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SPEEKK/polyaniline (PANI) composite membranes for direct methanol fuel cell usages

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Abstract

SPEEKK/PANI composite membranes were prepared and characterized for direct methanol fuel cell (DMFC) usages. The morphology change of membranes after the addition of PANI was studied in detail. The result show that: PANI showed very good compatibility with SPEEKK polymers due to the formation of hydrogen bond between the sulfonated acid and anion groups. The composite membranes' structure becomes more compact than that of SPEEKK, which may lead to the decrease of methanol diffusion. The proton conductivity and fuel cell performance of membranes changed a little after the addition of PANI. SPEEKK/PANI composite membranes showed very good prospective in DMFC usages.

Keywords: DMFC; Proton exchange membranes; Morphology

1. Introduction

The direct methanol fuel cell (DMFC) is a type of fuel cell, which is especially interesting for the application in automobile (cars, trucks, buses) or portable (cell phones, laptops) applications because of the simple fuel cell setup (easy storage of methanol, no reformer required), low emissions and low operating temperatures [1,2]. Proton exchange membrane as proton conductive material plays an important role in DMFC. So far only a few membrane types have been used as the proton conductor in DMFC, such as Nafion. Although they show good performance in fuel cells, the high cost, low conductivity at low humidity and high methanol permeability of Nafion limited their usages. For this reason, many researchers hope to develop high performance and low cost proton conductive electrolyte membranes. In our previous work, series SPEEK, SPEEKK were developed for proton exchange membranes [3–6]. Although they show relatively good properties, the brittleness of the membranes at evaluated temperatures and the relatively high methanol crossover in membranes at high sulfonated degrees have limited their usages. Recently acid–base composite membranes were widely studied to solve these problems [7–9]. The blend of the SPEEKK with amine group polymers was widely investigated due to the formation of hydrogen bond between the sulfoanted acid groups and amine groups. The hydrogen bond will lead to the following results [7,9]:

(1) The interaction will lead to the compatibilization of the blend polymers. This will be in favor of swelling reduction, improvement of mechanical property and further decreasing the methanol crossover of membranes.
(2) Mixing of acidic and basic molecular generally forms a proton conductive pathway. Blending with amine polymers will lead to the protons transfer from protonated-amine groups to the sulfonated groups of the blend polymers [8].

In this paper, we have prepared SPEEKK/PANI composite membranes. The purpose of this work is to decrease the methanol crossover and improve the mechanical properties. The SPEEKK used in this paper has high sulfonated degree or high water

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swelling. The object of this paper is to explore excellent membranes for DMFC usages.

2. Experiment

2.1. Polymer preparation

SPEEKK polymers were prepared by direct aromatic nucleophilic substitution step polymerization. Detailed synthesis procedures and characterization of these copolymers were reported previously [3–6]. The analytical data of SPEEKK is used in this paper. The sulfonated degree (D_s) is 1.2, and the ion exchange capacity (IEC) is 1.48 meq. The structure of SPEEKK is shown in Scheme 1. PANI powder was synthesized by chemical oxidation in an acidic solution using ammonium persulfate (APS) as oxidant.

2.2. Preparation of composite membranes

The pure SPEEKK and the SPEEKK/PANI composite membranes were prepared by solution casting. The SPEEKK with different weight ratio of PANI (0.5% and 1%) were dissolved in DMF to form a 10 wt% solution. The resulting mixture was stirred for about 6 h and cast onto a glass plate. The membranes (50–150 μm) of the sulfonated polymers were prepared and dried at 85 °C for 10 h and dried in a vacuum oven at 100 °C for 48 h.

2.3. Membrane properties

The water uptake of the membrane was calculated by setting the weight difference between the dry and swollen membranes. A detailed procedure was reported previously [3–6]. The titration technique was used to determine the IEC of the membranes at room temperature. Firstly, the membranes in the acid form (H^+) were converted to the sodium form by immersing the membranes in a 1 M NaCl solution for 24 h to exchange the H^+ ions with Na^+ ions. Then, the exchanged H^+ ions within the solutions were titrated with a 0.01N NaOH solution.

The water desorption measurement was tested by Pyris 1TGA (Perkin-Elmer). During measurement the temperature was kept at 80 °C, the pressure of the test cell was kept constant. Pyris 1TGA was used to determine the weight changes of samples with time.

