

Short communication

A novel H₃PO₄/Nafion–PBI composite membrane for enhanced durability of high temperature PEM fuel cells

Yunfeng Zhai^{a,b}, Huamin Zhang^{a,*}, Yu Zhang^{a,b}, Danmin Xing^a

^a Lab of PEMFC Key Materials and Technology, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Received 9 January 2007; received in revised form 5 March 2007; accepted 5 March 2007

Available online 12 March 2007

Abstract

A novel phosphoric acid doped Nafion–polybenzimidazole (H₃PO₄/Nafion–PBI) composite membrane was prepared and the H₂/O₂ single cell durability was tested at 150 °C without humidification. The durability was improved 55% compared with that of phosphoric acid doped polybenzimidazole (H₃PO₄/PBI). During the durability test, the hydrogen permeability of the membrane and the internal resistance of the single cell were detected using linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS), respectively. Before and after the durability test, the mechanical strength of the membranes was measured by stress–strain tests. The results of characterization indicated that the enhanced durability of the membrane attributed to the improved mechanical strength, which benefited from the presence of Nafion in the Nafion and PBI matrix. The preliminary results suggested that the novel H₃PO₄/Nafion–PBI composite membrane is a good candidate in high temperature PEMFC for achieving longer cell lifetime.

© 2007 Elsevier B.V. All rights reserved.

Keywords: High temperature PEMFC; H₃PO₄/Nafion–PBI; Acid–base polymer complex; Durability; Mechanical failure

1. Introduction

The proton exchange membrane fuel cells (PEMFCs) have been considered as one of the most promising clean energy technologies and suitable primary power sources for transportation and stationary applications [1]. Considering some technical and economic challenges, such as the production and storage of fuel, water-thermal management in the PEMFC system, recently, more and more attentions have been paid on high temperature PEMFC (>100 °C) due to its faster electrode kinetics, greater tolerance to impurities in the fuel stream and easier water-thermal management [2]. But the typical membranes (Dupont's Nafion series or other perfluorosulfonic acid membranes) only perform properly below 100 °C because that the membranes dehydrate at higher temperature and the proton conductivity decays sharply [3,4]. Therefore, many different approaches have been carried

out to develop novel PEM membranes for high temperature operation.

Phosphoric acid doped polybenzimidazole (H₃PO₄/PBI) membrane has been investigated intensively and used more successfully [5] in high temperature PEMFC because of the excellent thermo-chemical stability, lower gas permeability [6] and mechanical property of PBI, and good proton conductivity after doped with H₃PO₄ at elevated temperature (200 °C) [7,8]. Most of the research works were focused on fuel cell demonstration [9–11], catalyst activity [12–14] and physicochemical characterization of H₃PO₄/PBI membrane [15–19], such as proton conductivity, proton transfer mechanisms and permeability. Considering the importance of the proton exchange membrane (PEM) durability for the real application and commercialization of fuel cells, the life tests of single cells with H₃PO₄/PBI membrane were performed by continuous and intermittent operation at 150 °C without humidification in our previous work [20,21]. The results showed that the durability of the single cell was about 500 h, which was much shorter than the requirement of application. The main reason for the poor durability was the mechanical failure of the H₃PO₄/PBI membrane. That is to say,

* Corresponding author. Tel.: +86 411 8437 9072; fax: +86 411 8466 5057.
E-mail address: zhanghm@dicp.ac.cn (H. Zhang).

the endurance of H₃PO₄/PBI membrane should be improved to meet the real commercial application of high temperature PEMFCs.

In the present works, the Nafion–PBI composite membrane was prepared by casting from a blend solution of Nafion–Na and PBI in *N,N'*-dimethylformamide (DMF) solution, according to the acid/basic complexes polymer concept developed by Kerres et al. [22]. The properties of the composite membrane were studied by LSV, EIS and stress–strain test. The durability test of PEMFC with the H₃PO₄/Nafion–PBI composite membrane was performed by intermittent operation at 150 °C without humidification.

