



Short communication

Alkali doped polybenzimidazole membrane for high performance alkaline direct ethanol fuel cell

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ABSTRACT

An anion exchange membrane for alkaline direct ethanol fuel cell (ADEFEC) was prepared by doping KOH in polybenzimidazole (PBI) membrane. The distributions of nitrogen, oxygen and potassium in the membrane were analyzed by means of XRD and SEM-EDX, respectively. It was found that free or combined KOH molecules may exist in the PBI matrix, which was helpful for the ionic conductivity of PBI/KOH. Ethanol permeability through this membrane was much lower than that of Nafion[®]. For ADEFEC based on this PBI/KOH membrane electrolyte, the power density was 3 to 6 times of the results in literatures. In addition, the micro-structure of alkali doped PBI and the interaction between KOH and PBI matrix were also speculated logically.

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1. Introduction

Recently, increasing interest has been attracted by alkaline direct ethanol fuel cell (ADEFEC) because of its many merits [1,2]. Firstly, it is well known that ethanol is less toxic than methanol [3]. Secondly, during the operation of ADEFEC, the charge carrier in the membrane is anion and it moves from the cathode to the anode, opposite to the movement of the proton in acid membrane. Thus a reversed electro-osmotic effect is formed, which may depress ethanol crossover through the membrane accordingly [4]. Finally, both electrochemical oxidation of ethanol and oxygen reduction reaction are more facile in alkali medium than in acid medium [5–7]. The cost can also be reduced since non-platinum catalysts can be used in alkaline medium.

The quaternized polymers based on anion exchange membranes have been developed as electrolyte in alkali direct alcohol fuel cells [4,8–11]. However, the quaternized polymer is unstable in alkaline medium at temperatures above 60 °C and the performance of ADEFEC based on this type of membrane is still poor, most of which is less than 20 mW cm⁻². Therefore, the development of anion exchange membranes for an improved performance of ADEFEC is still urgent.

PBI membrane is well known to possess excellent endurance both in alkali medium and at high temperature [12]. It is an electronic and ionic insulator, however, there are two imide groups (–N=) in one repeat unit of PBI. Therefore, it can become proton conductor when doped with the acids. For instance, phosphoric acid doped PBI membrane is a very promising candidate for high temperature proton exchange membrane fuel cells (PEMFCs) [13–17]. Although PBI is a weakly basic polymer, the amine groups (–NH–) in its structure allow it to be an ionic conductor by introducing inorganic hydroxides [12]. However, compared with the acid doped PBI, there is fewer reports about alkali doped PBI for fuel cell applications. Up to now, the experimental evaluation of alkali doped PBI for ADEFEC applications has not been reported in literatures. In this paper, PBI-based anion exchange membrane was prepared and characterized by XRD, SEM-EDX and ac impedance spectroscopy. Finally, the single cell performance of ADEFEC based on KOH doped PBI membrane was investigated with 2 M ethanol as the fuel.

2. Experimental details

2.1. Materials

The PBI film (50 μm) was friendly supplied by Northeastern University in China. Potassium hydroxide pellet was used as received without being purified.

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2.2. Characterization of the alkali doped PBI membrane

The adsorption dynamics of PBI in KOH solution was studied by monitoring the membrane's weight at different time during doping with 6 M KOH solution. XRD pattern was obtained with a Rigaku X-3000 X-ray ($\lambda = 1.54 \text{ \AA}$) powder diffractometer using Cu $K\alpha$ radiation with a Ni filter. The scan range was from 5° to 85° , and the scan rate was 5° min^{-1} . The cross-section of the membrane was investigated with a JEOL JSM-6360LV SEM. The element distribution in the cross-section was determined by Oxford Instrument X-ray Microanalysis 1350. Before measuring the ionic conductivity, the sample was firstly rinsed with deionized (D.I.) water several times in order to remove KOH on the surface of the membrane. It was then sandwiched between two Teflon plates with platinum wires as electrodes. The ionic conductivity was measured at room temperature on the potentiostat (EG&G Model 273A) and Lock-in Amplifier (EG&G Model 5210) from 100 mHz to 100 KHz with oscillating voltage of 10 mV. Ethanol permeability through the membrane was determined using a glass diffusion cell [18], which was separated into two reservoirs (A and B). The membrane was placed vertically between A and B as a barrier. One compartment of the cell ($V_A = 50 \text{ mL}$) was filled with an aqueous solution of ethanol (80 mL L^{-1}) and *n*-butanol (2 mL L^{-1}). The other ($V_B = 20 \text{ mL}$) was filled with an aqueous solution of *n*-butanol (2 mL L^{-1}). Each reservoir was equipped with a stirrer for stirring during the measurement. The increase in ethanol concentration in B reservoir was measured at different time using gas chromatography (Shimadzu GC-14B).

