Preparation and characterization of the PVDF-based composite membrane for direct methanol fuel cells

Qian Liu, Laizhou Song, Zhihui Zhang, Xiaowei Liu

Department of Environmental & Chemical Engineering, Yanshan University, Qinhuangdao 066004, China.

Abstract
The polyvinylidene fluoride-sulfonated polystyrene composite membrane with proton exchange performance, denoted as PVDF-SPS, was prepared using a thermally induced polymerization technique. The thermal stability of the PVDF-SPS composite membrane was investigated using thermogravimetric (TG) analysis. The complex formation of the composite membrane was ascertained by Fourier transform infrared spectroscopy (FTIR). The surface compositions of the PVDF-SPS membrane were analyzed using X-ray photoelectron spectroscopy (XPS). The morphology of the composite membrane was characterized by environmental scanning electron microscopy (ESEM). The proton conductivity of the PVDF-SPS membrane was measured using impedance spectroscopy in the hydrated condition. The PVDF-SPS membrane has a stronger hydrophilic character than the pristine PVDF membrane and the polyvinylidene fluoride-polystyrene composite membrane (PVDF-PS), which is caused by the incorporation of sulfonic acid groups. The proton conductivity and the methanol permeability of the PVDF-SPS membrane measured at 298 K are 29.3 mS.cm^{-1} and 8.6×10^{-8} cm^2.s^{-1}, respectively. Although PVDF-SPS composite membrane possesses the lower oxidative stability than Nafion-117 membrane, the composite membrane displays lower methanol permeability than the Nafion-117 membrane, and the selectivity (the ratio of proton conductivity and methanol permeability) of the composite membrane is almost 20 times than that of Nafion-117.
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Keywords: Polyvinylidene fluoride-based composite membrane, Thermally induced polymerization, Proton conductivity, Methanol permeability, Oxidative stability.

1. Introduction
The proton exchange membranes (PEMs) have played an important role in direct methanol fuel cells (DMFCs). Membranes with high proton conductivity are potentially useful in electrochemical cells including fuel cells. Normally, the widely used membranes in DMFCs are still perfluorinated membranes, such as Nafion membranes, due to their high specific conductivity at room temperature, as well as good mechanical and chemical stability. However, the cost and high methanol permeability are the main difficulties for using them in DMFCs [1].
A number of studies have been performed with the goal of developing alternative membranes, focusing on the reduction of the methanol permeability. Some of them have focused on developing new synthetic polymeric membranes that have ionic clusters [2-11], and the modification of the Nafion membranes by surface treatment or by blending them with other polymer/inorganic materials [12-21]. Polyvinylidene

fluoride (PVDF) with excellent stability, is a kind of partial fluorinated polymer and has been widely used in the battery field [22, 23]. It has been reported that PVDF-based composite membrane with nano-sized ceramic powders could exhibit high proton conductivity when doped with some small molecular weight acid [24]. Polyvinylidene fluoride grafted polystyrene sulfonated acid proton exchange membranes based on a radiation-grafting technique were found that they have a higher proton conductivity, water-uptake and lower methanol permeability compared to Nafion membranes [25].

In this work, based on the method of thermally induced polymerization and phase inversion technique [26], the PVDF-based composite membrane (denoted as PVDF-SPS) with the performance of proton conductivity was prepared. Styrene was used to be polymerized and blended with the PVDF polymer. A kind of copolymer, polyvinylidene fluoride (PVDF)/sulfonated polystyrene (SPS) was adopted to prepare the PVDF composite membrane. The structure and the morphology of the PVDF-SPS composite membrane were characterized. The proton conductivity and the methanol permeability of the PVDF-SPS composite membrane were also investigated.

2. Experimental

2.1 Materials

In the study, PVDF powders (reagent grade) were obtained from Chen Guang Chemical Plant (China). Nafion-117 membrane with thickness of 230 μm, was provided by He Sen Electrical Plant (Shanghai, China). The PVDF composite membrane was made in our laboratory using a combination technique of thermally induced polymerization and phase inversion, and all of the other reagents were analytical grade.

2.2 Preparation of the PVDF-based composite membrane

The PVDF powders were basified firstly, and the double bond was formed [27]. The PVDF powders were dissolved in N, N-dimethylacetamide (DMAc) firstly, and then styrene, divinylbenzene (DVB) and benzoyl peroxide (BPO) were added to the solution and stirred with water bath at 343 K. The dosage of PVDF, styrene, DVB and BPO was that PVDF was 80 g.L^{-1}, styrene acted as 140 ml.L^{-1}, DVB was 7.5 ml.L^{-1}, and BPO was 2 g.L^{-1}, respectively. After the blending polymerization reaction, the polyvinylidene fluoride/polystyrene copolymer were sulfonated in a ClSO$_3$H acid/1,2-dichloroethane mixture at 313 K for 4 h. When the solution was cooled to the room temperature, the solution was immersed in deionized water for 48 h, and then the sulfonated copolymer washed with deionized water and dried for usage.

The sulfonated copolymer with weight of 15 g and 2.5 g polyvinyl pyrrolidine powders were dissolved in 100 mL DMAc. The mixture was heated at 343 K and stirred to obtain a viscous solution. After 2 h, the cast solution was degassed in a water bath at 313 K for 6 h. The PVDF-based composite membrane was prepared by a phase inversion process, and deionized water used as the non-solvent. The cast solution was cast onto a clean glass plate, and a flexible composite membrane was obtained. The membrane was washed several times with deionized water and then immersed in 0.5 mol.L^{-1} sulfuric acid solution for 24 h. The resulted membrane was washed with deionized water to remove the remaining sulfuric acid. The final proton exchange membrane was denoted as PVDF-SPS. The thickness of the swelled membrane is about 160 μm. The pristine PVDF membrane and the polyvinylidene fluoride/polystyrene membrane (PVDF-PS) were prepared with the phase inversion method referring to our previous work [26, 28].