The morphology of SPEEKK and its composite membranes was determined by tapping mode atomic force microscopy (AFM, SPA300HV/SPI3800N Probe Station, Seiko Instruments Inc., Japan in tapping mode). A silicon microcantilever (spring constant 2 N/m and resonance frequency ~70 kHz Olympus Co., Japan) with an etched conical tip (radius of curvature ~40 nm as characterized by scanning over very sharp needle array, NT-MDT, Russia) was used for scan. The scan rate was ranged from 1.0 to 2.0 Hz to optimize the image quality. Each scan line contains 256 pixels, and a whole image is composed of 256 scan lines.

2.3.1. Small-angle X-ray scattering (SAXS)

SAXS was performed on swollen SPEEKK and its composite membranes. The swollen state membranes were prepared by immersing in water for 24 h at room temperature. All the measurements were carried out at room temperatures with Kratky small-angle X-ray scattering, with Cu Kα (Philips) radiation. The UV spectrum could be gotten by SHIMADIU-UV2501.

The diffusion coefficient, D (cm^2/s), of methanol was determined using the electrochemical monitoring technique; the detailed procedure was reported by Xing et al. [10]. The measurement was performed by one diffusion cell basically consisting of two half cells separated by the membrane, which was fixed between two rubber rings. The membrane was supported by a platinum mesh, which served as a current collector for the working electrode. An Ag/AgCl electrode was used as a reference electrode and a platinum foil as a counter electrode. The potential of working electrode was kept at a constant value of 0.7 V where the complete methanol oxidation is controlled by the transport of methanol through membrane. Then the current was recorded as a function of time and the diffusion coefficient, D (cm^2/s), of methanol was determined via the following formula:

$$D = \frac{i \times d}{nFAC}$$

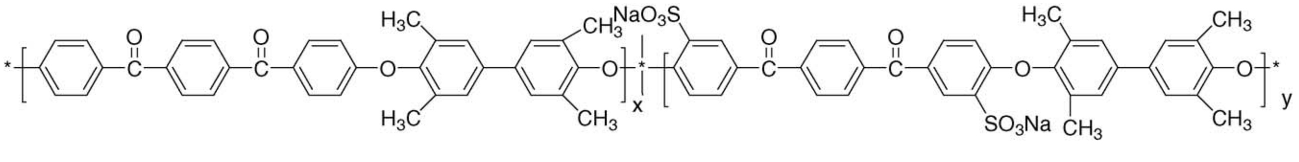
i is the limiting current (mA); d the thickness of membrane (cm); n the electron number of methanol oxidized completely; F the Faraday constant (C/mol); A the area of membrane (cm^2); C is the concentration of methanol (mol/cm^3).

2.3.2. Proton conductivity and fuel cells test

The measurements of proton conductivity of the membranes were carried out via the ac impedance spectroscopy using a Princeton Applied Research Model 273A potentiostat with a Model 5210 Frequency Response Detector (EG&G PARC, Princeton, NJ) from 100 mHz to 100 KHz. During testing the humidity was kept at 100%, the proton conductivity was calculated by formula

$$\sigma = \frac{L}{RA}$$

where σ is the proton conductivity, L the membrane thickness, R the membrane resistance and A is the membrane area.



Scheme 1. The structure of SPEEKK.

Cell performance was evaluated by using a DMFC unit cell, the catalysts used at the anode and the cathode were Pt-Ru/C and Pt/C, respectively. The catalyst loadings at the anode and the cathode based on the catalyst weight without polymers were 2.5 mg/cm^2. Two molar methanol at the cathode, was supplied by a Masterflex liquid micro-pump at 0.082 L/min while the cathode was fed with dried O_2 at a rate of 2 L/min by a flow meter. The cell temperature was kept at 70 °C.

