

Short communication

# Surface-modified Nafion<sup>®</sup> membrane by casting proton-conducting polyelectrolyte complexes for direct methanol fuel cells

Zhiming Cui<sup>a,b</sup>, Nanwen Li<sup>a,b</sup>, Xiaochun Zhou<sup>a,b</sup>, Changpeng Liu<sup>a</sup>,  
Jianhui Liao<sup>a</sup>, Suobo Zhang<sup>a</sup>, Wei Xing<sup>a,\*</sup>

<sup>a</sup> Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street,  
Changchun 130022, Jilin, PR China

<sup>b</sup> Graduate School, Chinese Academy of Sciences, Beijing, 100039, PR China

Received 24 June 2007; received in revised form 3 August 2007; accepted 3 August 2007

Available online 8 August 2007

## Abstract

Surface-modified Nafion<sup>®</sup> membrane was prepared by casting proton-conducting polyelectrolyte complexes on the surface of Nafion<sup>®</sup>. The casting layer is homogeneous and its thickness is about 900 nm. The proton conductivity of modified Nafion<sup>®</sup> is slightly lower than that of plain Nafion<sup>®</sup>; however, its methanol permeability is 41% lower than that of plain Nafion<sup>®</sup>. The single cells with modified Nafion<sup>®</sup> exhibit higher open circuit voltage (OCV = 0.73 V) and maximal power density ( $P_{\max} = 58 \text{ mW cm}^{-2}$ ) than the single cells with plain Nafion<sup>®</sup> (OCV = 0.67 V,  $P_{\max} = 49 \text{ mW cm}^{-2}$ ). It is a simple, efficient, cost-effective approach to modifying Nafion<sup>®</sup> by casting proton-conducting materials on the surface of Nafion<sup>®</sup>.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Polyelectrolyte complexes; Chitosan; Phosphotungstic acid; Methanol permeation; Proton-conducting

## 1. Introduction

Direct methanol fuel cells (DMFCs) are promising candidates for portable devices or transportation applications in view of their high energy density, easy manipulation, and high efficiency [1–3]. Perfluorosulfonic acid membranes, such as Nafion<sup>®</sup> membranes, are the primary membranes applied in the DMFCs presently. However, commercial Nafion<sup>®</sup> membranes do not meet the requirement for low methanol permeability especially at low temperatures (<100 °C) [4]. The methanol permeation results in reducing the open-circuit potential (OCP) and poisoning the electrocatalysts at the cathode. Various attempts have been made to overcome the drawbacks of Nafion<sup>®</sup> membranes for DMFC applications. The approaches described are diverse, ranging from doping with inorganic materials such as sulfonated montmorillonite [2], silica [5], silica/phosphotungstic acid [6], zeolite [7], zirconium phosphate [8], etc., modifying the

surface of Nafion<sup>®</sup> [9–12] to in situ polymerization with poly(1-methylpyrrole) [13] or polyfurfuryl alcohol [14]. Most modified Nafion<sup>®</sup> membranes indeed reduce methanol permeation, but the proton conductivity of modified Nafion<sup>®</sup> membranes is often markedly lower than that of plain Nafion<sup>®</sup> membranes. Among these modified Nafion<sup>®</sup> membranes, only a few of them meet the requirements for practical DMFC applications. Generally, oppositely charged polyions (polycations or polyanions) interact electrostatically to form polyelectrolyte complexes. We have reported the polyelectrolyte complexes formed between cationic chitosan and anionic phosphotungstic acid, which exhibit relatively high proton conductivity and low methanol permeability [15].

In the present work, we report a new approach to modifying Nafion<sup>®</sup> membranes by casting proton-conducting polyelectrolyte complexes formed between chitosan and phosphotungstic acid on the surface of Nafion<sup>®</sup> membranes. The performance of modified Nafion<sup>®</sup> for direct methanol fuel cells (DMFCs) was evaluated in terms of proton conductivity, methanol permeability, and a single cell test.

\* Corresponding author. Tel.: +86 431 5262223; fax: +86 431 5685653.  
E-mail address: [xingwei@ciac.jl.cn](mailto:xingwei@ciac.jl.cn) (W. Xing).