2.3 Structural characterization

The thermogravimetric analysis (TG) of the membranes were carried out by a STA 449C thermogravimetric thermal analyzer under the dry argon atmosphere, and the samples were heated from 300 K to 973 K at a rate of 20 K.min^{-1}. The FTIR spectra of the pristine PVDF membrane, PVDF-PS membrane and the PVDF-SPS membrane were measured on E55+FRA106 FTIR spectrometer. Each spectrum was collected by cumulating 16 scans at a resolution of 4 cm^{-1}. The surface and cross-section morphologies of the PVDF-SPS membrane were analyzed using the XL30 environmental scanning electron microscopy (ESEM). VG ESCA250 X-ray photoelectron spectroscopy (XPS) was used to characterize the elements of the PVDF-SPS composite membrane.

2.4 Water uptake

Water uptake is defined by $(W_{wet} - W_{dry})/W_{dry}$, where W_{dry} is the weight of the sample membrane dried in a vacuum oven under 373 K for 12 h and W_{wet} is the weight of the sample membrane saturated with deionized water for 48 h and weighed immediately after removing surface water with filtration paper.

2.5 Measurement of proton conductivity
The proton conductivity of the PVDF-SPS membrane and Nafion-117 membrane was measured using the ac impedance technology. The sample of the given membrane was sandwiched between two stainless steel electrodes. A spring loaded Teflon plunger was used to ensure an intimate contact between the end of the probe and the membrane. The impedance tests were carried out in 10^5 Hz-10^{-2} Hz frequency range at a maximum perturbation amplitude of 5 mV, using a Solartron 1250 Impedance Analyzer coupled with a Solartron 1286 Electrochemical Interface. Before each measurement was carried out, the membrane was equilibrated in deionized water for 12 h at ambient temperature. The measurements of conductivity at high temperature were carried out in an oven. The proton conductivity of the membrane (σ, S.cm^{-1}) was calculated according to Eq. (1)

$$\sigma = \frac{L}{R \cdot A} \tag{1}$$

where L is the membrane thickness between the two electrodes (cm), R is the membrane resistance (ohm) and A is the cross-sectional area of membrane (cm^2).

2.6 Methanol permeability
A two-reservoir cell was used for the measurement of methanol permeability at 298 K. The left reservoir was filled with an aqueous solution of 1 mol.L^{-1} methanol, while the right reservoir was filled with deionized water. The two reservoirs had a circularly symmetrical transport channel with the membranes separated between them. The methanol flux was established across the membrane driven by the concentration difference between the two reservoirs. The change of methanol concentration with time in the right reservoir was measured using a gas chromatographic instrument (Agilent 6890N, USA). The methanol permeability of the membrane was then calculated using Eq. (2)

$$P = \frac{V_B L}{A C_A} \times \alpha \tag{2}$$

where C_A is the methanol concentration in the feed compartment (mol.L^{-1}). V_B is the volume of right reservoir (cm^3). A and L are the membrane cross-sectional area and thickness, respectively. α is the slope of the linear plot of methanol concentration in the right reservoir (C_B) versus time t.

2.7 Oxidative stability
The oxidative stability was investigated by measuring the weight change of the membrane with a size of 3cm × 3cm, and the membrane was immersed in 3wt.% H_2O_2 aqueous solution at 333K. Every 12 h, the sample was taken out and the excessive surface water was quickly wiped with a tissue paper. The weight of the membrane was measured using an electronic balance immediately. The stability of the membrane was evaluated using the reduction of its weight.

3. Results and discussion
3.1 Thermal analysis of the PVDF-SPS composite membrane
The TG analysis curve is presented in Figure 1 for the investigation of the thermal stability of the PVDF membrane, PVDF-PS membrane, and the PVDF-SPS composite membrane. For the pristine PVDF membrane (curve Figure 1a), the PVDF polymer is stable up to about 630 K and suffers a weight loss of less than 5 % at 673 K [28]. The PVDF-PS membrane is thermally stable up to about 610 K (curve Figure 1b), and the last weight loss step at temperatures above 710 K corresponds to the bulk decomposition of the PVDF polymer. The PVDF-SPS membrane (curve Figure 1c) shows intermediate weight loss behavior in comparison to that of the pristine PVDF membrane (curve Figure 1a) and the PVDF-PS composite membrane (curve Figure 1b). A distinct two-step degradation process is observed for the PVDF-SPS sample. The onset of the first major weight loss at about 520 K corresponds to the decomposition of the PS polymer component. The second major weight loss commences at about 710 K, corresponding to the decomposition of the PVDF main chains [28].
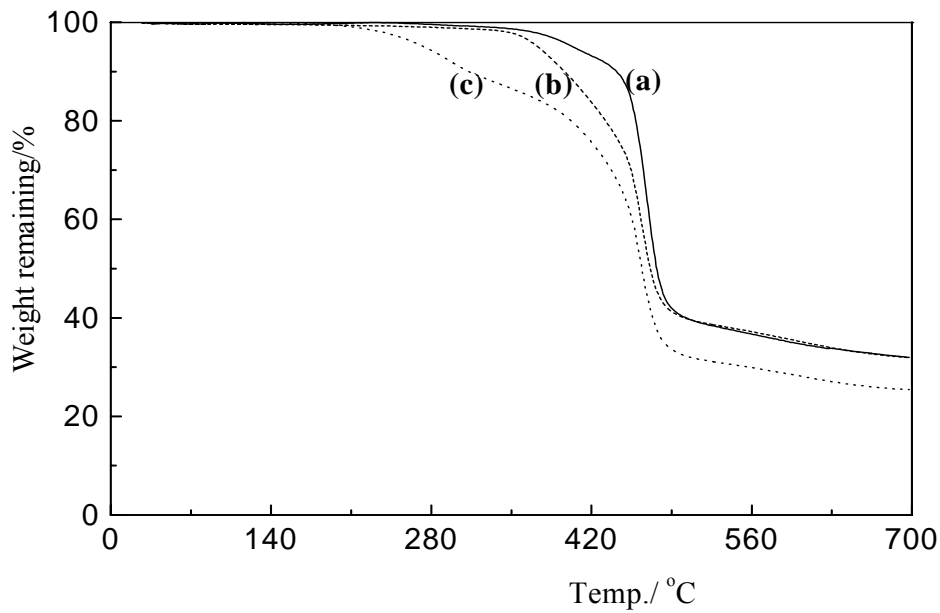
Figure 1. TG curve of the membranes: (a) PVDF, (b) PVDF-PS, (c) PVDF-SPS