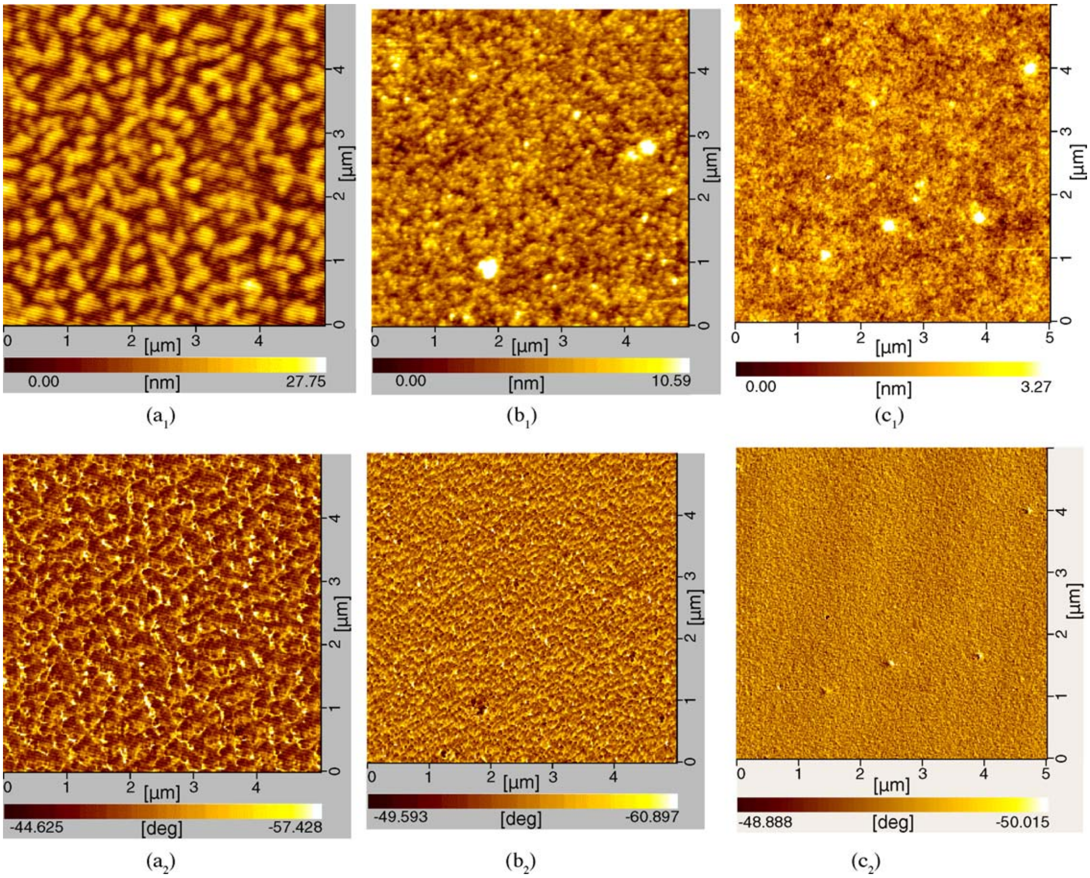
3. Result and discussion

3.1. The morphology of the membranes

The properties of membranes were closely related to their microstructures especially the spatial distribution of ionic site. To the state of aggregation of ionic polymers, extensive studies have been carried out by SAXS, AFM, TEM, etc. [11–13]. From the analysis of Eisenberg, the sulfonated groups may aggregate into clusters, which can provide cation transport pathway or ionic transport channel [14]. The proton conductivity of membranes is dependent on the distribution and connectivity of the conductive pathways through the cluster network [21]. Tapping-mode images of SPEEKK membranes were recorded under ambient conditions. The topgraphic images (a_1–c_1 in Fig. 1) indicate the surfaces of SPEEKK and its composite membranes. The softer domains surrounded by dark domains are regarded as hydrophilic segments embedded in the hydrophobic matrix. The topgraphic images indicate the good compatible of SPEEKK with PANI. With increasing of the PANI content, the microstructures of membrane become more and more compact due to the formation of hydrogen bond in Scheme 2. To the phase images of the membranes (a_2–c_2 in Fig. 1), light regions were assigned to a softer region, which represent the hydrophilic sulfonated groups. And the dark regions were assigned to hydrophobic polymer backbone. The connectivity and the size of hydrophilic regions have great influence on the transport properties of membrane. The connectivity and domain size vary depending on the content of PANI in SPEEKK. The size of hydrophilic and hydrophobic domains shows decreasing tendency with the content of PANI increasing from the result. This may be due to the formation of hydrogen bond between the sulfonated groups amine groups (Scheme 2). The decreasing hydrophilic domains will lead to the changes of properties of membranes, such as water uptake, methanol diffusion and proton conductivity.

