COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Nafion–polyfurfuryl alcohol nanocomposite membranes with low methanol permeation†

Jin Liu, Huanting Wang,* Shaoan Cheng and Kwong-Yu Chan*
Department of Chemistry, The University of Hong Kong, Hong Kong, China.
E-mail: huanting@hkucc.hku.hk; hrsccky@hku.hk; Fax: (852) 2857-1586; Tel: (852) 2859-7917

Received (in Cambridge, UK) 3rd December 2003, Accepted 29th January 2004
First published as an Advance Article on the web 19th February 2004

Nafion-polyfurfuryl alcohol nanocomposite membranes with low methanol permeability and high proton conductivity were synthesized by in-situ polymerisation of furfuryl alcohol inside commercial Nafion membranes.

Perfluorosulfonic polymers such as Nafion are most extensively studied as proton electrolyte membranes for fuel cells because of their outstanding chemical, mechanical and thermal stability and their high proton conductivity. In the operation of direct methanol fuel cells (DMFCs), however, high methanol permeation through Nafion membranes significantly lowers fuel efficiency and cell performance, and thus impedes the commercial development of DMFCs.[1] Significant efforts have been made to modify Nafion by using a variety of materials such as Pd,[2] Pd alloy,[3] polyvinyl alcohol,[4] polypyrrole,[5] zeolite,[6] silica and molybdophosphoric acid[7] and montmorillonite.[8] However, conventional modified Nafion membranes cannot meet the requirements for practical DMFC applications. The research on Nafion modification remains very active.

In this communication, we report a novel approach to Nafion modification by *in situ* polymerization of furfuryl alcohol (FA) within the Nafion structure. FA is miscible with mixtures of water and alcohols, and it can readily penetrate into the hydrophilic zones of the Nafion structure. After FA polymerization *via* acid catalysis,[9] PFA becomes more hydrophobic. With the prescence of chemically stable PFA, homogenous Nafion–PFA nanocomposite membranes possess higher resistance to methanol permeation.

Commercial Nafion 115 membranes were used in this study. The Nafion 115 membrane was first sodium exchanged by boiling in 0.5 M NaOH solution, followed by rinsing with deionized water and drying. The dried membranes (2 cm × 2 cm) were immersed in a mixture of 6 g furfuryl alcohol (FA, 98%, Lancaster), 12 g isopropanol, and 6 g deionized water. The fully swollen and saturated Nafion membranes were transferred into 1.0 M sulfuric acid at room temperature for 2 min. Subsequently, the polymerization of furfuryl alcohol was carried out at 80 °C in an oven. The resulting PFA–Nafion membrane contains approximately 1.0% by weight of PFA. By repeating this procedure, Nafion–PFA nanocomposite membranes with different contents of PFA were obtained. The membranes were washed with ethanol, and boiled with 1.0 M sulfuric acid to convert to the acid form. Then the dark brown membranes were finally anealed at 140 °C for 10 min.[10] The Nafion–PFA nanocomposite membranes containing 1.0, 3.9,4.7, 5.4, 8.0, and 12.4 wt% PFA were prepared and denoted as Nafion–1.0PFA, Nafion–3.9PFA, Nafion–4.7PFA, Nafion–5.4PFA, Nafion–8.0PFA, and Nafion–12.4PFA, respectively.

The membranes were characterized by a BIO-RAD FTS165 FT-IR spectrometer (32 scans, 2 cm^{-1} resolution). FT-IR spectra for plain Nafion 115, PFA, and Nafion–12.4PFA are shown in Fig. 1. The peaks at 1200, 1147, 1056, 981 and 969cm^{-1} are ascribed to characteristic functional groups in Nafion.[11] Additional peaks at 598, 735, 1018 cm^{-1} are observed in the spectrum of Nafion–12.4PFA, and they are attributed to furan rings of PFA.[12] It is clear that the PFA was successfully introduced into commercial Nafion115 membrane.

The microstructures of Nafion 115 membrane and Nafion–PFA nanocomposite membranes were examined with a scanning electron microscope (SEM, Philips Cambridge S360). The membranes were freeze-fractured in liquid N_2 for SEM observations. A low voltage (5 kV) was operated to lower the electron beam energy and avoid damage to the membranes. The representative cross-sectional images of the samples are shown in Fig. 2. All samples exhibit the characteristic clusters of super-molecular structure of ionomeric materials due to microphase separation of hydrophilic and hydrophobic domains. The cluster sizes are estimated to be around a few tens of nanometers which is consistent with the results obtained by AFM.[13] A protruded or rugged texture is observed in plain Nafion 115 (Fig. 2a). A flake-interlaced compact morphology develops when PFA is incorporated, and uniformly dispersed in Nafion structures (Fig. 2b,c). The dimensions of cluster aggregates evidently increase, and the thickness of interstitial regions in Nafion significantly decreases as the amount of PFA increases. Interestingly, Nafion–5.4PFA (Fig. 2b) shows smaller interlaced flakes that pack more densely as compared with Nafion–12.4PFA (Fig. 2c).