3.2 FTIR spectra of the PVDF-SPS composite membrane

In order to investigate the complex formation in the PVDF-SPS membrane, FTIR studies have been carried out. FTIR spectra of the pristine PVDF membrane, the PVDF-PS membrane and the PVDF-SPS membrane are shown in Figure 2. The absorption peaks appearing at 3025 cm⁻¹, 471 cm⁻¹ and 1200 cm⁻¹ are assigned to CF stretching, CF wagging, and CF bending vibration modes of PVDF [28]. The peak at 1200 cm⁻¹ is found to be weak in the PVDF-based composite membranes. Blending of styrene is confirmed by the presence of aromatic ring features at 1493 and 1602 cm⁻¹ corresponding to the presence of skeletal C=C in plate stretching vibrations [25]. A characteristic peak of a mono-substituted benzene ring is also shown at 750 cm⁻¹. The peak at 699 cm⁻¹, shown in Figure 2b and 2c, originates from the benzene groups of PS [29]. In the PVDF-SPS membrane, as shown in Figure 2c, the new peak appearing at 1126 cm⁻¹ corresponds to the vibrations of the sulfonic acid groups (—SO₃H) attached to the benzene rings, and the peak at 1007 cm⁻¹ corresponds to those of the benzene groups containing the sulfonic acid groups [30, 31]. The broad peak at 3410 cm⁻¹ is assigned to the —OH species of water molecules that are involved in hydrogen bonding with the —SO₃⁻ groups [30, 32]. The FTIR spectra showed that the PVDF-SPS proton exchange membrane was prepared successfully.
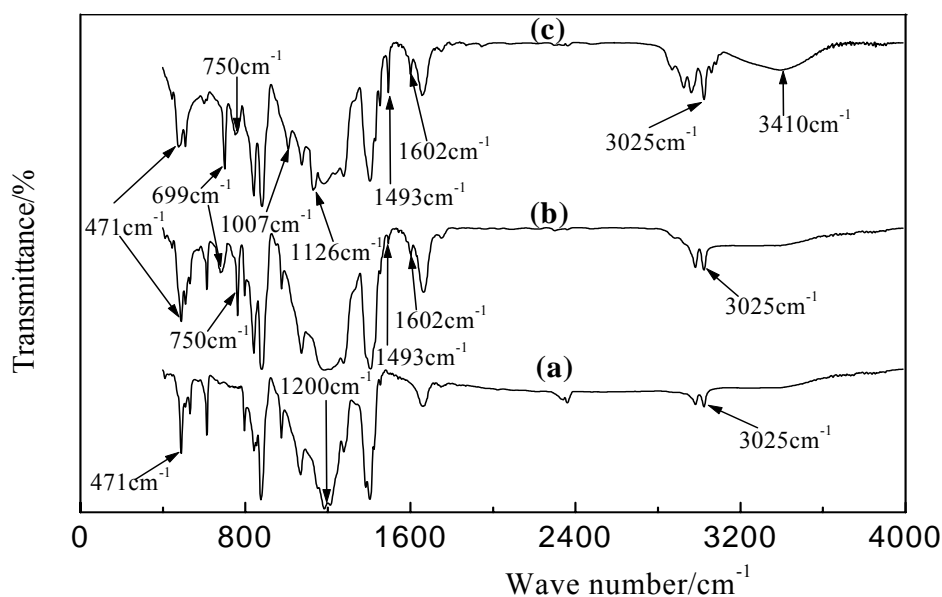

Figure 2. FTIR spectra of the membranes: (a) PVDF, (b) PVDF-PS, (c) PVDF-SPS

3.3 XPS analysis of the PVDF-SPS composite membrane

The surface compositions of the PVDF-SPS composite membrane are investigated using XPS measurements (Figure 3). Figure 3a, Figure 3b and Figure 3c show the C_{1s} core-level spectra, O_{1s} core-level spectra and S_{2p} core-level spectra of the PVDF-SPS membrane, respectively.