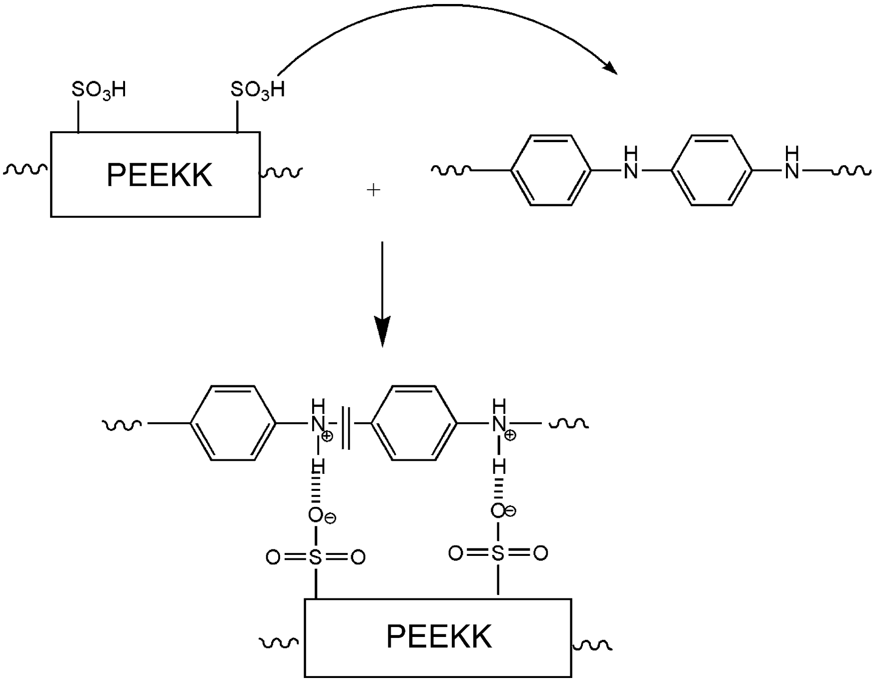
3.2. The small-angle X-ray scattering (SAXS)

To the internal structures ionic polymers, much work was carried out to study the ion clusters by using small-angle neutron scattering (SANS), small-angle X-ray scattering, etc. In SAXS, the existence of a scattering maximum was related to the difference of electron cloud density. To proton exchange membrane,



(a_1) (b_1) (c_1)
(a_2) (b_2) (c_2)

Fig. 1. The topographic and phase images of membranes. (a_1–c_1) The topographic images of SPEEKK, SPEEKK/PAN (0.5%), SPEEKK/PAN (1%). (a_2–c_2) The phase images of SPEEKK, SPEEKK/PAN (0.5%), SPEEKK/PAN (1%).



Scheme 2. The formation of hydrogen bond.

the phase separation of hydrophilic and hydrophobic domains may lead to the scattering maximum at low angles in SAXS. And at large angles, the Porod analysis will reflect the nature of interface between the hydrophilic and hydrophobic regions [11,17,20]. Hashimoto, etc. have analyzed the structure of perfluorinated ionomer (Nafion) membranes with SAXS. All these studies indicated the relationship between cluster size and scatter vector (q). Ionic scattering maximum shifts towards larger q indicating the decrease in intercluster distance, which further decreased cluster size [15,16]. From SAXS of the SPEEKK and its composite membranes (in Fig. 2), the ionic scattering maximum of composite membrane shifts to larger scattering vectors compared with SPEEKK membrane. This result indicated that decreasing size of ion clusters in SPEEKK/PANI membranes is compared with SPEEKK membranes. According to the Porod analysis of SAXS [11,17], the slope of $\ln[s^4 I(s)]$ versus $10s^2$ line can give the information about the distance between the two phase interface (hydrophilic and hydrophobic), which can further confirm the size change of clusters. The $\ln[s^4 I(s)]$ versus $10s^2$ curves of the SPEEKK and its composite membranes are shown in Fig. 3. The slope of the SPEEKK and its composite membranes was 1.56 and 1.43 × 10^{-20} m^2 (1.56 and 1.43 Å^2), respectively, the distance between the two phase's interfaces shows decreased tendency with the addition of PANI. All these results are consistent with the result of AFM. Both the results of AFM and SAXS have illustrated the formation of hydrogen bond in the blending polymers.

