ELSEVIER

Composite Nafion/polyphenylene oxide (PPO) membranes with phosphomolybdic acid (PMA) for direct methanol fuel cells

Junho Sauk, Jungyeon Byun, Hwayong Kim*

*School of Chemical Engineering and Institute of Chemical Processes, Seoul National Universty, San 56-1,
Shinlim-dong, Kwanak-Ku, Seoul 151-744, Korea*

Abstract

The preparation and characterization of new polymer composite membranes containing polyphenylene oxide (PPO) thin films with phosphomolybdic acid (PMA) are presented. PPO thin films with PMA (PPO-PMA films) have been prepared by using the solvent mixture. In this study, methanol was used as a solvent dissolving PMA and chloroform was used as a solvent dissolving PPO. PPO-PMA solutions were cast onto a glass plate. The composite membranes were prepared by casting Nafion mixture on porous PPO-PMA films. The composite membranes were characterized by measuring their ion conductivity and methanol permeability. The morphology and structure of these PPO-PMA films were observed with scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and wave dispersive spectrometer (WDS). The composite membranes are tested as electrolytes in a direct methanol fuel cells (DMFCs). The performance tests have shown that they have a good perspective in this DMFCs. The methanol cross-over in the DMFC can be reduced by composite membranes containing PPO-PMA barrier films.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Polyphenylene oxide; Phosphomolybdic acid; PPO-PMA films; Direct methanol fuel cells; Methanol cross-over

1. Introduction

Fuel cells have emerged strongly as power sources for stationary and portable applications owing to their high-energy conversion efficiency, eco-friendly nature and low-temperature operation [1–3]. Recently, direct methanol fuel cells (DMFCs) uses methanol as the fuel because of cheap price and easy handling. Methanol can be oxidized directly to carbon dioxide and water in DMFC systems. It has a high energy density and can be generated from a variety of sources such as natural gas, coal and biomass. DMFC is expected to have high and compromising value as clean energy [4–6].

Despite the advantage of DMFCs, there are two major obstacles inhibit the use of DMFCs, namely, limited catalyst activity and methanol cross-over to the cathode. The perfor-mance of DMFCs is limited by the cross-over of methanol though the membrane electrolyte. The methanol cross-over causes performance losses at the cathode due to the consumption of oxygen and catalyst poisoning [7–9].

It is well known that Nafion membranes offer several advantages such as high conductivity, mechanical strength and good chemical properties. However, some significant disadvantages are also encountered such as high methanol permeability and temperature limitation [10,11].

In order to reduce the methanol cross-over in DMFCs, several new membrane structures have been studied by various authors. Hobson et al. [12] proposed a thin barrier layer of polybenzimidazol (PBI) on the Nafion 117 surface by screen printing to reduce methanol cross-over. Shao et al. [8] reported that the methanol cross-over can be reduced by a thin film containing polyvinyl alcohol (PVA) and Nafion. Hatanaka et al. [13] conducted grafted polymer membranes as an electrolyte using poly(ethylene-tetrafluoroethylene) film

* Corresponding author. Tel.: +822 880 7406; fax: +822 888 6695.
E-mail address: hwayongk@snu.ac.kr (H. Kim).

for DMFCs. In any case, it is highly desirable to find electrolyte membranes which reduce the methanol cross-over significantly.

Phosphomolybdic acid ($H_3PMo_{12}O_{40}$, PMA) is an inorganic acid, but at the same time can act as an oxidizing agent. PMA has shown high proton conductivity at room temperature and a high solubility in water and in many organic solvents. They are mostly soluble in polar solvents such as water and alcohols, but PMA is insoluble in non-polar chemical. A method for the preparation of PMA imbedded polymer films using mixed solvents is used in this work toward the immobilization of PMA. To overcome this leakage problem from membrane and to increase the proton conductivity of the cell, PMA was immobilized in polymer matrix. This work is to use mixed solvents comprising methanol and chloroform in order to prepare various PPO-PMA films [14–17].