2.3. Membrane electrode assemblies and fuel cell tests

The electrode catalysts, Pt-Ru/C (30% Pt, 15% Ru) for the anode and Pt/C (20% Pt) for the cathode, were purchased commercially from Johnson Matthey. The loadings of Pt-Ru at the anode and Pt at the cathode were 2.0 and 1.0 mg cm^{-2} , respectively. The MEA was prepared by sandwiching the membrane between two electrodes. It was then placed between two stainless steel plates with channels to form a single cell with an active area of 4 cm^2 . Single cell tests were performed using a commercial fuel cell test system (Arbin Instrument Corporation). Because the conventional anode with Nafion® solution as interface solution was used, 2 M KOH was fed into the anode along with 2 M ethanol at a flow rate of 1 mL min^{-1} in order to supply with three-phase boundary and enough OH^- . At the same time, the cathode was supplied with O_2 (0.2 MPa).

3. Results and discussions

3.1. The adsorption behavior of PBI in alkaline solution

Generally speaking, PBI film exhibits good proton conductivity after doped with H_3PO_4 by forming hydrogen bonds between H_3PO_4 and $-\text{N}=\text{}$ in imidazole rings. On the other hand, it was also reported that PBI had a remarkable absorbent capacity to KOH [12], thus possessing higher ionic conductivity. In this work, the alkali doped PBI was prepared by immersing PBI film in 6 M KOH solution for a period of time at room temperature. The adsorption dynamics of PBI in KOH solution was shown in Fig. 1. The results suggested that the doping equilibrium was reached after the PBI film was immersed in 6 M KOH solution for about 7 days. As PBI membrane prepared from a solution in *N,N*-dimethylacetamide was dense and non-porous [13], it is thus speculated that chemical interaction, such as dipole–dipole interaction (including hydrogen bonding) and induction forces, may take place between PBI backbone and KOH during alkali doping.

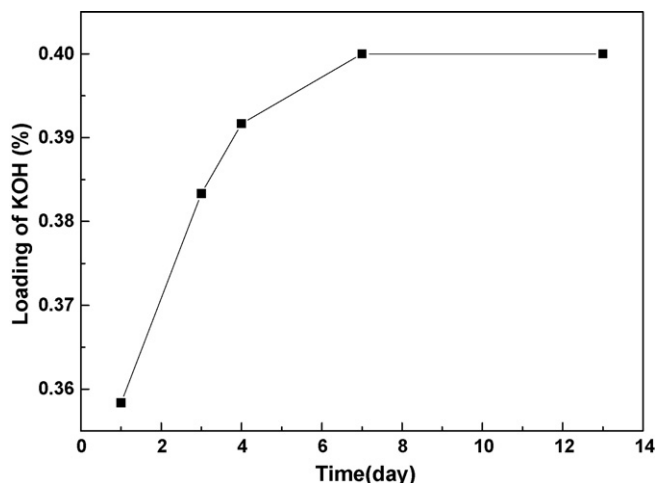


Fig. 1. The absorption behavior of the alkali doped PBI in 6 M KOH solution as a function of time at room temperature.

3.2. XRD characterization

XRD pattern of wet PBI/KOH with surface KOH removed was obtained as shown in Fig. 2. It was found that the XRD pattern of PBI/KOH was a coupling of two XRD patterns of PBI and inorganic KOH. From the outline of XRD pattern of PBI/KOH, a broad diffraction peak at $2\theta = 25.2^\circ$ was observed, which should be assigned to PBI according to the literature [19]. The rest narrower diffraction peaks were attributed to KOH. The result of XRD indicated that PBI can absorb KOH into its backbones.