The C_{1s} core-level spectrum of the PVDF-SPS membrane can be curve-fitted with four peak components, with binding energies at 285.8 eV for the CH_2 species, and at 290.43 eV for the CF_2 species [26, 28], the component peak at 286.44 eV is assigned for aliphatic C—H species of the polystyrene chain blended to the PVDF polymer. The peak with BE of 288.06 eV is attributed to C—S species which is in sulfonic acid group. In the XPS spectra of the PVDF-SPS membrane, The O_{1s} peak and the S_{2p} peak of the composite membrane appeared at 532.47 eV and 169 eV, respectively [30, 32]. It can be inferred that the sulfonated polystyrene polymer was blended to PVDF membrane completely, and the sulfonic acid functional group was grafted to the PVDF membrane.
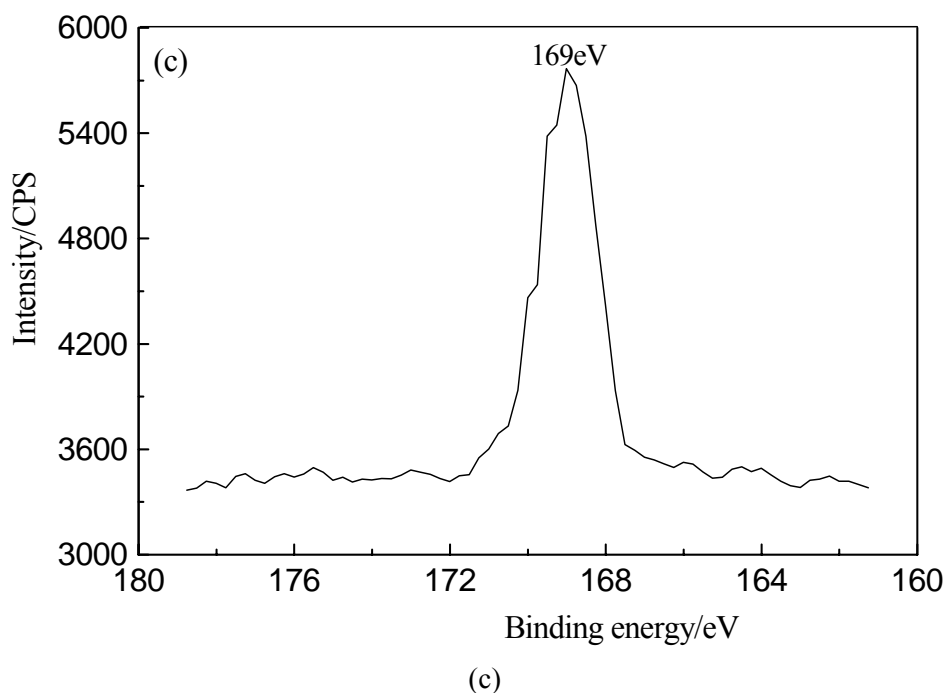

(a)

(b)

(c)
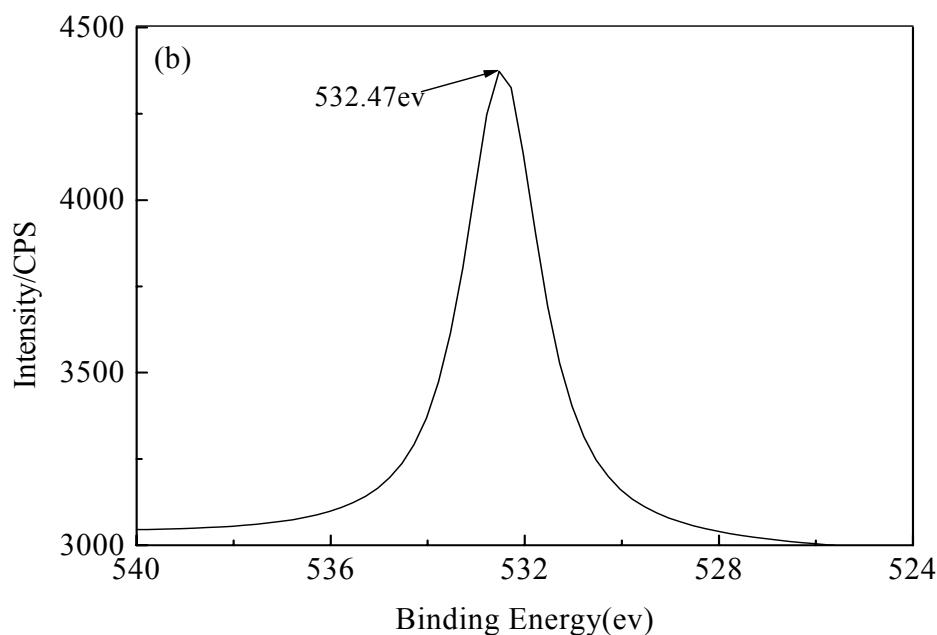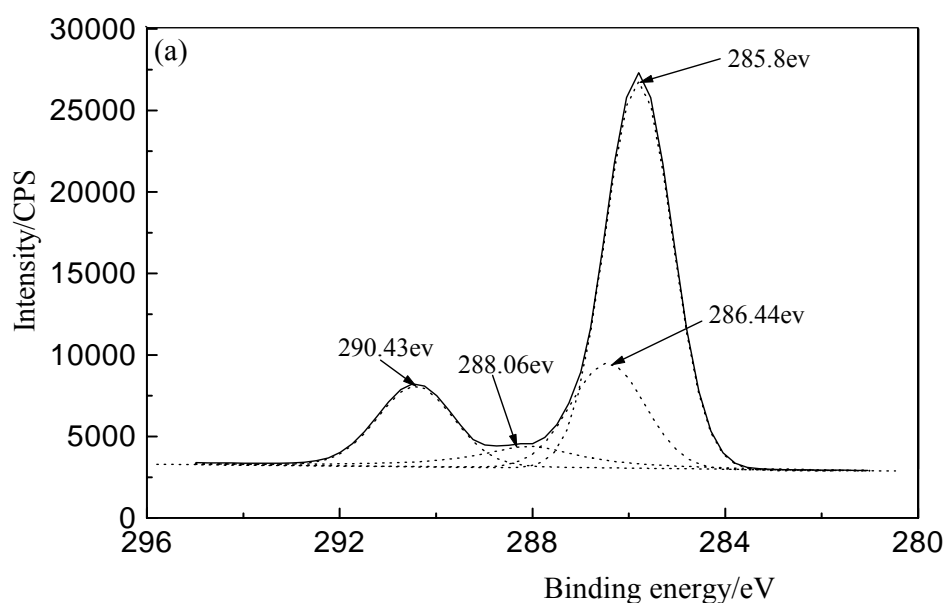
Figure 3. XPS spectra of the PVDF-SPS membrane: (a) C_{1s}, (b) O_{1s}, (c) S_{2p}