2. Experimental

2.1. Preparation of composite membranes

The Nafion–PBI composite membrane was prepared by the following process. The sodium from Nafion (Nafion–Na) resin was firstly obtained by adding appropriate amount of NaOH solution (aqueous 10 wt.%) into the Nafion solution (5.4 wt.%, Du Pont, with nominal equivalent weight, EW of 1100), stirring for 30 min to neutralize, and then evaporating at 80 °C to remove the solvent. An appropriate amount of PBI (prepared by my co-worker according to US005525436A) solution (5 wt.%) in DMF was mixed with the Nafion–Na/DMF solution (10 wt.%) by stirring vigorously for 12 h. In this blend solution, the weight ratio of PBI to Nafion is 4:1. After eliminating bubbles in an ultrasonic bath for 30 min, the Nafion–PBI/DMF blend solution was poured onto a glass tray with designed dimension, and then evaporated in air at 50 °C to remove solution. After being annealed at 160 °C in a vacuum oven for 3 h, the Nafion–PBI composite membrane was removed from the glass tray by adding some de-ionized water. The Nafion–PBI composite membrane was dried at 105 °C in a vacuum oven for 12 h.

The Nafion–PBI composite membrane (32 μm in dry thickness, 20 wt.% Nafion and 80 wt.% PBI) was post-treated by immersing in 85% H₃PO₄ at 60 °C for 60 min. After the H₃PO₄ on the membrane surface was removed with filter paper, the H₃PO₄/Nafion–PBI membrane was stored between two pieces PTFE films for later use.

2.2. Electrode preparation and single cell test

The processes of the electrode preparation and the single cell test were same to the description in our previous report [20,21]. Catalyst ink was prepared by mixing catalyst powder (commercial 47.6% Pt/C from TKK, Japan) with PBI and PVDF blend solution in *N*-methyl-2-pyrrolidone (NMP). The catalyst ink was spread onto the wet-proofed GDL (SGL GDL 31 BC, 300 μm of thickness) evenly. The average thickness of catalyst layer was 30 μm, and the mean platinum loading in the electrode was 0.75 mg cm⁻². In this work, the same electrode was used in both the anode and cathode. The electrodes and H₃PO₄/Nafion–PBI membrane were assembled in layer-placed model under 3 Nm torque in a single cell with graphite bipolar plates and gold-plated copper end plates. The utilizable

areas of electrodes were 7.0 cm². The single cell was tested in our homemade test platform at 150 °C with hydrogen and oxygen without humidification at 0.1 MPa pressure and a flow rate of 100 ml min⁻¹. The single cells were operated intermittently (running from 8:00 to 20:00 everyday) at constant current (700 mA cm⁻²). During the test, the cell voltage was recorded every 2 h, and the polarization curve was recorded every 24 h. For comparison, a single cell with H₃PO₄/PBI (the dry thickness of PBI membrane was 36 μm) was also tested simultaneously under the same condition.

2.3. Physical and chemical characterization of the membranes

2.3.1. Electrochemical characterization

The H₂ permeability and proton conductivity of the membranes were measured by the LSV and EIS analysis using electrochemical working station (EG&G model 1025 FRA and model 263A) once every 24 h. In three-electrode configuration, working electrode (WE) was the cathode and the anode acted as reference electrode (RE) and counter electrode (CE) simultaneously. During the H₂ permeability test, the cathode side was purged by nitrogen and the anode side by hydrogen at 150 °C and 0.1 MPa pressure. The LSV curves were recorded with the scan rate of 4 mV s⁻¹ from 0 V to 0.8 V (versus standard hydrogen electrode). Under an H₂/O₂ open current condition, the internal resistance of single cell was obtained by EIS analysis from 100 kHz to 100 mHz with the AC amplitude at 10 mV. All inlet gases were maintained at a flow rate of 100 ml min⁻¹.

2.3.2. Stress–strain test

Before the durability tests, the tensile properties of the membranes were measured using a vertical material testing frame (GMT 4503, SANS, China) with a speed of 5 mm min⁻¹ in atmosphere at room temperature. Before immersing in H₃PO₄, the initial dimensions of all samples were 60 mm in length, 5 mm in width and 0.032 mm in thickness. After the durability tests, the tested membranes were peeled carefully off the tested MEAs and measured the tensile strength properties under the same condition. The samples had an original length of 30 mm and width of 5 mm. Considering the effect of mechanical disturbance during disassembly, a blank stress strain test was also taken following the process: tow assembled single cells (with the composite membrane and H₃PO₄/PBI membrane, respectively) were held for 24 h at 150 °C in nitrogen atmosphere, and then disassembled and retake membranes stress strain.