In this work, we aim to improve the cell performance and inhibit the methanol permeation by the composite membranes using PPO-PMA thin films. PPO-PMA thin films are used to reduce methanol permeability while maintaining proton conductivity at the composite membranes. The morphology and structure of porous thin films were determined using scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and wave dispersive spectrometer (WDS). Furthermore, the ion conductivity and methanol permeation were measured and compared with those of Nafion 115 membrane. DMFC performances were also tested on the purpose-built equipment.

2. Experimental

2.1. Materials

Phosphomolybdic acid ($H_3PMo_{12}O_{40}$, PMA) was obtained from Fluka chemicals. These PMA was purified and calcined at $300\,^\circ$C for the precise quantification. Polyphenylene oxide (PPO, poly-2,6-dimethyl-1,4-phenylene oxide from Aldrich Co.) was used as a blending polymer. Methanol (M) and chloroform (C) were used as blending solvents. Dupont supplied Nafion 15 wt.% solution to cast membranes. Their chemical structures are shown in Fig. 1.

2.2. Preparation of composite membranes

The PMA and PPO can be blended using the solvent mixture, because PPO and PMAs are not soluble in the same solvent. In this study, PPO-PMA thin films were prepared according to procedures described in the literature [14]. Chloroform was used as a solvent dissolving PPO. PMA (0–1 g) was first dissolved in 3 ml of methanol. 0.9 g of PPO was completely dissolved in 16 ml of chloroform solution and then PMA-M solution was added into this PPO-C solution. The PPO-PMA-MC solution was stirred with a magnetic stirrer until it was completely mixed. PPO-PMA solutions were cast onto a glass plate with uniform thickness. PPO-PMA films
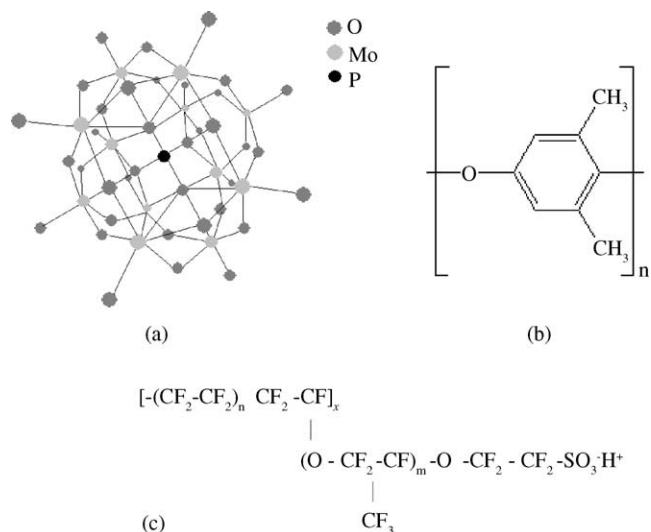

Fig. 1. Chemical structure of (a) $H_3PMo_{12}O_{40}$ (PMA), (b) poly-2,6-dimethyl-1,4-phenylene oxide, (c) Nafion.