3.4 Morphology of the PVDF-SPS composite membrane

The morphologies of the pristine PVDF membrane, the PVDF-PS membrane and the PVDF-SPS membrane were revealed by ESEM. SEM surface and cross-section micrographs of the membranes are shown in Figure 4. It is clearly seen from Figure 4a to Figure 4c, that the pristine PVDF membrane has the larger pores than the PVDF-PS membrane and the PVDF-SPS membrane. The mean pore diameter of the PVDF membrane, the PVDF-PS membrane and the PVDF-SPS membrane is 0.25 μm, 0.12 μm and 0.16 μm, respectively. It can be seen that the polymerization of styrene and the blending of PS and SPS polymers have affected the surface structure of the PVDF membrane obviously. The cross-section morphologies of the PVDF membrane, the PVDF-PS membrane and the PVDF-SPS membrane are shown in Figure 4d, Figure 4e and Figure 4f, respectively. Using water as the coagulant, as can been seen, Figures 4d - 4f show that the long finger-like structures with small pore opening are present under the outer skin layer of the membranes, and the sponge-like structures appear in the inner part of the membranes. As shown in Figure 4e, many big aggregates appear in the middle part of the PVDF-PS membrane. The hydrophobic property of PS polymer promoted the formation of these polymer aggregates.

As can be seen, the thermally induced polymerization of styrene, as well as the blending of PS and SPS polymers, causes reduction in the remaining pores of the PVDF membrane overwhelmingly. It also reduces the mean pore diameter on the surface of the PVDF membrane. It also can be seen that the structure of PVDF-SPS membrane appears a uniform pore size distribution with no distinction between the sulfonated polystyrene polymer and the PVDF matrix.