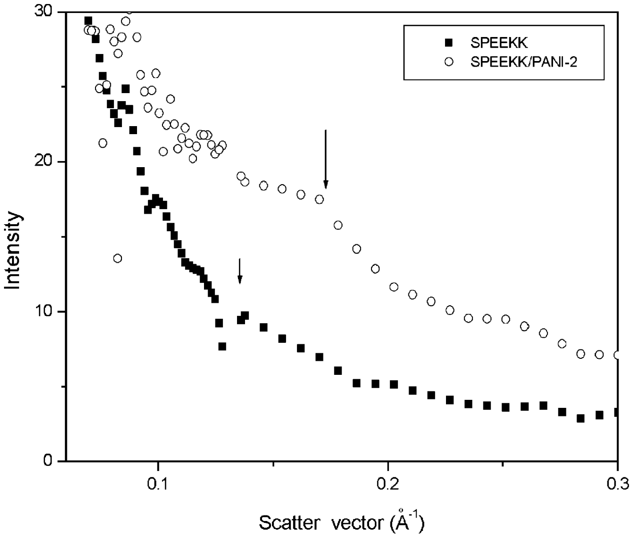


Fig. 2. The SAXS of SPEEKK and its composite membranes.

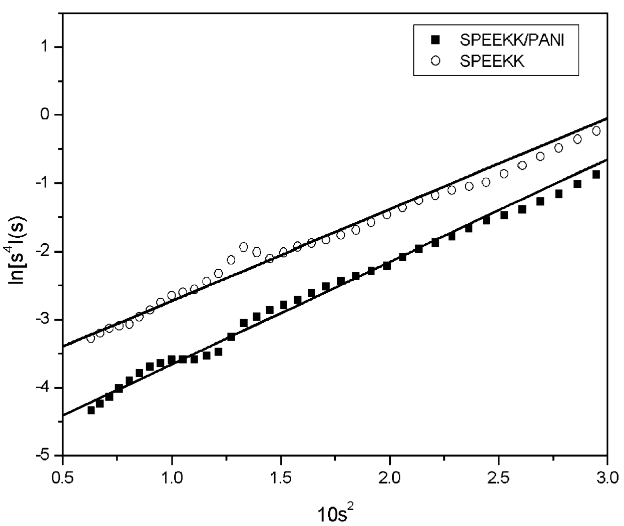


Fig. 3. $\mathrm{Ln}[s^4 I(s)]$ vs. $10s^2$ curves.

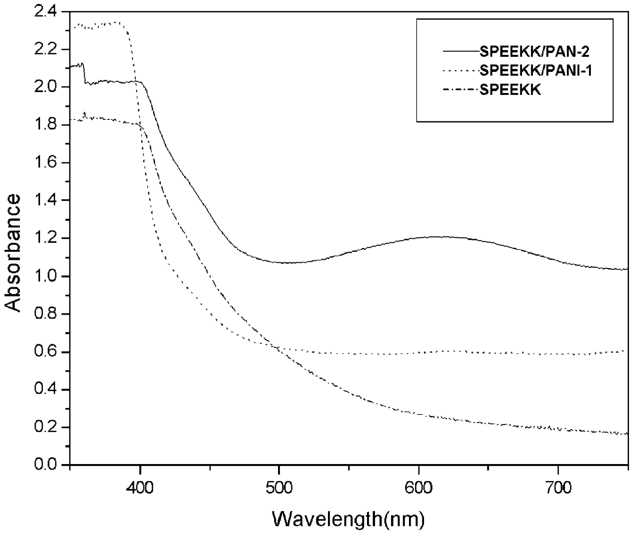


Fig. 4. UV curves of SPEEKK and its composite membranes.