3.3. SEM and EDX characterization

Prior to the experiment, the sample was rinsed with D.I. water to remove KOH on its surface, then it was freeze-fractured in the liquid nitrogen. Fig. 3 showed the cross-section SEM image of alkali doped PBI and its corresponding EDX mappings for potassium, oxygen and nitrogen elements. In the EDX mapping image, the highlighted bright dots revealed high element concentration. It was found that the distributions of potassium, oxygen and nitrogen elements were homogeneous, which implied that KOH was well dispersed throughout PBI membrane. Furthermore, the EDX mapping of potassium element exhibited much higher concentration than that of oxygen element. The reason may be as follows:

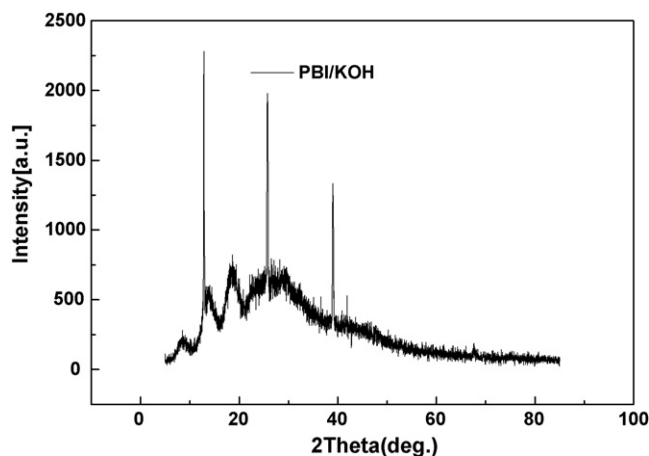


Fig. 2. XRD pattern of the alkali doped PBI.

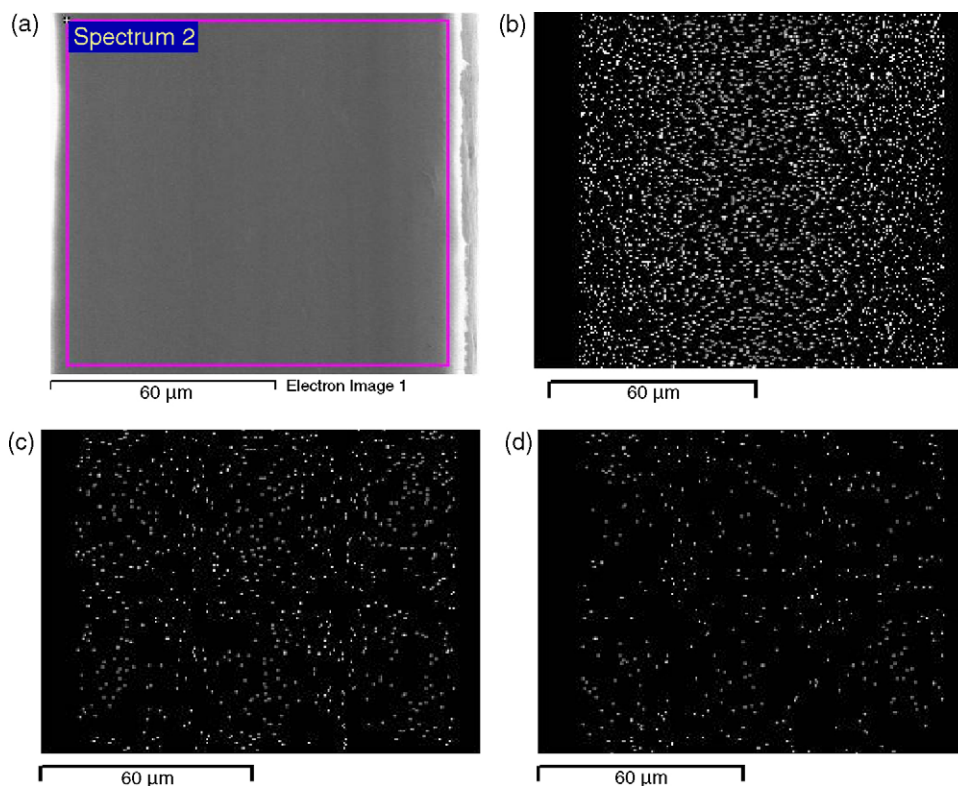


Fig. 3. (a) SEM image of PBI/KOH. EDX mapping of (b) potassium element, (c) oxygen element and (d) nitrogen element within PBI/KOH.