were dried at room temperature overnight. Then it was soaked in water/ethanol mixture (volumetric ratio 1:1) for 10 min to separate the films from the glass plate. The film thickness was 3–4 μm. The Composite membranes were prepared by casting the Nafion on porous PPO-PMA films. PPO-PMA films were extended over a flat glass plate, and then the Nafion mixture was poured on it. The glass plate was dried in an oven at $80\,^\circ$C for 8 h, and finally dried in a vacuum oven for a day. After the evaporation of solvent, Nafion resin can completely wrapped the PPO-PMA films. The membranes are peeled off the bottom by the addition of some water. These membranes were converted to the proton form by treating for 1 h at $80\,^\circ$C in 0.5 M H_2SO_4 (98%, Aldrich). The membranes were then soaked in deionised water for 1 h at $80\,^\circ$C in order to remove the excess of acid. The thickness of the composite membranes is easily controlled by the amount of the Nafion solution. Fig. 2 shows the preparation procedure of composite Nafion/PPO-PMA membranes.
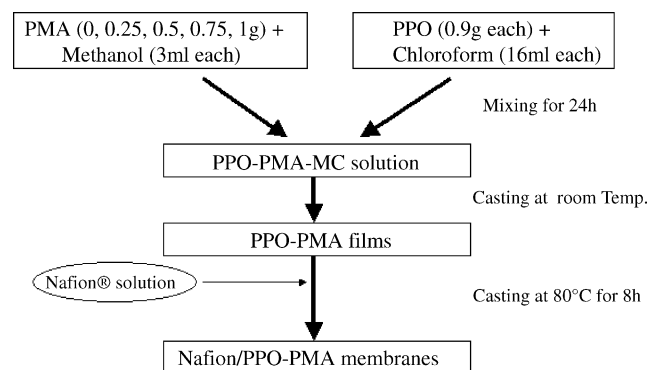

Fig. 2. Preparation procedures of Nafion/PPO-PMA composite membranes.

2.3. Membrane characterization

The phase morphological characteristic of PPO-PMA films were observed by means of field emission scanning electron microscope (FE-SEM, JSM-6700F). Representative samples of the film were cut into 0.5 cm lengths, attached with carbon tape to aluminium plate. The surface was coated with platinum to avoid charge. Cross-section image mapping of the PPO-PMA films were measured with energy dispersive spectrometer (INCA Energy, Oxford Instruments). And then wave dispersive spectrometer (JXA-8900R) was also used to monitor the structure and composition of PPO-PMA porous films.

Ion conductivity measurements of each sample were carried out using AC electrochemical impedance spectroscopy (EG&G model 273A potentiostat/galvanostat) at room temperature. The amplitude of the AC voltage was 10 mV. In our experiment, the four-probe method was used to determine the area resistance of each membrane [18]. The methanol permeability of each membrane was measured using an in-house diffusion cell at room temperature. The concentration of methanol in the permeate stream increased with time and it was measured by a reflective index detector (NAR-3T, ATAGO) to calculate methanol permeability across composite membranes [19].

2.4. Fuel cell experiments

The performance was evaluated with composite membranes as electrolytes in fuel cell conditions (methanol concentration = 2 M; cell temperature = 80 °C; 2 kgf cm^{-2} pressure between cathode and anode). Air was supplied at 300 ml min^{-1}. The flow rate of air was controlled by mass-flow controller. The membrane electrode assembly (MEA) was fabricated by hot pressing the composite membranes with the Pt black as cathode and a Pt–Ru electrode as anode by compaction with a pressure of 13.8 MPa at 125 °C for 2 min. The electrode surface area was 1 cm^2. The electrode (catalyst loading of 4.0 mg cm^{-2}) was supplied by E-TEK.