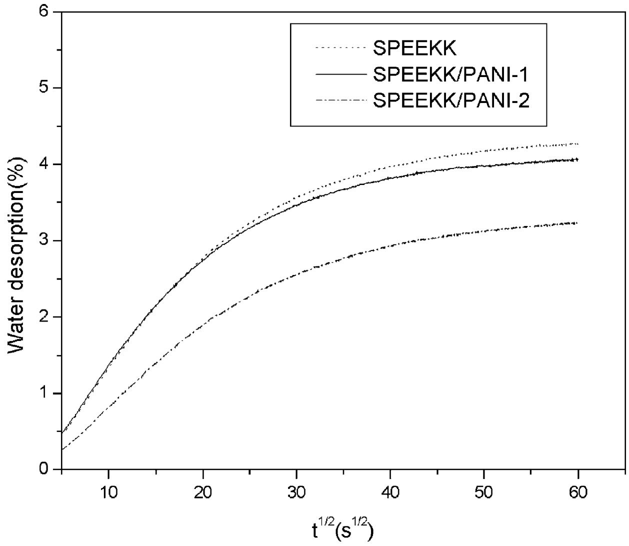


Fig. 5. Water desorption isotherm of membranes.

3.3. UV–vis spectroscopy

The UV–vis spectrums of the SPEEKK/PANI composite membranes (in Fig. 4) have two peaks at about 390–400 and 630 nm. However, the SPEEKK membrane only has one peak at 390–400 nm. The first peak corresponds to the π–π* transition of the benzenoid rings. While the second peak at about 630 nm is attributed to the exciton absorption of the quinoid rings of PANI [18]. SPEEKK/PAN-1 does not show a clear absorbance peak at about 630 nm. This may be due to the hydrogen bond between the sulfonated acid groups and amnion. But with the increasing of PANI content, the peak become clear. The UV result further confirmed that we have successfully introduced the PANI into SPEEKK membranes.

3.4. Water uptake, water desorption and IEC

The water uptake and IEC may have very great influence on the proton conductivity of proton exchange membranes. The proton exchanging reaction requires a significant amount of water to coordinate with proton as it moves through the membrane. Also the protons that participate in the conduction are derived from the sulfonated acid groups. Water uptake and IEC of SPEEKK and its composite membranes are shown in Table 1. Both of them show decreased tendency with the increasing of PANI content. For example, the composite membranes with the content of PANI increasing from 0.5% to 1%, respectively, show the water uptake of 25.02% and 23%, otherwise the IEC decreased from 1.16 to 1.00. This may be due to the formation of hydrogen bond of the composite membranes, the hydrogen bond made the membrane structure more compact. The hydrophilic domain size becomes smaller than the SPEEKK membrane without PANI, which can be concluded from AFM. In addition the formation of hydrogen bond ensures that part of the sulfonated groups cannot exchange with ions, which leads to the decreased IEC. The velocity of water evaporation in membranes may give the information about water retention of membranes. Water desorption of SPEEKK and its composite membranes are shown in Fig. 5. The relationships between the water desorption and times may follow the Ficker diffusion [19]. The desorption isotherm in Fig. 5 shows that the water in composite membranes evaporates more quickly than SPEEKK membranes, which may be resulted from the formation of hydrogen bond. The water diffusion calculated from the slope of the initial liner between the M_t/M_∞ and $t^{1/2}$ of SPEEKK and its composite membranes were 2.72×10^{-10}, 3.89×10^{-8} and 5.09×10^{-6} cm^2/s, respectively. With the addition of PANI the more compact structure of membranes makes the decreasing of water retention of membranes, which can be explained by the AFM and SAXS study.

Table 1
Water uptake and IEC of SPEEKK and its composite membranes

	Polymer		
	SPEEKK	SPEEKK/PANI-1	SPEEKK/PANI-2
PANI content (%)	0	0.5	1
Water uptake (%)	27	25.02	23.03
Water diffusion (cm^2/s)	2.72×10^{-10}	3.89×10^{-8}	5.09×10^{-6}
IEC	1.48	1.16	1.00
Methanol diffusion coefficient (cm^2/s, 25 °C)	6.6×10^{-7}	4.8×10^{-7}	3.8×10^{-7}
Proton conductivity (s/cm)	0.048	0.049	0.051

Methanol permeability plays a very important role in DMFC, the permeability of methanol was determined by the potential–time curves. The membranes show decreased methanol diffusion coefficient with the content of PANI increased. SPEEKK and its composite membranes show the methanol diffusion of 6.6×10^{-7}, 4.8×10^{-7}, 3.8×10^{-7}, with the content of PANI 0%, 0.5%, 1%, respectively. The result was consistent with our suggestions. With the PANI content increasing, the formation of hydrogen bond will lead to the compact structure of membranes, which was confirmed by AFM and SAXS. All this will lead to the decreasing of methanol diffusion, which further confirmed our suggestions.