3. Results and discussion

3.1. Preparation of H₃PO₄/Nafion–PBI composite membrane

The novel composite membrane was synthesized according to the acid–base polymer complexes concept developed by Kerres et al. [22], which consists of mixing polymeric acid with polymer bearing basic sites. The formation of acid–base poly-

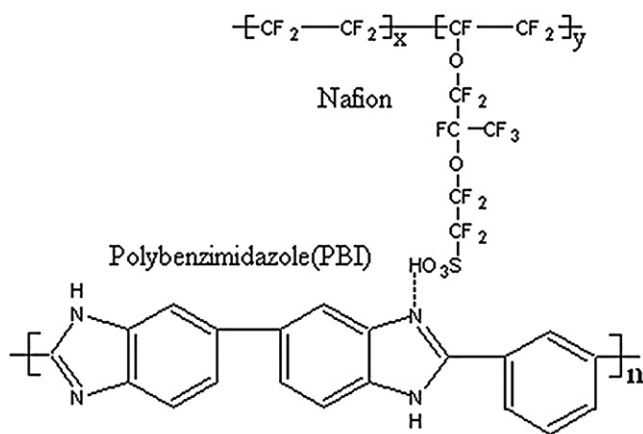


Fig. 1. Acid–base complex formation mechanism between the sulfonic acid group of Nafion and the imidazole nitrogen of PBI.

mer complex presented in this study was shown in Fig. 1. The sulfonic acid groups of Nafion interact with the N-base of PBI either by formation of hydrogen bridges or by protonation of the basic N-sites. In the polymer complex, Nafion not only plays as a crosslinking agent but also improves the chemical stability of the polymer matrix.

The transformation of Nafion resin from H form to Na form was the most important step for the composite membrane fabrication. The Nafion resin must be fully transformed into sodium form to obtain a clear casting solution and a transparent and strong film. When the Nafion/DMF solution contained H form Nafion resin, a turbid suspension formed immediately when it was mixed with PBI/DMF solution. The particle precipitate in the suspension was considered a result of the crosslinking of the acid form of Nafion and PBI, as shown in Fig. 1. After solvent evaporation and annealing, an opaque and brittle film was obtained.

During the acid immersing step, all Na^+ is removed from the composite membrane; the Nafion–Na in the Nafion–PBI composite membrane was protonated and then interacted with PBI component formed Nafion–PBI crosslinked complex. In this step, the composite membrane was also doped with H_3PO_4 . According to the weight analysis method reported in Ref. [23], the acid doping levels (the number of H_3PO_4 molecules per PBI repeat unit) were measured about 7.94 ± 0.08 for the H_3PO_4 /Nafion–PBI composite membrane and 8.64 ± 0.07 for the H_3PO_4 /PBI membrane. The acid doping level of H_3PO_4 /Nafion–PBI composite membrane was lower about 8% than that of the H_3PO_4 /PBI membrane, which accorded with the molar ratio (about 7%) of $-\text{SO}_3\text{H}$ to PBI repeat unit. This result indicated that the reaction, as shown in Fig. 1, occurred certainly between the sulfonic acid group of Nafion and the imidazole nitrogen of PBI.

3.2. Single cell life test

The polarization curves of the H_2/O_2 single cell with the composite membrane were shown in Fig. 2. It is obvious that the performance of the single cell reached its maximum at

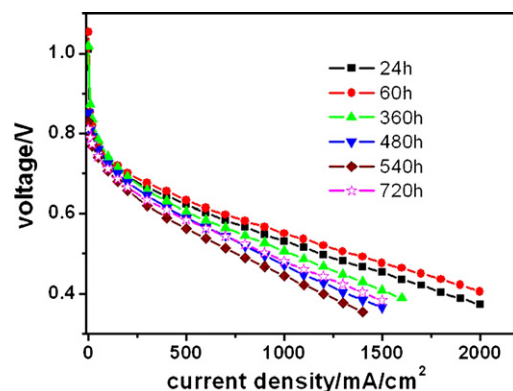


Fig. 2. The polarization curves of the H_3PO_4 /Nafion–PBI composite membrane single cell at different test time.

60 h, and then degraded a lot during the following test, for example, the voltage of the single cell at 1000 mA cm^{-2} fell from 0.55 V at 60 h to 0.45 V, at 540 h, but it increased a little again at 720 h. After about 60 h, the single cell reached its maximum performance. The degradation in the single cell performance during the test was results of the degradation of the electrocatalyst and membrane. The little increase at 720 h was due to the increase in the membrane proton conductivity, which was a result of the increase in permeability of membrane [20].