3. Results and discussion

3.1. SEM measurement

The morphological changes in the surface of the PPO-PMA thin films were presented in the set of FE-SEM micrographs. Fig. 3 shows SEM images of PPO-C (without methanol and PMA), PPO-MC (without PMA) and PPO-PMA-MC films. When thin films were cast without PMA-M solutions, the morphology of PPO-C, Fig. 3(a), is significantly different from those of other thin films. PPO-C thin film shows non-porous structure. In case of PPO-MC (without PMA), Fig. 3(b) shows porous structure in the film surface. The morphology of the surface of PPO-MC is caused by the difference of solvent evaporation. To enhance ion conductivity and PMA immobilization, we added various composition of PMA-M solution in PPO-C solutions. Fig. 3(c–f) shows effect of various amounts (0.25, 0.5, 0.75 and 1 g) of PMA on PMA-PPO-MC films, respectively. As these figures show, micropores developed on the surface during evaporation and the average pore size was less than 2 μm. It is also expected that the effect of mixed solvents on the PPO-PMA films can be optimized to meet the need for desirable property. Fig. 3(d) shows that PMA is uniformly and finely dispersed
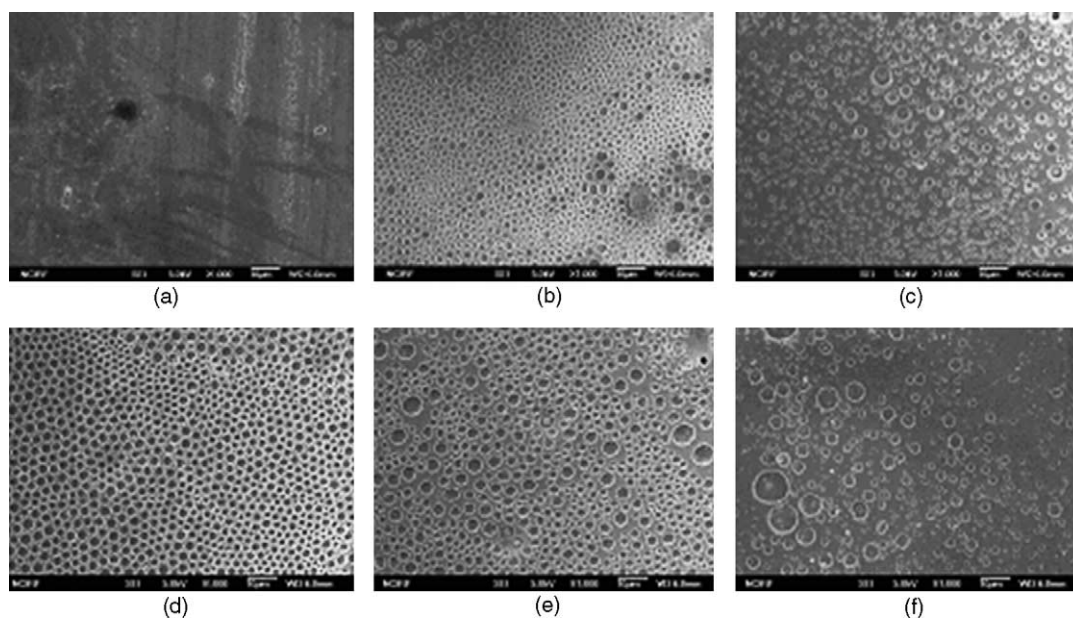

Fig. 3. Scanning electron micrographs of (a) PPO-C (without methanol and PMA), (b) PPO-MC (without PMA) and (c) 0.25 g, (d) 0.5 g, (e) 0.75 g, (f) 1 g amounts of PMA on PPO-PMA-MC films.
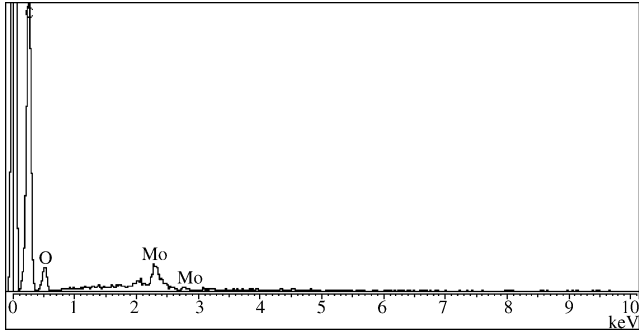
Fig. 4. EDS spectra of PPO-PMA thin films.

Fig. 5. Cross-sectional EDS image of PPO-PMA thin films by mapping on molybdenum (Mo).

in the thin film. No visible evidence representing PMA was found in SEM images of PPO-PMA-MC.