The proton conductivities of Nafion 115 membrane and Nafion–PFA nanocomposite membranes were obtained by measuring the membrane impedance at room temperature.[14,15] The membrane was fixed in an electrochemical cell connected to an AUTOLAB FRA2 impedance analyzer. As expected, the proton conductivity of the membranes decreases when PFA is incorporated (Table 1). The proton conductivity drops by 11.02%, 6.51%, 26.13%, and 41.45% for Nafion–1.0PFA, Nafion–3.9PFA, Nafion–8.0PFA, and Nafion–12.4PFA, respectively, as compared to plain Nafion 115 membrane. By optimizing the amount of PFA, Nafion–PFA nanocomposite membranes still remain highly proton conducting, which is essential for fuel cell applications.

The methanol permeabilities of Nafion 115 and Nafion–PFA nanocomposite membranes were measured by a potentiometric method recently reported in the literature.[16] The membrane was clamped between the two compartments of a permeation cell; the

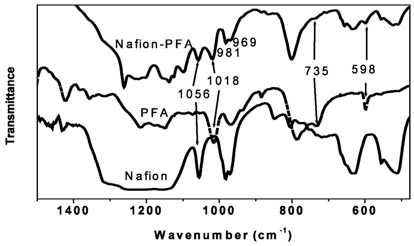

Fig. 1 FT-IR spectra of Nafion 115, PFA and Nafion–12.4PFA.

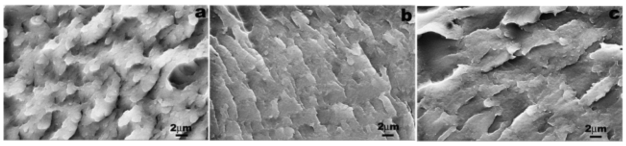

Fig. 2 SEM images of Nafion 115 and Nafion–PFA nanocomposite membranes. (a) Nafion 115, (b) Nafion–5.4 PFA, (c) Nafion–12.4PFA.

---

† Electronic Supplementary Information (ESI) available: Preparation and test methods of membrane electrode assemblies. See http://www.rsc.org/suppdata/cc/b3/b315742c/

DOI: 10.1039/b315742c

This journal is © The Royal Society of Chemistry 2004

Table 1 Proton conductivity and methanol permeability of Nafion 115 and Nafion–PFA membranes measured at room temperature

	Nafion 115	Nafion–1.0PFA	Nafion–3.9PFA	Nafion–8PFA	Nafion–12.4PFA
Proton conductivity/S cm^{-1}	0.0953	0.0848	0.0891	0.0704	0.0558
Methanol permeability/ $\mu mol\ cm^{-2}\ min^{-1}$	4.66	2.69	2.16	1.72	4.35

required volume of a solution of 1 M methanol and 0.5 M H_2SO_4 in deionized H_2O was added to one compartment, and an equal volume of a solution of 0.5 M H_2SO_4 in deionized H_2O to the other compartment. These were kept stirred using magnetic stir bars during experiments. The potential of a Pt/C gas diffusion electrode against Ag/AgCl, KCl (3 M) reference electrode was recorded by a Radiometer Copenhagen /Dynamic-Eis Voltalab PGZ301potentiostat/galvanostat.

The variation of potential as a function of permeation time for Nafion 115 and Nafion–3.9PFA is shown in Fig. 3. The potential for Nafion–3.9PFA is much higher than that for plain Nafion 115. This clearly indicates the methanol crossover through Nafion–3.9PFA is significantly reduced as compared to plain Nafion 115. The methanol permeability was determined by calibrating a standard curve of potential shift against given methanol concentration. The methanol permeability of Nafion 115 and Nafion–PFA nanocomposite membranes with different amounts of PFA is summaried in Table 1. The methanol crossover of Nafion membrane is apparently suppressed *via* PFA modification. The reduction of methanol permeability varies with the amount of PFA incorporated. The methanol permeability drops by a factor of 1.7, 2.2, 2.7, and 1.1 for Nafion–1.0PFA, Nafion–3.9PFA, Nafion–8.0PFA and Nafion–12.4PFA, respectively as compared to Nafion 115. When a small amount of PFA is incorporated, methanol permeability is significantly reduced. However, when a large amount of PFA (*e.g.* 12.4 wt%) is introduced, blockage of methanol crossover becomes less pronounced. This may be explained by the PFA molecules filling hydrophilic and lower-density regions of Nafion, giving rise to densely packed polymer chains that effectively block methanol permeation through ionic channels. But too much PFA (*e.g.* 12.4 wt%) expands greatly the hydrophilic channels of Nafion, leading to looser structures. These are also evident from microstructural differences of Nafion and Nafion–PFA nanocomposite membranes as observed by SEM (Fig. 2). The performance of Nafion–PFA nanocomposite membranes was also evaluated in a DMFC at 60 °C. The nanocomposite membrane exhibits much higher cell performance than the plain Nafion membrane (Table 2).

