, S.M. Jo, A. Manthiram, J. Power Sources 180 (2008) 167–171.
[5] H.S. Park, Y.J. Kim, W.H. Hong, H.K. Lee, J. Membr. Sci. 272 (2006) 28–36.
[6] B.G. Choi, H. Park, H.S. Im, Y.J. Kim, W.H. Hong, J. Membr. Sci. 324 (2008) 102–110.
[7] H. Wu, B. Zheng, X. Zheng, J. Wang, W. Yuan, Z. Jiang, J. Power Sources 173 (2007) 842–852.
[8] Z. Liu, B. Guo, J. Huang, L. Hong, M. Han, L.M. Gan, J. Power Sources 157 (2006) 207–211.
[9] Q. Deng, C.A. Wilkie, R.B. Moore, K.A. Mauritz, Polymer 39 (1998) 5961–5972.
[10] R. Jiang, H.R. Kunz, J.M. Fenton, J. Membr. Sci. 272 (2006) 116–124.
[11] D.H. Jung, S.Y. Cho, D.H. Peck, D.R. Shin, J.S. Kim, J. Power Sources 106 (2002) 173–177.
[12] B.P. Ladewig, R.B. Knott, D.J. Martin, J.C.D. da Costa, G.Q. Lu, Electrochem. Commun. 9 (2007) 781–786.
[13] C.Y. Yen, C.H. Lee, Y.F. Lin, H.L. Lin, Y.H. Hsiao, S.H. Liao, C.Y. Chuang, C.C.M. Ma, J. Power Sources 173 (2007) 36–44.
[14] S.W. Tay, X. Zhang, Z. Liu, L. Hong, S.H. Chan, J. Membr. Sci. 321 (2008) 139–145.
[15] C. Li, G. Sun, S. Ren, J. Liu, Q. Wang, Z. Wu, H. Sun, W. Jin, J. Membr. Sci. 272 (2006) 50–57.
[16] S.Z. Ren, G.Q. Sun, C.N. Li, Z.X. Liang, Z.M. Wu, W. Jin, X. Qin, X.F. Yang, J. Membr. Sci. 282 (2006) 450–455.
[17] R.A. Zoppi, I.V.P. Yoshida, S.P. Nunes, Polymer 39 (1998) 1309–1315.
[18] D. Kim, J. Sauk, J. Byun, K.S. Lee, H. Kim, Solid State Ionics 178 (2007) 865–870.
[19] M. Poliakoff, S.M. Howdle, S.G. Kazarian, Angew. Chem. Int. Ed. Engl. 34 (1995) 1275–1295.
[20] J.J. Watkins, T.J. McCarthy, Macromolecules 28 (1995) 4067–4074.
[21] D. Li, Z.M. Liu, B.X. Han, L.P. Song, G.Y. Yang, T. Jiang, Polymer 43 (2002) 5363–5367.
[22] C.D. Saquing, D. Kang, M. Aindow, C. Erkey, Micropor. Mesopor. Mater. 80 (2005) 11–23.
[23] R.H. Sui, A.S. Rizkalla, P.A. Charpentier, Cryst. Growth Des. 8 (2008) 3024–3031.
[24] E.N. Gribov, E.V. Parkhomchuk, I.M. Krivobokov, J.A. Darr, A.G. Okunev, J. Membr. Sci. 297 (2007) 1–4.
[25] Y. Luan, H. Zhang, Y. Zhang, L. Li, H. Li, Y. Liu, J. Membr. Sci. 319 (2008) 91–101.
[26] C.R. Martin, T.A. Rhoades, J.A. Ferguson, Anal. Chem. 54 (1982) 1639–1641.
[27] S. Tan, D. Belanger, J. Phys. Chem. B 109 (2005) 23480–23490.
[28] Z.X. Liang, W.M. Chen, J.G. Liu, S.L. Wang, Z.H. Zhou, W.Z. Li, G.Q. Sun, Q. Xin, J. Membr. Sci. 233 (2004) 39–44.
[29] M. Lavorgna, L. Mascia, G. Mensitieri, M. Gilbert, G. Scherillo, B. Palomba, J. Membr. Sci. 294 (2007) 159–168.
[30] C.Y. Chen, J.I. Garnica-Rodriguez, M.C. Duke, R.F. Dalla Costa, A.L. Dicks, J.C.D. da Costa, J. Power Sources 166 (2007) 324–330.
[31] K.L. Toews, R.M. Shroll, C.M. Wai, N.G. Smart, Anal. Chem. 67 (1995) 4040–4043.
[32] S.G. Kazarian, M.F. Vincent, F.V. Bright, C.L. Liotta, C.A. Eckert, J. Am. Chem. Soc. 118 (1996) 1729–1736.
[33] W.H. Tuminello, G.T. Dee, M.A. McHugh, Macromolecules 28 (1995) 1506–1510.
[34] T.A. Zawodzinski, J. Davey, J. Valerio, S. Gottesfeld, Electrochim. Acta 40 (1995) 297–302.
[35] T.A. Zawodzinski Jr., C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 1041–1047.
[36] J. Lin, P.H. Wu, R. Wycisk, A. Trivisonno, P.N. Pintauro, J. Power Sources 183 (2008) 491–497.
[37] N. Miyake, J.S. Wainright, R.F. Savinell, J. Electrochem. Soc. 148 (2001) A905–A909.
[38] Z. Wu, G. Sun, W. Jin, H. Hou, S. Wang, J. Membr. Sci. 325 (2008) 376–382.
[39] B.S. Pivovar, Y. Wang, E.L. Cussler, J. Membr. Sci. 154 (1999) 155–162.
[40] A. Regina, E. Fontananova, E. Drioli, M. Casciola, M. Sganappa, F. Trotta, J. Power Sources 160 (2006) 139–147.
[41] A.F. Ismail, N.H. Othman, A. Mustafa, J. Membr. Sci. 329 (2009) 18–29.
[42] J. Pang, H. Zhang, X. Li, L. Wang, B. Liu, Z. Jiang, J. Membr. Sci. 318 (2008) 271–279.
[43] L. Li, J. Zhang, Y.X. Wang, J. Membr. Sci. 226 (2003) 159–167.