3.2. EDS/WDS analysis

Fig. 4 shows the EDS spectrum of the molybdenum (Mo) on the surface of PPO-PMA thin films. The Mo peaks were detected at 2.3 and 2.8 keV. It is obvious that some Mo exits on the thin film. WDS and EDS mapping are usually considered more accurate for locating heavy element. The particles could be easily detected as bright spots in the EDS image. The composition of the metal-containing polymer films after evaporation was determined by analysing cross-sections. Fig. 5 shows that Mo particles are uniformly distributed in cross-sectional area of PPO-PMA films. The uniform distribution of Mo in the cross-sectional thin films was conformed by EDS analysis. Surfaces of PPO-PMA thin films (0.5 g and 1 g PMA loadings) were inspected by WDS to monitor the distribution of Mo particles. Fig. 6 shows distribution images of 0.5 g and 1 g PMA loadings on the surface of PPO-PMA thin films. An inspection of the distribution maps suggest that the Mo enriched among the pores (Fig. 6(a)).
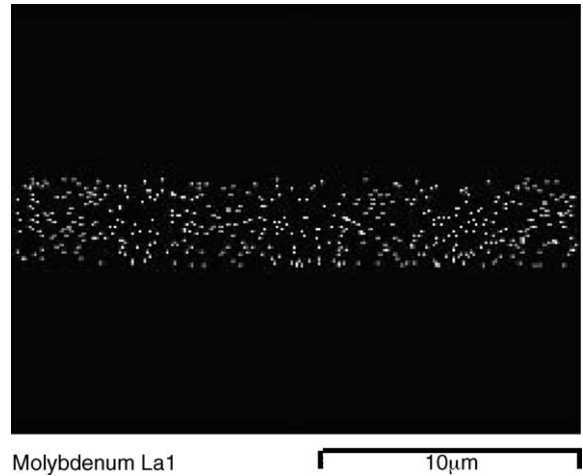
Table 1
Comparison of ion conductivity and methanol permeability of composite membranes at room temperature

Amount of PMA (g)	Methanol permeability ($cm^2\,s^{-1}$)	Ion conductivity ($S\,cm^{-1}$)
Nafion 115	3.29×10^{-6}	0.0385
0	2.10×10^{-6}	0.0280
0.25	1.89×10^{-6}	0.0176
0.5	2.01×10^{-6}	0.0341
0.75	1.61×10^{-6}	0.0242
1	4.41×10^{-7}	0.0274

3.3. Ion conductivity and methanol permeability

To prevent the PMA leakage and to increase the proton conductivity, PMA was immobilized in thin films. The change of ion conductivity as a function of PMA amount on composite membranes was shown in Table 1. The thickness of the composite membranes is $100 \pm 5\,\mu m$. The value of Nafion 115 itself was measured in this experiment for a reference value and showed $0.0385\,S\,cm^{-1}$. As shown in Table 1,
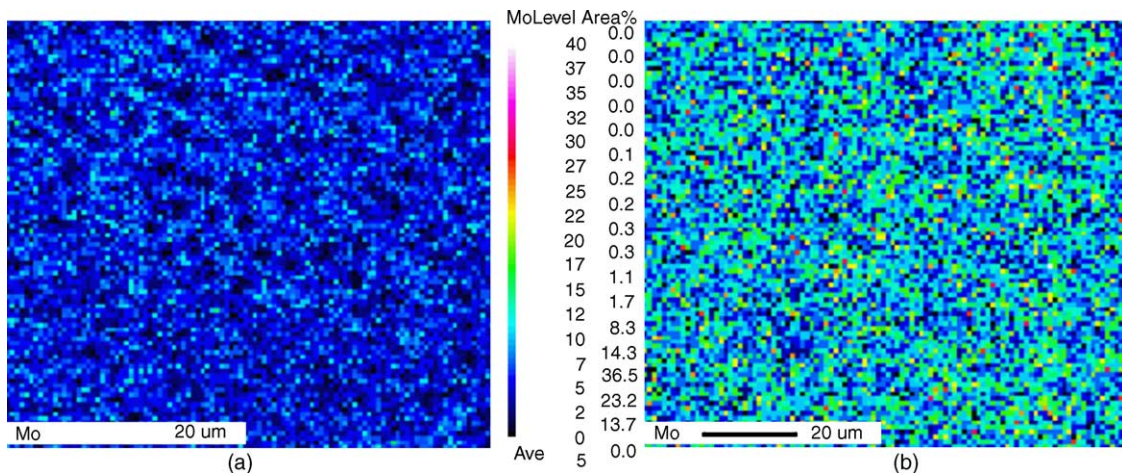