## 2. Experimental

### 2.1. Preparation of modified Nafion®

Nafion® 115 membranes (Du Pont Co.) were pretreated by boiling them in 5 wt.% peroxide solution at 80 °C, 1 M aqueous sulfuric acid solution at 80 °C, and deionized water, in that order. 1% (w/v) chitosan solution was prepared by dissolving chitosan powder (degree of deacetylation: 95%; molecular weight: 50,000 g mol<sup>-1</sup>, Haidebei Ltd., China) in 2% (v/v) acetic acid solution. The pretreated Nafion® 115 were immersed in chitosan solution mentioned above for 2 h, followed by a drying step at 60 °C in drying oven for 2 h. As a result, a layer of chitosan was formed on the surface of the Nafion® membranes. Nafion® membranes coated with a layer of chitosan were immersed in 0.05 M phosphotungstic acid solution for 6 h, and then were washed with deionized water and stored in deionized water prior to the different measurements.

### 2.2. Scanning electron microscopy

The morphology of the membranes was characterized by a LEO 1525 FE-SEM scanning electron microscope.

### 2.3. Fourier transform infrared spectroscopy

IR spectra (4000–500 cm<sup>-1</sup>, resolution 4 cm<sup>-1</sup>) were recorded with a Bruker Vertex 70 RTIR spectrometer.

### 2.4. Measurements of proton conductivity

The proton conductivity of plain Nafion® and modified Nafion® membranes was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage. Impedance spectra were recorded using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The membranes were fixed in a measuring cell made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops [16]. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. The proton conductivity ( $\sigma$ ) of the membranes was calculated using the following equation:

$$\sigma = \frac{L}{RA} \quad (1)$$

where  $L$ ,  $R$ , and  $A$  denote the distance between the two inner gold wires, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

### 2.5. Measurements of methanol permeability

The methanol permeability of these membranes was determined and calculated by the method described in the reference [15]. The methanol concentration in the receptor chamber was measured versus time by using a gas chromatograph

(Shimadzu GC-14B) equipped with a thermal conductivity detector.

### 2.6. Performance tests for a single cell

The Pt–Ru/C with 40 wt.% Pt + 20 wt.% Ru/C and the Pt/C catalyst with 20 wt.% Pt were used as the anodic and cathodic catalysts, respectively. Nafion® 115 and the composite membrane prepared were used as the electrolyte. The fabrication of the membrane electrode assembly (MEA) is the same as that in the literature [17]. The catalyst loading was 4 mg cm<sup>-2</sup> for both the anode and the cathode and the effective electrode area of the single cell was 10 cm<sup>2</sup>. The performance of the single cell was measured at 80 °C with a Fuel Cell Test System (Arbin Co.). 2.0 M CH<sub>3</sub>OH solution with a flow rate of 20 mL min<sup>-1</sup> and oxygen with a flow rate of 0.5 L min<sup>-1</sup> at 0.05 MPa were used. Each single cell was operated for three times.

## 3. Results and discussion

### 3.1. Scanning electron microscopy

Parts A and B of Fig. 1 show the surface images of plain Nafion® and modified Nafion®. From the both images, it can be observed that the polyelectrolyte complexes formed on the smooth surface of Nafion® are homogeneous, and have no obvious phase separation. From the cross-sectional image of modified Nafion® membrane in Fig. 2, it is found that the thickness of the casting layer is about 900 nm.