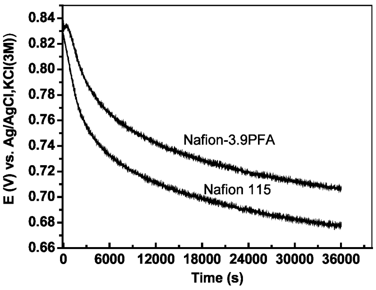

Fig. 3 Variation of potential (*E*) of Pt/C electrode *versus* time during methanol permeation.

Table 2 Steady-state performance of DMFCs (MEAs) with plain Nafion 115 and Nafion–4.7PFA operated at 60 °C with 1 M methanol and ambient air

		Current density/mA cm^{-2}			
		0	20	30	40
Nafion 115	Cell voltage/mV	624	238	140	58
Nafion–4.7PFA	Cell voltage/mV	705	349	277	209

In conclusion, we have successfully fabricated Nafion–polyfurfuryl alcohol nanocomposite membranes by *in situ* polymerization of furfuryl alcohol inside commercial Nafion 115 membranes. The Nafion–PFA membranes have 2.2–2.7 times lower methanol permeability and maintain high proton conductivity when 3.9–8.0 wt% PFA is incorporated. It is expected that sulfonation of PFA[17] will further increase proton conductivity of PFA–Nafion membranes. The approach developed here is simple, efficient, cost-effective for the fabrication of Nafion–PFA nanocomposite membranes that show great potential for improving the performance of direct methanol fuel cells.

This work is supported by The University of Hong Kong and The Research Grants Council (RGC) of Hong Kong (HKU 7005/03P, HKU 7072/01P).

Notes and references

1 A. Heinzel and V. M. Barragan, *J. Power Sources*, 1999, **84**, 70.
2 Y. M. Kim, K. W. Park, J. H. Choi, I. S. Park and Y. E. Sung, *Electrochem. Commun.*, 2003, **5**, 571.
3 Z. Q. Ma, P. Cheng and T. S. Zhao, *J. Membr. Sci.*, 2003, **215**, 327.
4 Z. G. Shao, X. Wang and I. M. Hsing, *J. Membr. Sci.*, 2002, **210**, 147.
5 M. A. Smit, A. L. Ocampo, M. A. Espinosa-Medina and P. J. Sebastian, *J. Power Sources*, 2003, **124**, 59.
6 V. Tricoli and F. Nannetti, *Electrochim. Acta*, 2003, **48**, 2625.
7 P. Dimitrova, K. A. Friedrich, U. Stimming and B. Vogt, *Solid State Ionics*, 2002, **150**, 115.
8 D. H. Jung, S. Y. Cho, D. H. Peck, D. R. Shin and J. S. Kim, *J. Power Sources*, 2003, **118**, 205.
9 H. T. Wang, L. M. Huang, B. A. Holmberg and Y. S. Yan, *Chem. Commun.*, 2002, 1708.
10 L. A. Zook and J. Leddy, *Anal. Chem.*, 1996, **68**, 3793.
11 M. Ludvigsson, J. Lindgren and J. Tegenfeldt, *Electrochim. Acta*, 2000, **45**, 2267.
12 Z. Wang, Z. Lu, X. Huang, R. Xue and L. Chen, *Carbon*, 1998, **36**, 51.
13 A. Lehmani, S. Durand-Vidal and P. Turq, *J. Appl. Polym. Sci.*, 1998, **68**, 503.
14 J. T. Müller and P. M. Urban, *J. Power Sources*, 1998, **75**, 139.
15 T. A. Davis, J. D. Genders and D. Pletcher, *Ion Permeable Membranes*, The Electrochemical Consultancy, New York, 1997.
16 N. Munichandraiah, K. McGrath, G. K. Surya Prakash, R. Aniszfeld and G. A. Olah, *J. Power Sources*, 2003, **117**, 98.
17 X. S. Chen, G. D. Zheng, J. P. Xu and L. F. Shen, *Acta Chim. Sin.*, 1992, **50**, 44.