Fig. 6. WDS maps of the molybdenum (Mo) distribution in (a) 0.5 g and (b) 1 g amounts of PMA on PPO-PMA thin films.

when PPO-PMA porous barrier film was used for composite membranes, their ion conductivities decreased compared that of Nafion 115. For 0.5 g amount of PMA, the highest ion conductivity ($0.0341\,\mathrm{S\,cm^{-1}}$) was observed in this experiment. Various amounts of PMA led change in pore distribution. Bad distribution is not favourable to increasing the ion conductivity because of increasing membrane resistance. Otherwise, increasing amount of PMA should enhance the ion conductivity. These two competing factors result in an optimum in the curves. On the other hand, in Table 1, the methanol permeability is also shown as a function of PMA amount. The samples used for methanol permeability measurement were composite membranes including PPO-PMA films. The methanol permeability was determined from equation developed by Tricoli [20]. The permeability of methanol in the Nafion 115 membrane was higher, with a value of $3.29 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ than those of composite membranes. The permeability of the composite membranes showed similar values ranged from 2.10×10^{-6} to $1.61 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ excepted 1 g PMA loaded composite membrane. For the 0.5 g amount of PMA, permeability decreased as much as 39% from 3.29×10^{-6} to $2.01 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$. We can also be observed that 1 g amount of PMA has the lowest permeability ($4.41 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$) due to bad pore distribution as shown in Fig. 3(f) and Fig. 6(b).

3.4. Cell performance test

Fig. 7 shows that the composite membrane system by inserting PPO-PMA films provided higher open circuit voltage (O.C.V) than that of Nafion 115 in DMFC system. When 0.5 g of PMA was loaded, the composite membrane showed the highest O.C.V value due to change pore distribution and methanol permeability. The effect of various amounts of PMA in composite membranes on the performance of the single cell DMFC at 0.35 V is presented in Fig. 8. The five composite membranes differ only on amount of PMA. As seen from this figure, 0.5 g PMA loaded composite membrane has the best cell performance at 0.35 V because this membrane
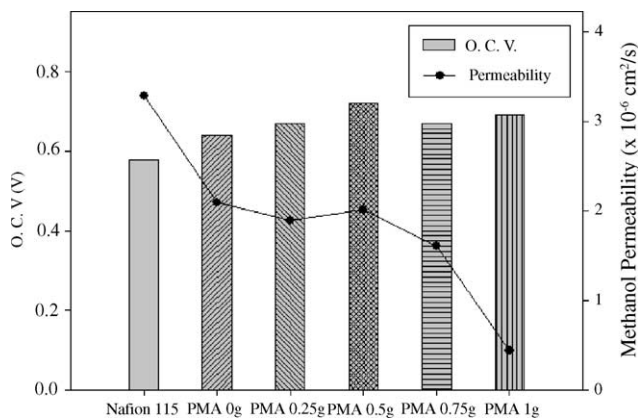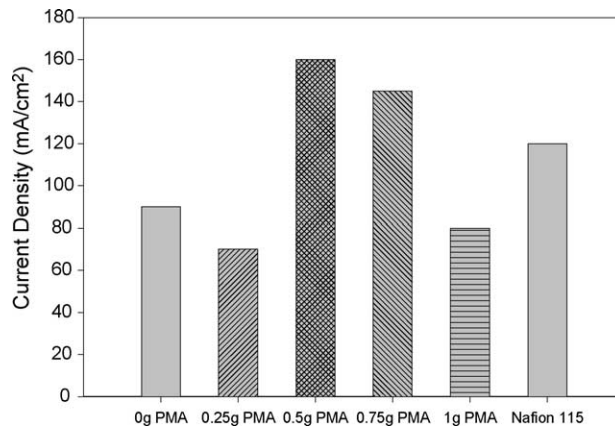