OH^- in KOH may react with H atom of $-\text{NH}-$ in PBI matrix to generate water, while K^+ was left behind to combine with N atom in the backbones of the polymer. Taking 2-phenylbenzimidazole aqueous solution as a reference, its secondary dissociation constant pK_a is 11.91 at 25°C . The amine groups in PBI may act as proton donors to react with strong alkali of KOH although this reaction may take place incompletely. In addition, the water was also adsorbed by PBI membrane during alkali doping. Some of KOH molecules probably were taken into the polymer by water molecules. Therefore, the EDX mappings of both potassium and oxygen were higher than that of nitrogen element. This result suggested that free or combined KOH molecules by long-distance interaction may exist in the PBI matrix, which was helpful for the ionic conductivity of PBI/KOH. According to the results of XRD and SEM-EDX, two possible combinations between PBI and KOH were presumed: (1) combination between K^+ and $-\text{NH}-$ in imidazole ring of PBI may occur as a result of neutralization or interaction; (2) hydrogen bonding possibly existed between OH^- and $-\text{N}=\text{C}$ in imidazole ring of PBI, while K^+ was introduced into the polymer connecting with OH^- to form a charge balance, as shown in Fig. 4. The first com-

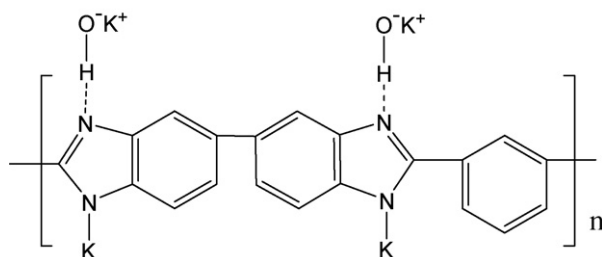


Fig. 4. Micro-structure of the alkali doped poly[2,2-(*m*-phenylene)-5,5'-bibenzimidazole], PBI/KOH.

ination between them may occur step by step, as displayed in Fig. 5.

3.4. The ionic conductivity and ethanol permeability

For ADEFC, the ionic conductivity and fuel permeability are two important parameters, which are highly correlative to the cell performance. Generally speaking, it is essential that an electrolyte membrane for ADEFC should have higher ionic conductivity and lower ethanol permeability. In this work, these two parameters for alkali doped PBI were determined at room temperature and listed in Table 1. The ionic conductivity of the membrane was 0.0184 S cm^{-1} , which was acceptable and reasonable, even if it was much lower than 0.10 S cm^{-1} of H-Nafion[®] in literatures [20–22]. This result may be due to the fact that the transfer number of OH^- is inherently much lower than that of H^+ , which is only 0.25 times of the transfer number of H^+ . Ethanol permeability through PBI/KOH was $6.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which was much lower than that of Nafion[®] [23]. The reason may be as follows: there are many hydrophilic groups of $-\text{SO}_3\text{H}$ in H-Nafion[®] structure, and Nafion[®] is usually swollen more significantly than PBI and PBI/KOH in the presence of ethanol and water. The less expanded space among PBI backbones than that of the Nafion[®] probably resulted in lower ethanol permeability of PBI/KOH [24].

Table 1

The ionic conductivity and ethanol permeability of the alkali doped PBI at room temperature

ionic conductivity (S cm^{-1})	Ethanol permeability ($\text{cm}^2 \text{ s}^{-1}$)
0.0184	6.5×10^{-7}