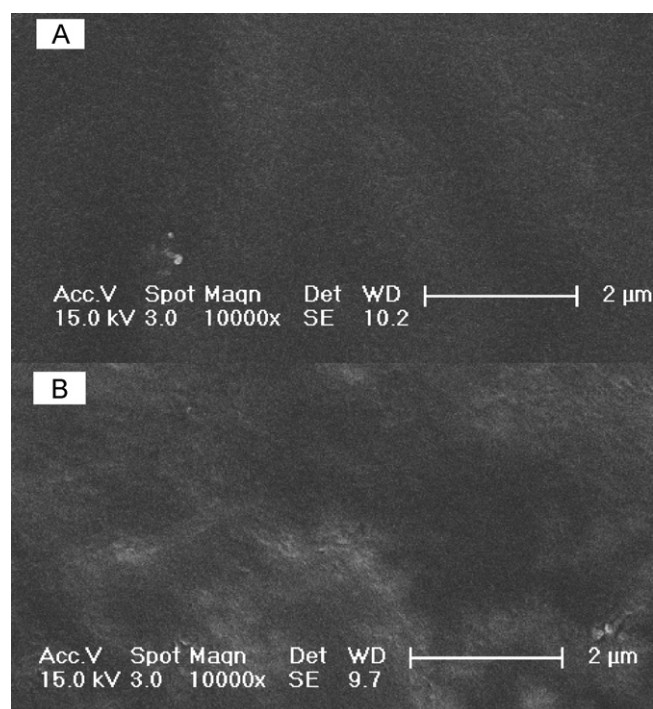


Fig. 1. SEM picture of the membranes: (A) surface of plain Nafion® membrane and (B) surface of modified Nafion® membrane.

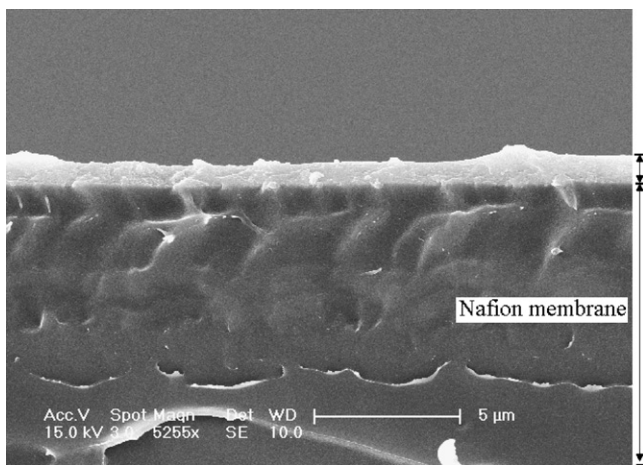


Fig. 2. SEM picture of the cross-section of modified Nafion<sup>®</sup> membrane.

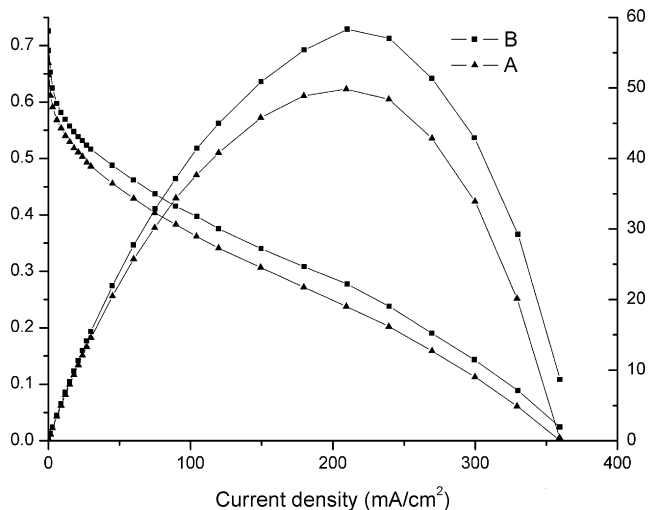


Fig. 4. Polarization curves for the MEA made with plain Nafion<sup>®</sup> (A) and modified Nafion<sup>®</sup> (B).

the existence of the polyelectrolyte complexes on the surface of Nafion<sup>®</sup>.

### 3.3. Proton conductivity and methanol permeability

The proton conductivity and methanol permeability of plain Nafion<sup>®</sup>, modified Nafion<sup>®</sup> and washed Nafion<sup>®</sup> are given in Table 1 (all the values in Table 1 are the average of three measurements). The proton conductivity of modified Nafion<sup>®</sup> is slightly lower than that of plain Nafion<sup>®</sup>, which is easy to understand because the conductivity of the casting layer (polyelectrolyte complexes) is inferior to that of plain Nafion<sup>®</sup> membranes [15]. However, the methanol permeability of modified Nafion<sup>®</sup> is reduced by 41% compared with that of plain Nafion<sup>®</sup>. This indicates that methanol permeation can significantly be reduced by casting the polyelectrolyte complexes on the surface of Nafion<sup>®</sup>.