### 3.5 Water uptake of the PVDF-SPS composite membrane

Table 1 shows the water uptake of the pristine PVDF membrane, the PVDF-PS membrane and the PVDF-SPS composite membrane. The blending of PS polymer reduces the water uptake of the PVDF membrane decreasing from 22.05% to 14.31%, which can explain the hydrophobic property of PS polymer. However, the water uptake of PVDF-SPS membrane is larger than that of the pristine PVDF membrane, which is caused by the hydrophilicity of the sulfonated polystyrene (SPS) polymer. The SPS polymer helps promote the liquid retention in the PVDF membrane due to it property of hydrophilicity. It has been shown that the SPS polymer absorbs water on the surface through a strong interaction with surface —SO_3^- groups and formation of hydrogen bonds, which increases the water retention.
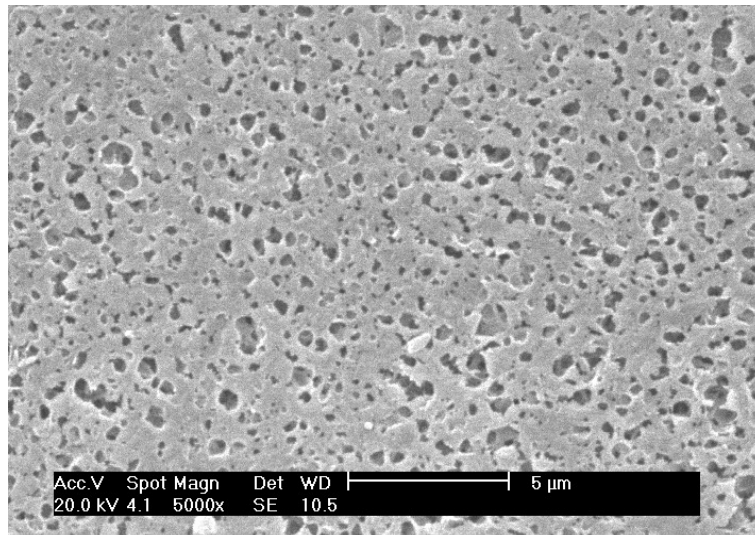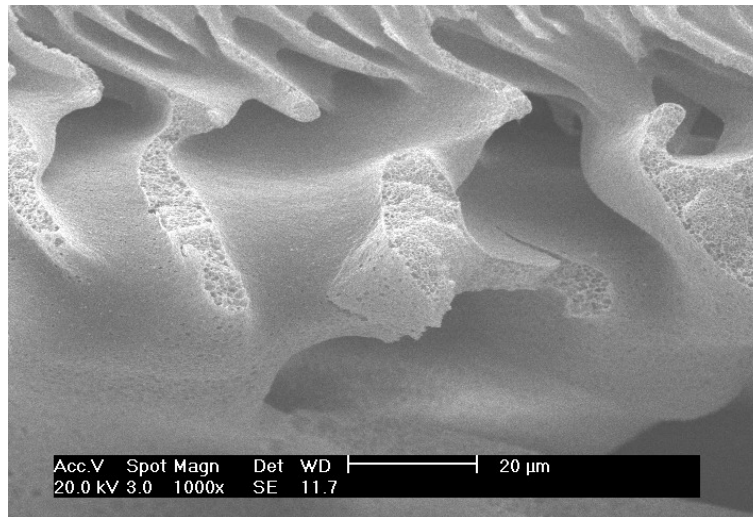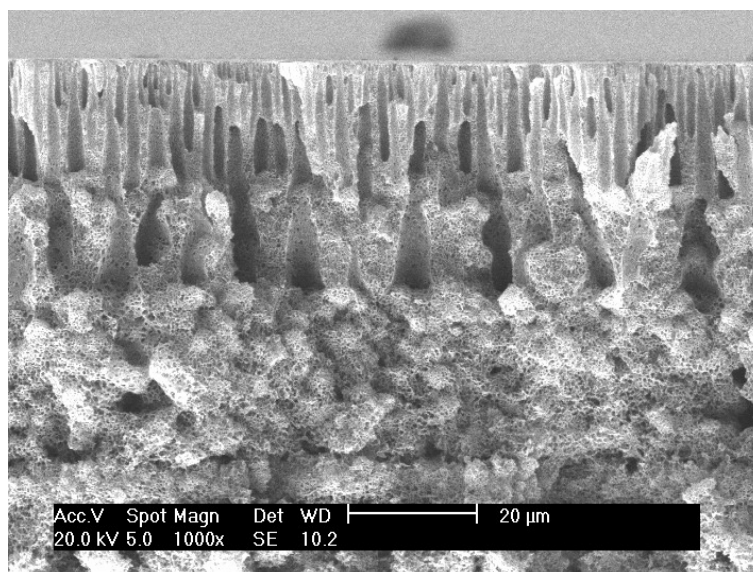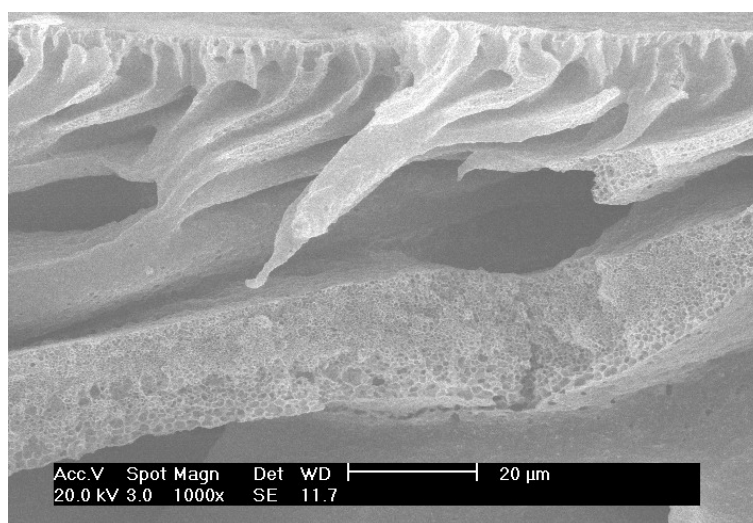
(a)
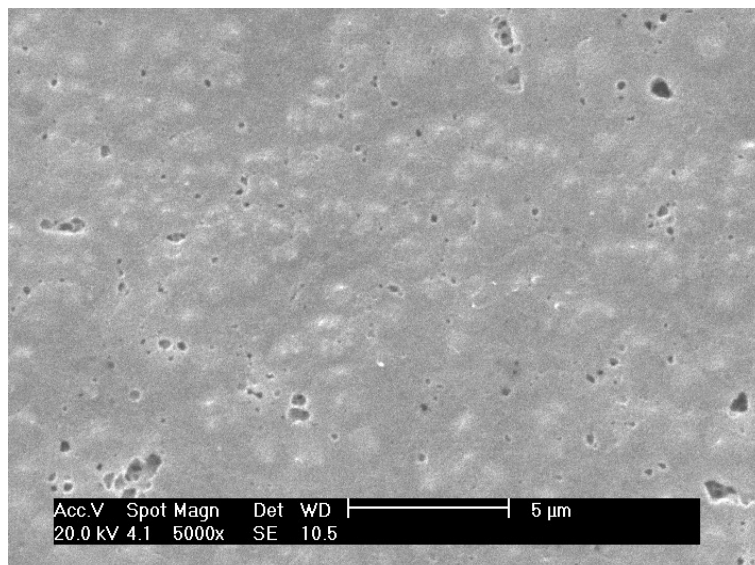
(b)
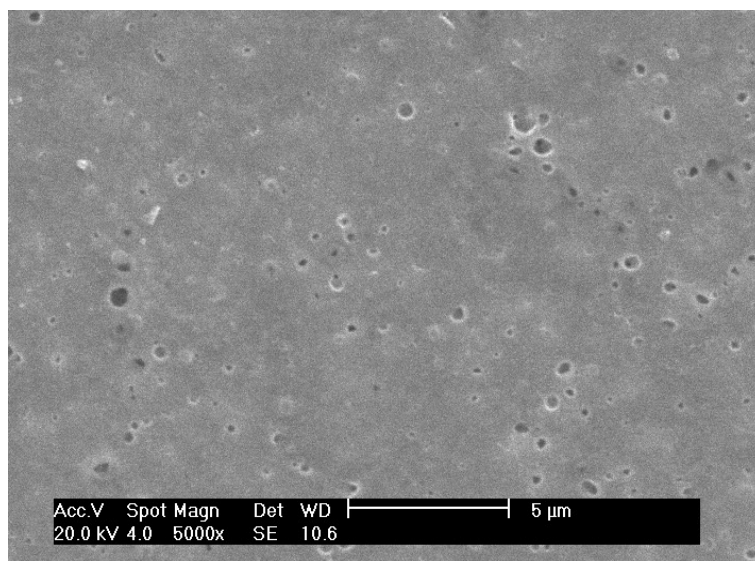
(c)

(d)

(e)

(f)

Figure 4. SEM micrographs of the membranes: (a - c) surface micrograph of PVDF, PVDF-PS, PVDF-SPS respectively; (d - f) cross-section of micrograph of PVDF, PVDF-PS, PVDF-SPS respectively