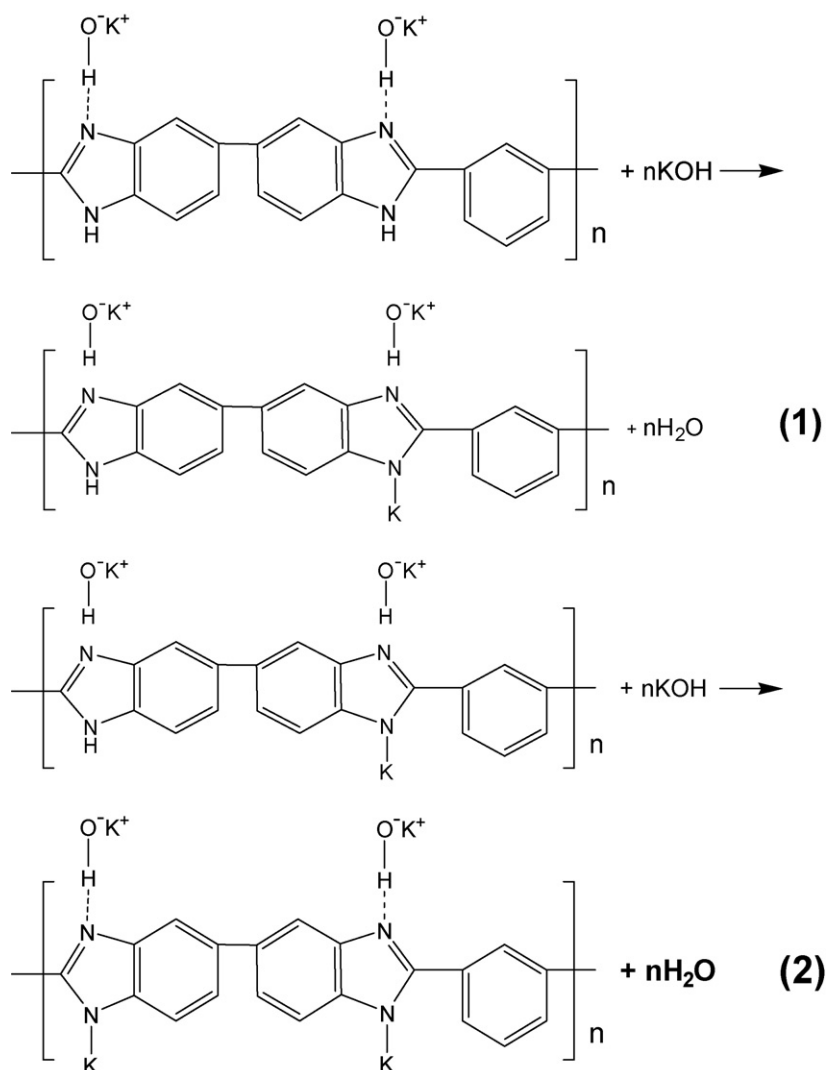


Fig. 5. The scheme of combination between KOH and -NH- in the matrix of PBI.

3.5. Single cell performance

Fig. 6 showed the single cell performance of ADEFC with PBI/KOH as anion membrane electrolyte at 75 °C and 90 °C. The

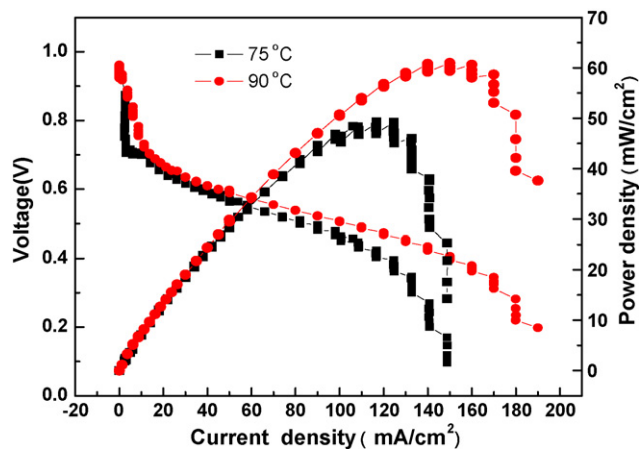


Fig. 6. The i - v curves of ADEFC with alkali doped PBI as an electrolyte membrane at 75 °C and 90 °C.

solution containing 2 M ethanol and 2 M KOH was fed into the anode of the fuel cell. The open circuit potentials (OCPs) and power densities of ADEFC at 75 °C and 90 °C were listed in Table 2. The OCPs of single cell at 75 °C and 90 °C were 0.9236 V and 0.9797 V, respectively. These favorable results should be owed to much lower ethanol permeability of PBI/KOH membrane. In addition, during ADEFC operation, the anion moves from the cathode to the anode, opposite to the movement of the proton in acid membrane. A reversed electro-osmotic effect is thus formed, which may further depress ethanol crossover through the membrane accordingly. The loss of OCP due to ethanol permeability can be minimized. The peak power densities of ADEFC at 75 °C and 90 °C were 49.20 and 60.95 mW cm^{-2} respectively, which were much better than the corresponding values in literatures [1,2]. The corresponding values in above literatures were usually lower than 20 mW cm^{-2} , due to lower stability above 60 °C for their anion exchange membranes.

Table 2

The OCPs and the power densities of ADEFC at 75 °C and 90 °C

Temperature (°C)	OCP (V)	Power density (mW cm^{-2})
75	0.9236	49.20
90	0.9797	60.95

In this work, as an anion exchange membrane, PBI/KOH exhibited excellent endurance both in basic solution and at higher temperatures. Therefore, the operation temperature of single cell can be increased to 90 °C. Wang et al. [25] reported that the elevating temperature can accelerate electrochemical reaction kinetics, and depress negative effect of pH difference between the anode and the cathode in alkaline direct methanol fuel cell. In summary, low ethanol permeability, fast electrochemical reaction kinetics and reduced negative effect of pH difference between two electrodes made the performance of ADEFC reach a much higher power density. The optimization of the electrode structure about ADAFC based on PBI/KOH membrane without aqueous KOH fed into the anode will be our next target.