The performance at constant current (700 mA cm^{-2}) and the open current voltage (OCV) of the H_2/O_2 single cell with the composite membrane were shown in Fig. 3(a), as a contrast, those of the H_2/O_2 single cell with the H_3PO_4 /PBI membrane were shown in Fig. 3(b). It can be seen that the performance curves have four regions: in the first about 60 h, the voltage of the H_3PO_4 /Nafion–PBI single cell increased to 0.608 V and that of the H_3PO_4 /PBI single cell increased to 0.591 V, because of the activation of electrocatalyst and the decrease in the internal resistance of the single cell. In the following stage, the voltage of the H_3PO_4 /Nafion–PBI single cell decreased to 0.521 V at 580 h with a degradation rate of 0.17 mV h^{-1} and that of the H_3PO_4 /PBI single cell decreased to 0.527 V at 340 h with a degradation rate of 0.23 mV h^{-1} , due to the degradation of the electrocatalyst and the membranes. In the third stage, the voltages of the both cells have a little increase, which was a result of the increase in permeability and water content of the membranes. In the last stage, from about 720 h for the H_3PO_4 /Nafion–PBI single cell and 480 h for the H_3PO_4 /PBI single cell, the performances decreased rapidly to failure because the membranes were mechanical failure. Comparing the steady performance curves of the two single cells, it is definite that the stability and durability of the H_3PO_4 /Nafion–PBI composite membrane is much higher than that of the H_3PO_4 /PBI membrane in high temperature PEMFCs.

With respect to the OCV curves, three regions can be partitioned: rising stage, steady stage and falling stage. The detailed explanation for OCV variation of the single cell with the composite membrane will be discussed with the permeability of the composite membrane subsequently.

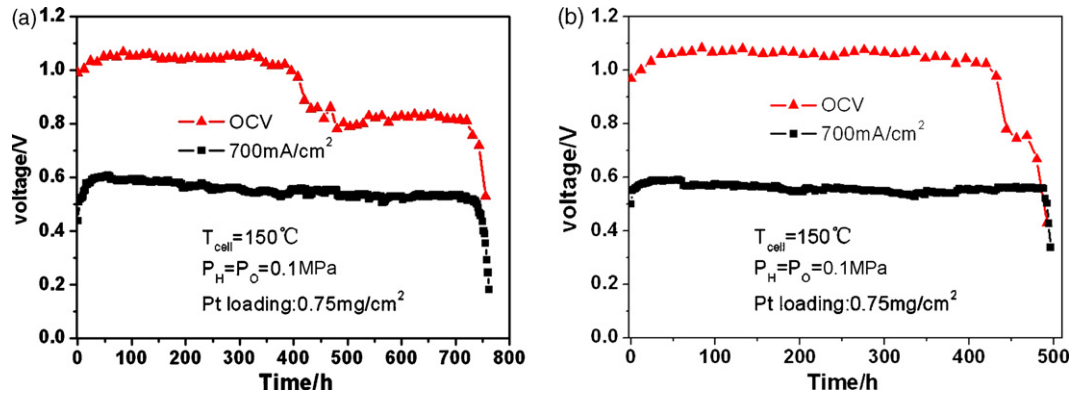


Fig. 3. The steady state performance and OCV variations of single cell with $\text{H}_3\text{PO}_4/\text{Nafion-PBI}$ composite membrane (a) and $\text{H}_3\text{PO}_4/\text{PBI}$ membrane (b) during life test.