3.5. Proton conductivity and fuel cell test

The proton conductivity of the SPEEKK and its composite membranes are shown in Table 1. Two factors may influence the composite membranes' proton conductivity. Firstly, the structure of membranes becomes compact and the water uptake of composite membranes decreases with the introduction of PANI and further lead to the decreasing of proton conductivity. Secondly, the formation of hydrogen bond may favor forming proton transport way, which will lead to the improvement of proton conductivity. In this paper, the proton conductivity of membranes increases very little, which may be due to the lower content of PANI. The polarization of the DMFC for SPEEKK and its composite membranes is shown in Fig. 6 for 2 M methanol solution at 70 °C. The cell performance of the SPEEKK membrane was a little better than its composite membranes. The membranes exhibited steep ohmic loss because higher bulk resistance and poor physical contact, which made such steep decrease in the cell potential. All the membranes show relatively lower cell performance due to the poor compatibility with catalyst.

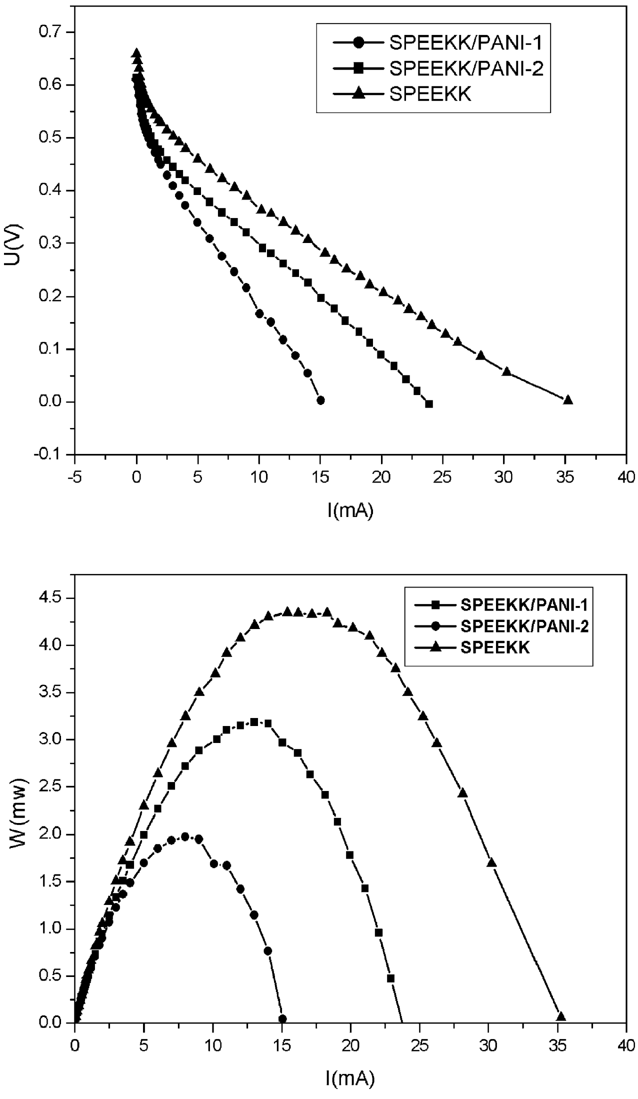


Fig. 6. The cell performance of SPEEKK and its composite membranes.

4. Conclusion

PANI was introduced into the SPEEKK membranes to improve methanol resistance. The structures of the SPEEKK and its composite membranes were studied in detail. The relationship between the properties and microstructures was characterized. The work will favor to explore excellent membranes that were suitable for DMFC usages. The SPEEKK/PANI composite membranes show good prospective usages in DMFC.

References

[1] K.Y. Cho, J.Y. Eom, H.Y. Jung, N.S. Choi, Y.M. Lee, J.K. Park, J.H. Choi, K.W. Park, Y.E. Sung, Characteristics of PVdF copolymer/Nafion blend membrane for direct methanol fuel cell (DMFC), Electrochim. Acta 50 (2004) 583–588.

[2] P. Dimitrova, K.A. Friedrich, B. Vogt, U. Stimming, Transport properties of ionomer composite membranes for direct methanol fuel cells, J. Electroanal. Chem. 532 (2002) 75–83.