4. Conclusion

Alkali doped PBI membrane for high performance ADEFC was prepared and characterized. The results suggested that KOH was distributed evenly in the matrix of PBI. The ionic conductivity of PBI/KOH was markedly enhanced compared to that of unmodified PBI membrane. Ethanol permeability of PBI/KOH was $6.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, which was much lower than that of H-Nafion®. For ADEFC based on this PBI/KOH membrane electrolyte, the power density was 3 to 6 times of the results in literatures.

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References

- [1] A. Verma, A.K. Jha, S. Basu, *J. Power Sources* 141 (2005) 30–34.
- [2] A. Verma, S. Basu, *J. Power Sources* 145 (2005) 282–285.
- [3] S.Q. Song, P. Tsiakaras, *Appl. Catal. B* 63 (2006) 187–193.
- [4] L. Li, Y.X. Wang, *J. Membr. Sci.* 262 (2005) 1–4.
- [5] C.W. Xu, L.Q. Cheng, P.K. Shen, Y.L. Liu, *Electrochem. Commun.* 9 (2007) 997–1001.
- [6] J.P. Liu, J.Q. Ye, C.W. Xu, S.P. Jiang, Y.X. Tong, *Electrochem. Commun.* 9 (2007) 2334–2339.
- [7] H. Meng, P.K. Shen, *Electrochem. Commun.* 8 (2006) 588–594.
- [8] J. Fang, P.K. Shen, *J. Membr. Sci.* 285 (2006) 317–322.
- [9] A.B. Huang, C.Y. Xia, C.B. Xiao, L. Zhuang, *J. Appl. Polym. Sci.* 100 (2006) 2248–2251.
- [10] J.R. Varcoe, R.C.T. Slade, *Fuel Cells* 5 (2) (2005) 187–200.
- [11] J.R. Varcoe, R.C.T. Slade, *Electrochem. Commun.* 8 (2006) 839–843.
- [12] B. Xing, Q. Savadogo, *Electrochem. Commun.* 2 (2000) 697–702.
- [13] R.H. He, Q.F. Li, A. Bach, J.O. Jensen, N.J. Bjerrum, *J. Membr. Sci.* 272 (2006) 38–45.
- [14] M.Y. Jang, Y. Yamazaki, *J. Power Sources* 139 (2005) 2–8.
- [15] Q.F. Li, R.H. He, J.O. Jensen, N.J. Bjerrum, *Chem. Mater.* 15 (2003) 4896–4915.
- [16] R.H. He, Q.F. Li, J.O. Jensen, N.J. Bjerrum, *J. Polym. Sci. Part A Polym. Chem.* 45 (2007) 2989–2997.
- [17] H.T. Pu, Q.Z. Liu, G.H. Liu, *J. Membr. Sci.* 241 (2004) 169–175.
- [18] C.N. Li, G.Q. Sun, S.Z. Ren, J. Liu, Q. Wang, Z.M. Wu, H. Sun, W. Jin, *J. Membr. Sci.* 272 (2006) 50–57.
- [19] P. Staiti, F. Lufrano, A.S. Arico, E. Passalacqua, V. Antonucci, *J. Membr. Sci.* 188 (2001) 71–78.
- [20] P. Costamagna, C. Yang, A.B. Bocarsly, S. Srinivasan, *Electrochim. Acta* 47 (2002) 1023–1033.
- [21] Z.M. Wu, G.Q. Sun, W. Jin, H.Y. Hou, S.L. Wng, Q. Xin, *J. Membr. Sci.* 313 (2008) 336–343.
- [22] H.L. Tang, M. Pan, S.P. Jiang, Z.H. Wan, R.Z. Yuan, *Colloids Surf. A: Physicochem. Eng. Aspects* 262 (2005) 65–70.
- [23] Z.M. Wu, G.Q. Sun, W. Jin, Q.i. Wang, H.Y. Hou, K.Y. Chan, Q. Xin, *J. Power Sources* 167 (2007) 309–314.
- [24] Q.F. Li, R.H. He, R.W. Berg, H.A. Hjuler, N.J. Bjerrum, *Solid State Ionics* 168 (2004) 177–185.
- [25] Y. Wang, L. Li, L. Hu, L. Zhuang, J.T. Lu, B.Q. Xu, *Electrochem. Commun.* 5 (2003) 662–666.