The polymer electrolyte membranes applied in DMFCs should possess simultaneously high proton conductivity and low methanol permeability. Membrane performances can be estimated from the ratio of proton conductivity ( $\sigma$ ) to methanol permeability ( $P$ ). That is to say, the higher the value of  $\sigma/P$  is, the better the performance of the membrane would be [19]. Table 1 shows that the value of  $\sigma/P$  of modified Nafion<sup>®</sup> is much higher than that of plain Nafion<sup>®</sup>. Besides, the value of  $\sigma/P$  of modified Nafion<sup>®</sup> is nearly the same with that of washed Nafion<sup>®</sup>, which shows that modified Nafion<sup>®</sup> is stable and durable.

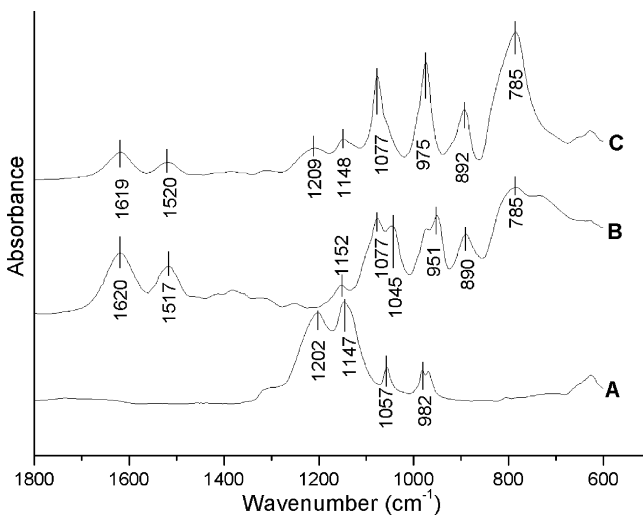


Fig. 3. The IR spectra of plain Nafion<sup>®</sup> (A), polyelectrolyte complexes (B) and modified Nafion<sup>®</sup> (C).

### 3.2. Fourier transform infrared spectroscopy

Fig. 3 presents the IR spectra of plain Nafion<sup>®</sup>, the polyelectrolyte complexes and modified Nafion<sup>®</sup>. The bands at 1202, 1147, 1057, 982, 969  $\text{cm}^{-1}$  are ascribed to characteristic functional groups in plain Nafion<sup>®</sup> [18]. The IR spectra of the polyelectrolyte complexes have already been discussed in detail in our previous works [15]. In comparison with the IR spectra of modified Nafion<sup>®</sup>, the characteristic bands of the polyelectrolyte complexes at 1619, 1520, 1077, 892, 785  $\text{cm}^{-1}$  are also presented in the spectra of the modified Nafion<sup>®</sup>, which indicates

Table 1

Thickness, proton conductivity ( $\sigma$ ), methanol permeability ( $P$ ) and selectivity factor ( $\sigma/P$ ) of modified Nafion<sup>®</sup> and plain Nafion<sup>®</sup>

Sample	Thickness ( $\mu\text{m}$ )	$\sigma$ ( $\text{S cm}^{-1}$ )	$P$ ( $\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ )	$\sigma/P$ ( $\times 10^5 \text{ S s cm}^{-3}$ )
Plain Nafion <sup>®</sup>	150	$0.085 \pm 0.02$	$11 \pm 0.3$	0.8
Modified Nafion <sup>®</sup>	151	$0.078 \pm 0.02$	$6.5 \pm 0.4$	1.2
Washed Nafion <sup>®a</sup>	151	$0.076 \pm 0.03$	$6.5 \pm 0.3$	1.17

<sup>a</sup> Modified Nafion<sup>®</sup> was boiled in water at 80 °C for 24 h, then the resulted membrane was termed washed Nafion<sup>®</sup>.

### 3.4. Performance tests for a single cell

Fig. 4 shows the plots of cell potential versus current density and power density versus current density for MEAs with plain Nafion<sup>®</sup> and modified Nafion<sup>®</sup>. As shown in Fig. 4, the maximum power density is 58 mW cm<sup>-2</sup> for modified Nafion<sup>®</sup> and 49 mW cm<sup>-2</sup> for plain Nafion<sup>®</sup>. The performance of the single cell with modified Nafion<sup>®</sup> membrane is better than that with plain Nafion<sup>®</sup>. The single cell with modified Nafion<sup>®</sup> membranes possesses a higher open circuit voltage (OCV = 0.73 V) than that with plain Nafion<sup>®</sup> (OCV = 0.67 V). It has been previously explained that higher methanol permeation leads to lower OCP [7].