[3] M. Gil, X.L. Ji, X.F. Li, H. Na, J. Eric Hampsey, Y.F. Lu, Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications, J. Membr. Sci. 234 (2004) 75–81.

[4] X.F. Li, C.P. Liu, H. Lu, C.J. Zhao, Z. Wang, W. Xing, H. Na, Preparation and characterization of sulfonated poly(ether ether ketone ketone) proton exchange membranes for fuel cell application, J. Membr. Sci. 255 (2005) 149–155.

[5] X.F. Li, H. Na, H. Lu, Novel sulfonated poly(ether ether ketone ketone) derived from bisphenol S, J. Appl. Polym. Sci. 94 (2004) 1569–1574.

[6] X.F. Li, C.J. Zhao, H. Lu, Z. Wang, H. Na, Direct synthesis of sulfonated poly(ether ether ketone ketone)s (SPEEKKs) proton exchange membranes for fuel cell application, Polymer 46 (2005) 5820–5827.

[7] W. Cui, J. Kerres, G. Eigenberger, Development and characterization of ion-exchange polymer blend membranes, Sep. Purif. Technol. 14 (1998) 145–154.

[8] M. Yamada, I. Honma, Anhydrous protonic conductivity of a self-assembled acid–base composite material, J. Phys. Chem. B 108 (2004) 5522–5526.

[9] D. Mecerreyes, H. Grande, O. Miguel, E. Ochoteco, R. Marcilla, I. Cantero, Porous polybenzimidazole membranes doped with phosphoric acid: highly proton-conducting solid electrolytes, Chem. Mater. 16 (2004) 604–607.

[10] W.L. Xu, C.P. Liu, X.Z. Xue, Y. Su, Y.Z. Lu, W. Xing, T.H. Lu, New proton exchange membranes based on poly (vinyl alcohol) for DMFCs, Solid State Ionics 171 (2004) 121–127.

[11] G. Gebel, J. Lambard, Small-angle scattering study of water-swollen perfluorinated ionomer membranes, Macromolecules 30 (1997) 7914–7920.

[12] J.F. Ding, C. Chuy, S. Holdcroft, Solid polymer electrolytes based on ionic graft polymer: effect of graft chain length on nano-structured, ionic networks, Adv. Funct. Mater. 12 (5) (2002) 389–394.

[13] B.B. Sauer, R.S. Mclean, AFM and X-ray studies of crystal and ionic domain morphology in poly(ethylene-co-methacrylic acid) ionomers, Macromolecules 33 (2000) 7939–7949.

[14] A. Eisenberg, Clustering of ions in organic polymers. A theoretical approach, Macromolecules 3 (1970) 147–154.

[15] M. Fujimura, T.J. Hashimoto, H. Kawai, Small-angle X-ray scattering study of perfluorinated ionomer membranes. Part 1. Origin of two scattering maxima, Macromolecules 14 (1981) 1309–1315.

[16] M. Fujimura, T.J. Hashimoto, H. Kawai, Small-angle X-ray study of perfluorinated ionomer membranes. Part 2. Models for ionic scattering maximum, Macromolecules 15 (1982) 136–144.

[17] Z.S. Mo, H.F. Zhang, Structure of Crystalline Polymers by X-ray Diffraction, Science Publishing Company in China, (October) 2003, pp. 307–311.

[18] K. Huang, H.J. Qiu, M.X. Wan, Synthesis of highly conducting polyaniline with photochromic azobenzene side groups, Macromolecules 35 (2002) 8653–8655.

[19] T. Watari, H.Y. Wang, K. Kuwahara, K. Tanaka, H. Kita, K. Okamoto, Water vapor sorption and diffusion properties of sulfonated polyimide membranes, J. Membr. Sci. 219 (2003) 137–147.

[20] G. Gebel, R.B. Moore, Small-angle scattering study of short pendant chain perfuorosulfonated ionomer membranes, Macromolecules 33 (2002) 4850–4855.

[21] Y.S. Kim, M.A. Hickner, L.M. Dong, B.S. Pivovar, J.E. McGrath, Sulfonated poly(arylene ether sulfone) copolymer proton exchange membranes: composition and morphology effects on the methanol permeability, J. Membr. Sci. 243 (2004) 317–326.