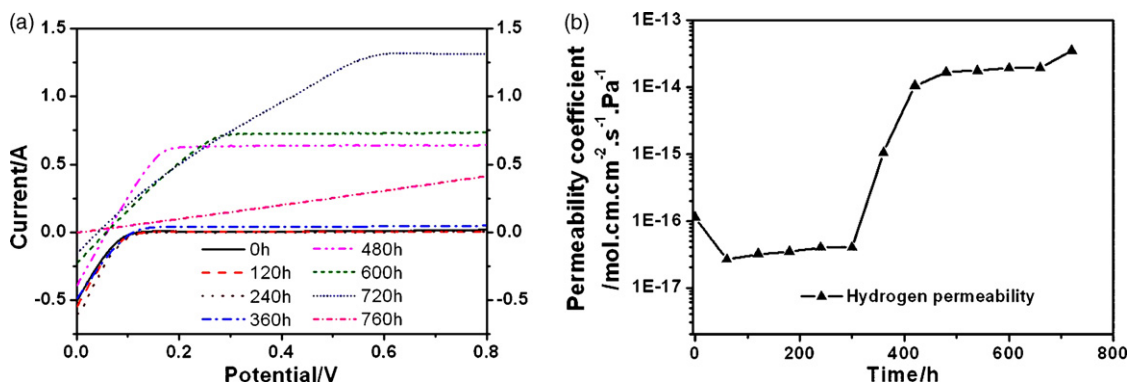


Fig. 4. The LSV curves of the MEA with $\text{H}_3\text{PO}_4/\text{Nafion-PBI}$ composite membrane (a) and the H_2 permeability variation of the composite membrane with time (b).

3.3. Physical and chemical characterization of the membranes

The permeability of the MEA with the composite membrane was tested by the LSV analysis during the life test. The representative LSV curves were shown in Fig. 4(a). The H_2 permeability of the composite membrane calculated from the LSV analysis was shown in Fig. 4(b). During the first about 360 h test, the H_2 crossover current was very small and the permeability of the membrane was very low, the permeability coefficient was about $\sim 10^{-17} \text{ mol cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. In the first about 60 h, the permeability of the membrane had a little decrease because that the swelling of the membrane decreased due to a little H_3PO_4 leaching [16]. From about 60 h to 300 h, it was nearly steady-going. From about 300 h, the permeability of the membrane increased rapidly to $\sim 10^{-15} \text{ mol cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, which maybe due to the blemish in the composite membrane. In the last life test, at about 760 h, the H_2 crossover current rose rapidly with the increase of working electrode potentials, and no the limiting current was found with increasing overpotential. These phenomenons represented that the permeability of the membrane was too much and the single cell was no longer in working order. These changes of H_2 crossover through the MEA should be responsible for the variation of the OCV of the single cell with the composite membrane. As shown in Fig. 3(a), the OCV increased with the decrease of H_2 crossover, contrarily, the OCV decreased; especially in the end-life, the dramatic

reduction of OCV was due to the mechanical failure of the membrane.

In order to investigate the proton conductivity of the $\text{H}_3\text{PO}_4/\text{Nafion-PBI}$ composite membrane, the internal resistance of the single cell with the composite membrane at OCV was detected using EIS analysis compared with that of the single cell with $\text{H}_3\text{PO}_4/\text{PBI}$ membrane during the life test. As shown in Fig. 5, on the whole, the internal resistance of the $\text{H}_3\text{PO}_4/\text{Nafion-PBI}$ single cell was close to, even lower a little than that of the $\text{H}_3\text{PO}_4/\text{PBI}$ single cell. During the life tests, both of them varied in a similar trend: a small decrease at the

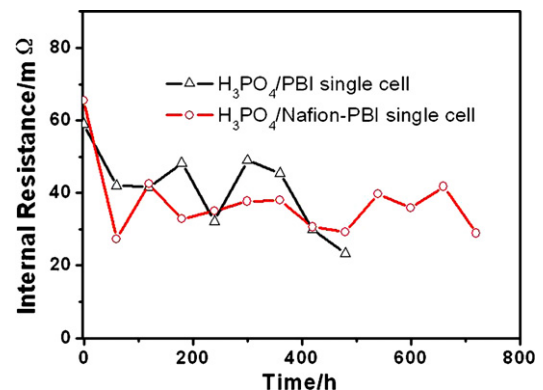


Fig. 5. The internal resistance variations of the single cells with $\text{H}_3\text{PO}_4/\text{PBI}$ membrane and $\text{H}_3\text{PO}_4/\text{Nafion-PBI}$ composite membrane during life test.