Table 1. Water uptake of the membranes

Membrane	Water uptake /%
PVDF	22.05
PVDF-PS	14.31
PVDF-SPS	49.22

3.6 Proton conductivity of the PVDF-SPS composite membrane

Figure 5 shows the conductivity of the PVDF-SPS membrane and Nafion-117 membrane at the different temperatures. It can be seen that the relationship of log (σ) and the parameter $1000/T$ satisfies an Arrhenius equation [29]. The conductive active energy (E_a) of the membranes were calculated, 18.58 kJ.mol^{-1} for Nafion-117 and 20.05 kJ.mol^{-1} for PVDF-SPS membrane, respectively. E_a of the PVDF-SPS membrane is close to that of the Nafion-117. The proton conductivity of the PVDF-SPS membrane and Nafion-117 is 29.3 mS.cm^{-1} and 54.3 mS.cm^{-1} at 298 K, respectively. It indicates that the proton conductivity performance of the PVDF-SPS membrane is good, although the proton conductivity of PVDF-SPS membrane is smaller than that of the commercial Nafion-117 membrane.
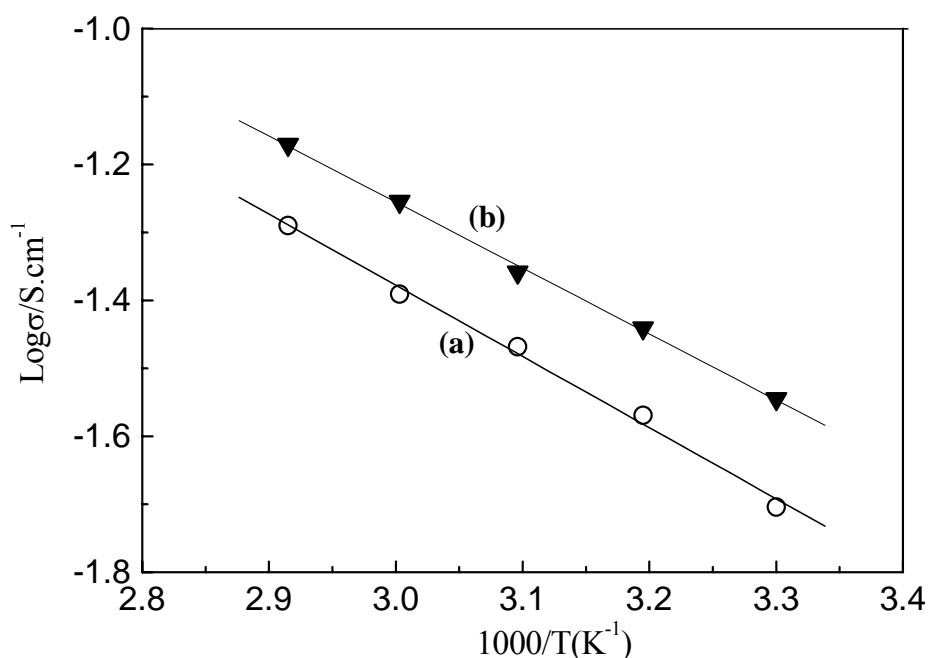

Figure 5. Relationship of the proton conductivity in the PVDF-SPS membrane (a), and in the Nafion-117 membrane (b) with temperature

3.7 Methanol permeability of the PVDF-SPS composite membrane

The variation of methanol concentration in the permeate compartment (C_B) with the time for PVDF-SPS membrane and Nafion-117 membrane were measured. Figure 6 shows that the two kind of membranes report a linear relationship between C_B and t, and the methanol permeability of the membranes can be calculated from the slopes of the linear curves according to Eq. (2). The methanol permeability of the PVDF-SPS membrane was measured to be 8.6×10^{-8} cm^2.s^{-1}, and the methanol permeability of Nafion-117 was 3.4×10^{-6} cm^2.s^{-1} under the same conditions. Compared with the Nafion-117, the PVDF-SPS membrane shows a better performance in restraining the methanol permeability.

As the proton conductive membranes of the direct methanol fuel cells, they must have both excellent proton conductivity and low methanol permeation. However, sometimes these have been mutually incompatible. In order to compare the comprehensive character of the membranes, the ratio of proton conductivity and methanol permeability, defined as the selectivity, was calculated. The selectivity of PVDF-SPS membrane was calculated to be 3.41×10^5 S.s.cm^{-3}, which is almost 20 times than that of Nafion-117 membrane.
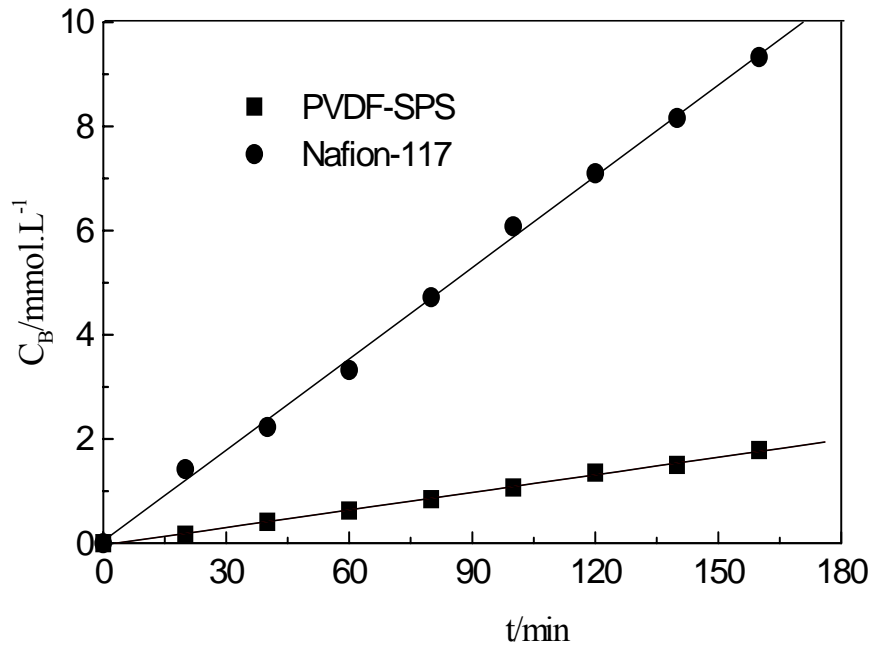
Figure 6. Variation of the methanol concentration in the permeate compartment (C_B) with time for
PVDF-SPS membranes and Nafion-117 membrane