Fig. 8. Effect of various amounts of PMA in composite membranes on performance of single-cell DMFC at 0.35 V.

probably has the highest ion conductivity among the composite membranes while showing lower methanol permeability than that of Nafion 115. Based on these results, the enhanced cell performance of DMFCs can be obtained by maintaining the ion conductivity and reducing methanol permeability of composite membranes using PPO-PMA porous barrier films. It implies that Nafion/PPO-PMA composite membrane is an alternative to increase the cell performance.

4. Conclusion

Composite membranes were prepared by casting Nafion mixture on PPO-PMA porous barrier films. We carried out the characterization and the cell performance test of these membranes. The morphology of PPO-PMA films can be controlled by amount of PMA in the PPO-PMA-MC solutions. Scanning electron micrographs allow assessing the effect of PMA amounts on morphology. EDS and WDS mapping of thin films confirm that PMA indeed imbedded onto barrier films. The Nafion/PPO-PMA composite membranes showed lower methanol permeability than that of Nafion 115. The best ion conductivity of composite membranes has shown the similar value to Nafion 115. The enhanced cell performance of DMFCs can be obtained by composite membranes using PPO-PMA porous barrier films.

Fig. 7. O.C.V and methanol permeability as a function of various amounts PMA on composite membranes.

References

[1] B. Smitha, S. Sridhar, A.A. Khan, J. Membr. Sci. 225 (2003) 63–76.
[2] A.J. Appleby, F.R. Foulkes, Fuel Cell Handbook, Van Nostrand Reinhold, New York, 1989.
[3] J. Yu, B. Yi, D. Xing, F. Liu, Z. Shao, Y. Fu, J. Power Sources 4937 (2002) 1–6.
[4] L. Jörissen, V. Gogel, J. Kerres, J. Garche, J. Power Sources 105 (2002) 267–273.
[5] K.V. Kordesh, J. Electrochem. Soc. 25 (1978) 77.
[6] W. Vielstich, A. Lamm, H.A. Gasteiger, Handbook of Fuel Cells, Wiley, England, 2003.

[7] K. Scott, W. Taama, J. Appl. Electrochem. 28 (1998) 289.

[8] Z. Shao, X. Wang, I.-M. Hsing, J. Membr. Sci. 210 (2002) 147.

[9] J. Cruickshank, K. Scott, J. Power Sources 70 (1998) 40.

[10] P. Dimitrova, K.A. Friedrich, U. Stimming, B. Vogt, Solid State Ionics 150 (2002) 115–122.

[11] P. Dimitrova, K.A. Friedrich, B. Vogt, U. Stimming, J. Electroanal. Chem. 532 (2002) 75–83.

[12] L.J. Hobson, Y. Nakano, H. Ozu, S. Hayase, J. Power Sources 104 (2002) 79–84.

[13] T. Hatanaka, N. Hasegawa, A. Kamiya, M. Kawasumi, Y. Morimoto, K. Kawahara, Fuel 81 (2002) 2173–2176.

[14] J.K. Lee, I.K. Song, W.Y. Lee, J. Mol. Catal. 120 (1997) 207–216.

[15] I.V. Kozhevnikov, K.I. Matveev, Appl. Catal. 5 (1983) 135.

[16] I.K. Song, J.K. Lee, W.Y. Lee, Appl. Catal. 119 (1994) 107.

[17] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.

[18] B.D. Cahan, J.S. Wainright, J. Electrochem. Soc. 140 (1993) 185.

[19] J. Sauk, J. Byun, H. Kim, J. Power Sources 132 (2004) 59–63.

[20] V. Tricoli, J. Electrochem. Soc. 145 (1998) 3799.