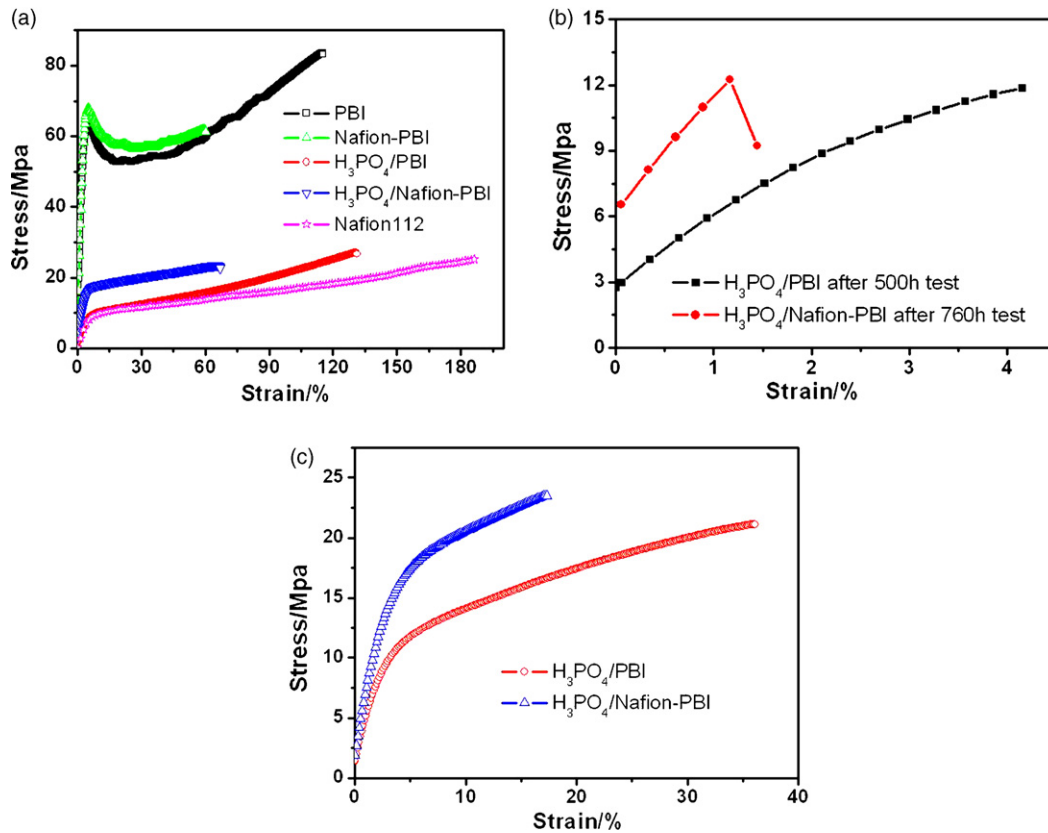


Fig. 6. The stress–strain curves of the composite membrane and H₃PO₄/PBI membrane before (a) and after (b) the life test and blank (c).

beginning, held almost in line, another small decrease nearly the end of the life test. The little lower internal resistance of the H₃PO₄/Nafion–PBI single cell maybe due to the thinner thickness of H₃PO₄/Nafion–PBI membrane than H₃PO₄/PBI membrane. The small decrease at the beginning of tests was a result of the H₃PO₄ leaching to the electrocatalyst layers from the membrane, and which improved the proton conductivity of the electrocatalyst layers [23]. But the second small decrease in internal resistance of single cells nearly the end of the life test because that the increase in permeability of membrane resulted in the water content increase in the membrane. The results indicated that the introduction of Nafion had not reduced the proton conductivity of the H₃PO₄/PBI membrane.

Before and after the life test, the mechanical tensile properties of the H₃PO₄/Nafion–PBI composite membranes were measured comparing with that of the H₃PO₄/PBI membrane, to attempt to search for the reason for the improved durability of the composite membrane in high temperature PEMFC. The typical stress–strain curves were shown in Fig. 6. It should be noted that when the membrane was peeled off the electrodes in the MEA, some part of catalyst layer adhered to the membrane. So the thickness of it is indeterminable. Therefore, in this test, the thicknesses of all membranes were based on that before immersing in H₃PO₄. The results in Fig. 6(a) indicated that the dry Nafion–PBI blend membrane had the same mechanical strength as PBI membrane except the less elongation at break; after doped with H₃PO₄, the H₃PO₄/Nafion–PBI membrane gave much better mechanical strength than that of

H₃PO₄/PBI membrane, although both of them had a significant reduction. Which because that when phosphoric acid was introduced, the membranes swelled and the molecular cohesion of PBI was decreased. With regard to the H₃PO₄/Nafion–PBI membrane, the non-linear additivity of the physical properties of Nafion suggested that the higher mechanical strength owed to the interaction between Nafion and the imidazole rings of PBI. From Fig. 6(b), it can be seen that even after the 760 h durability test, the composite membrane hold still better mechanical strength than the 500 h-tested H₃PO₄/PBI membrane. Considering the effect of mechanical disturbance during disassembly, the result of blank stress strain test was also shown in Fig. 6(c), the result indicated the both membranes had a little increase mechanical strength and large decrease in elongation at break because of a little H₃PO₄ leaching due to assembly force. All above results implied the H₃PO₄/Nafion–PBI composite membrane also had more mechanically robust than the H₃PO₄/PBI membrane.