### 4. Conclusions

In conclusion, we have successfully modified Nafion<sup>®</sup> by casting proton-conducting materials, polyelectrolyte complexes of chitosan and phosphotungstic acid, on the surface of plain Nafion<sup>®</sup>. The casting layer is homogeneous and its thickness is about 900 nm. The proton conductivity of modified Nafion<sup>®</sup> is slightly lower than that of plain Nafion<sup>®</sup>; however, its methanol permeability is 41% lower than that of plain Nafion<sup>®</sup>. The single cells with modified Nafion<sup>®</sup> exhibit a higher open circuit voltage (OCV = 0.73 V) and maximal power density ( $P_{\max} = 58 \text{ mW cm}^{-2}$ ) than the single cells with plain Nafion<sup>®</sup> (OCV = 0.67 V,  $P_{\max} = 49 \text{ mW cm}^{-2}$ ). It is a simple, efficient, cost-effective approach to modifying Nafion<sup>®</sup> by casting proton-conducting materials on the surface of Nafion<sup>®</sup>.

### Acknowledgments

This work was supported by High Technology Research Program (863 program 2001AA323060, 2003AA517060) of

Science and Technology Ministry of China, the National Natural Science Foundation of China (20373068 and Key Project 20433060).

### References

- [1] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466.
- [2] C.H. Rhee, H.K. Kim, H. Chang, J.S. Lee, Chem. Mater. 17 (2005) 1691.
- [3] B. Gurau, E.S. Smotkin, J. Power Sources 112 (2002) 339.
- [4] A. Heinzl, V.M. Barragan, J. Power Sources 84 (1999) 70.
- [5] N. Miyake, J.S. Wainright, R.F. Savinell, J. Electrochem. Soc. 148 (2001) A905.
- [6] P. Staiti, A.S. Ario, V.A. Baglio, F. Lufrano, E. Passalacqua, V. Antonucci, Solid State Ionics 145 (2001) 101.
- [7] Z. Chen, B. Holmberg, W. Li, X. Wang, W. Deng, R. Munoz, Y. Yan, Chem. Mater. 18 (2006) 5669.
- [8] C. Yang, S. Srinivasan, A.S. Aricò, P. Creti, V. Baglio, V. Antonucci, Electrochem. Solid State Lett. 4 (2001) A31.
- [9] B. Bae, D. Kim, H. Kim, T. Lim, I. Oh, H.Y. Ha, J. Phys. Chem. B 110 (2006) 4240.
- [10] S.P. Jiang, Z. Liu, Z.Q. Tian, Adv. Mater. 18 (2006) 1068.
- [11] T. Hejze, B.R. Gollas, B.K. Schmied, F. Hofer, J.O. Besenhard, J. Power Sources 140 (2005) 21.
- [12] Z. Shao, X. Wang, I.M. Hsing, J. Membr. Sci. 210 (2002) 147.
- [13] N. Jia, M.C. Lefebvre, J. Halfyard, Z. Qi, P.J. Pickup, Electrochem. Solid State Lett. 3 (2000) 529.
- [14] J. Liu, H. Wang, S. Cheng, K. Chan, Chem. Commun. (2004) 728.
- [15] Z. Cui, C. Liu, T. Lu, W. Xing, J. Power Sources 167 (2007) 94.
- [16] Y. Sone, P. Ekdunge, D. Simonsson, J. Electrochem. Soc. 143 (1996) 1254.
- [17] A.S. Aricò, A.K. Shukla, K.M. el-Khatib, P. Creti, V. Antonucci, J. Appl. Electrochem. 29 (1999) 671.
- [18] M. Ludvigsson, J. Lindgren, J. Tegenfeldt, Electrochim. Acta 45 (2000) 2267.
- [19] W. Xu, C. Liu, X. Xue, Y. Su, Y. Lv, W. Xing, T. Lu, Solid State Ionics 171 (2004) 121.