3.8 Oxidative stability of the PVDF-SPS composite membrane
Oxidative stability of proton exchange membranes is one of the most important factors that affect
membrane durability. It is known that the possible degradation of polymer electrolyte is caused during
fuel cell operation. In this study, the oxidative stability of the membranes were investigated in a 3% H_2O_2
aqueous solution at 333 K. Figure 7 shows the weight change of Nafion-117 membrane and the PVDF-
SPS composite membrane. The Nafion-117 membrane showed high stability, flexibility without any
changes in appearance after the testing for 180 h. As show in Figure 7, it was found that the weight of
PVDF-SPS composite membrane initially increases and then decreases, and there is a peak in the curve
at 60 h. The PVDF-SPS membrane continuously swells and decomposes. The swelling is due to the
degradation of the cross-linking structure of the membrane in the H_2O_2 solution [33]. The decomposition
rate is larger than the swelling effect after 60 h. The result indicates that the stability of PVDF-SPS
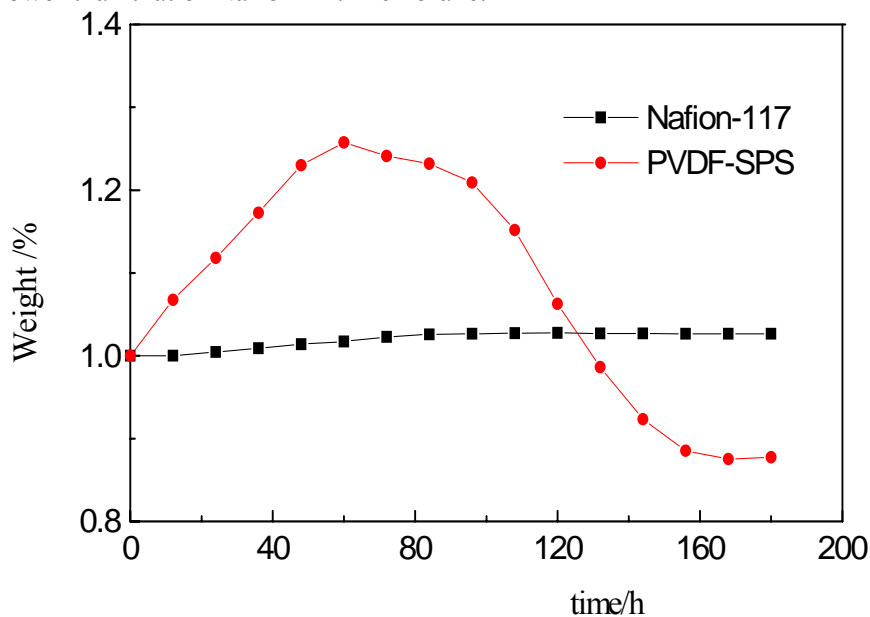membrane is lower than that of Nafion-117 membrane.

Figure 7. Oxidative stability of Nafion-117 membrane and PVDF-SPS membrane in the 3%H_2O_2
solution at 333 K

4. Conclusions

The PVDF-based composite membrane has been prepared using a simultaneous thermally induced polymerization and blending technique. Polystyrene and the sulfonated polystyrene polymers are blended into the PVDF polymer. Using the polyvinylidene fluoride-sulfonated polystyrene copolymer, the PVDF-SPS composite membrane with the performance of proton conductivity, has been prepared simply.

FTIR and XPS results confirm that the polystyrene and the sulfonated polystyrene polymers are blended into the PVDF matrix. SEM result shows that the PVDF-SPS composite membrane has a more uniform pore size distribution than the pristine PVDF membrane. The PVDF-SPS membrane has a strong hydrophilic character that is caused by the incorporation of sulfonic acid groups. The PVDF-SPS composite membrane displays lower methanol permeability than the Nafion-117 membrane. The selectivity of the PVDF-SPS composite membrane is almost 20 times than that of Nafion-117. However, the PVDF-SPS composite membrane possesses lower oxidative stability than Nafion-117 membrane, and the further research on increasing the anti-oxidation performance of PVDF-SPS composite membrane should be done.

The overall findings suggest that the PVDF-SPS membrane offers the potential for improving the performance of the DMFCs, this kind of membrane may still have the promising applications in DMFCs.

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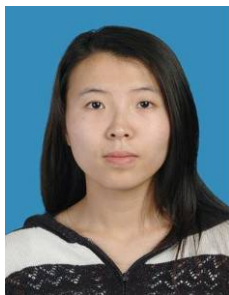
Qian Liu: a post graduate majoring in environmental engineering in Yanshan University situated in Qinhuangdao, China. Wastewater treatment is her current study field.
E-mail address: lqian_0310@163.com

Laizhou Song: the corresponding author, a professor in Yanshan University with a ph.D in applied chemistry. He is engaged in the wastewater treatment and new energy application, and has published some related articles and patents in this field.
E-mail address: songlz@ysu.edu.cn; Tel: 86-335-8061569.
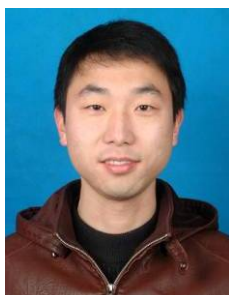
Zhihui Zhang: a post graduate majoring in environmental engineering in Yanshan University situated in Qinhuangdao, China. Wastewater treatment is his current study field.
E-mail address: jeasonhui@163.com

Xiaowei Liu: a post graduate majoring in environmental engineering in Yanshan University. Wastewater treatment is his current study interest.
E-mail address: huanjing82@126.com