4. Conclusions

A novel H₃PO₄/Nafion–PBI composite membrane was prepared and the single cell durability was tested in high temperature PEMFC. The single cell with the H₃PO₄/Nafion–PBI composite membrane had an improved (about 55%) durability and the same performance compared with the H₃PO₄/PBI system. The results suggested that the reasons for the enhanced durability of the composite membrane were the presence of

Nafion in the Nafion–PBI matrix. In brief, the preliminary results indicate that the novel H₃PO₄/Nafion–PBI composite membrane is a better candidate in high temperature PEMFC for achieving longer cell lifetime.

Acknowledgements

This work was partly supported by the National Natural Science Foundation of China (Grant no. 20476104) and the Innovation Foundation of Dalian Institute of Chemical Physics.

References

- [1] W.H.J. Hogarth, J.C.D. da Costa, G.Q.M. Lu, *J. Power Sources* 142 (2005) 223.
- [2] C. Yang, P. Costamagn, J. Benziger, A.B. Bocarsly, *J. Power Sources* 103 (2001) 1.
- [3] J.A. Asensio, S. Borros, G.R. Pedro, *Electrochem. Commun.* 5 (2003) 967.
- [4] Z.G. Shao, P. Joghee, I.M. Hsing, *J. Membr. Sci.* 229 (2004) 43.
- [5] Q.F. Li, R.H. He, J.O. Jensen, N.J. Bjerrum, *Chem. Mater.* 15 (2003) 4896.
- [6] O. Savadogo, *J. Power Sources* 127 (2004) 135.
- [7] J.T. Wang, R.F. Savinell, *Electrochim. Acta* 41 (1996) 193.
- [8] D. Mecerreyes, H. Grande, O. Miguel, R. Marcilla, I. Cantero, *Chem. Mater.* 16 (2004) 604.
- [9] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, *Fuel Cell* 4 (2004) 147.
- [10] C. Pan, R. He, Q. Li, J.O. Jensen, N.J. Bjerrum, H.A. Hjulmand, A.B. Jensen, *J. Power Sources* 145 (2005) 392.
- [11] J.O. Jensen, Q. Li, R. He, C. Pan, N.J. Bjerrum, *J. Alloys Compd.* 404 (2005) 653.
- [12] Q. Li, R. He, J. Gao, J.O. Jensen, *J. Electrochem. Soc.* 150 (2003) A1599.
- [13] Z. Liu, J.S. Wainright, R.F. Savinell, *Chem. Eng. Sci.* 59 (2004) 4833.
- [14] Q. Li, H.A. Hjuler, N.J. Bjerrum, *Electrochim. Acta* 45 (2000) 4219.
- [15] X. Glipa, B. Bonnet, B. Mula, D.J. Jones, J. Rozi  re, *J. Mater. Chem.* 9 (1999) 3045.
- [16] Q. Li, H.A. Hjuler, N.J. Bjerrum, *J. Appl. Electrochem.* 31 (2001) 773.
- [17] R. He, Q. Li, G. Xiao, N.J. Bjerrum, *J. Membr. Sci.* 226 (2003) 169.
- [18] J.S. Wainright, J.-T. Wang, D. Weng, R.F. Savinell, M. Litt, *J. Electrochem. Soc.* 142 (1995) L121.
- [19] C.E. Hughes, S. Haufe, B. Angerstein, R. Kalim, U. Ma1hr, A. Reiche, M. Baldus, *J. Phys. Chem. B* 108 (2004) 13626.
- [20] Y. Zhai, H. Zhang, G. Liu, J. Hu, B. Yi, *J. Electrochem. Soc.* 154 (2007) B72.
- [21] Y. Zhai, H. Zhang, D. Xing, Z. Shao, *J. Power Sources* 164 (2007) 126.
- [22] J. Kerres, A. Ullrich, F. Meier, T. H  ring, *Solid State Ionics* 125 (1999) 243.
- [23] R. He, Q. Li, A. Bach, J.O. Jensen, N.J. Bjerrum, *J. Membr. Sci.* 277 (2006) 38.