

Short communication

Porosity-graded micro-porous layers for polymer electrolyte membrane fuel cells

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Received 3 December 2006; received in revised form 26 December 2006; accepted 2 January 2007
Available online 17 January 2007

Abstract

In this paper, the effect of porosity-graded micro-porous layer (GMPL) on the performance of polymer electrolyte membrane fuel cells (PEMFCs) was studied in detail. The GMPL was prepared by printing micro-porous layers (MPL) with different content of NH_4Cl pore-former and the porosity of the GMPL decreased from the inner layer of the MPLs at the membrane/MPL interface to the outer layer of the MPLs at the gas diffusion electrode/MPL interface. The morphology and porosity of the GMPLs were characterized and the performance of the cell with GMPLs was compared with those having conventional homogeneous MPLs. The result demonstrates that the fuel cells consisting of GMPL have better performance than those consisting of conventional homogeneous MPLs, especially at high current densities. Micro-porous layer with graded porosity is beneficial for the electrode process of fuel cell reaction probably by facilitating the liquid water transportation through large pores and gas diffusion via small pores in the GMPLs.

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Keywords: Polymer electrolyte fuel cells; Micro-porous layer; Graded porosity; Gas diffusion layer

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been attracting enormous research interest as promising power sources for vehicles, stationary power generations and portable electronics devices [1–4]. The performance of a PEMFC is critically dependent on the electrocatalytic activity of the precious metal catalyst such as platinum and platinum alloy and performance of various components including the gas diffusion electrode (GDE) [5–7]. The gas diffusion electrode (GDE) is one of the key components of PEMFCs where the reactions of the diffusion of reactant gas and the discharge of the liquid water formed occur. As a result, the microstructure of the GDE has significant influence on the performance of the PEMFCs [6,8–10].

The performance of a GDE can be improved by attaching a micro-porous layer (MPL) consisting of carbon black and hydrophobic polytetrafluoroethylene (PTFE) [11–15]. Qi et al.

experimentally demonstrated the advantage of placing a MPL between the gas diffusing layer (GDL) and the catalyst layer [16]. Chang et al. [17] studied the effects of the pore size on gas transport and cell performance, and suggested that porosity distribution of GDL should be bimodal, facilitating the water discharge through large pores and gas diffusion through small pores. Wilkinson et al. [18] simulated the structure of the GDE, and concluded that both the operation parameter and the MEA structure should be graded. Based on the calculation of the capillary pressure, Nam et al. [19] indicated that a pore and water saturation “jump” in GDL would improve the water and gas transport. Chu et al. [20] investigated the effect of average porosity on the oxygen transport and suggested that a porosity-graded GDL should be beneficial to the fuel cell performance. The results of Roshandel et al. also revealed the important effects of porosity distribution on PEM fuel cell performance [21]. Recently, based on a two-phase flow in fuel cell electrode, Hotinen et al. [22] suggested a GDE with a graded porosity is more favorable for the liquid water removal from the catalyst layer. This conclusion was also supported by the computer simulation results [23].

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However, as shown above there is lack of experimental studies on the effect of the porosity-graded MPL on the electrocatalytic activities of catalyst layer and performance of PEMFCs. In this paper, MPL with graded porosity (GMPL) was prepared and the effect of graded porosity in the MPL on the cell performance was studied in detail. The results indicate that GMPL enhances the performance of PEM fuel cells.

2. Experimental

2.1. Preparation of GMPL

The wet-proofed carbon paper was prepared by immersing a carbon paper (Toray TGPH-060) in a polytetrafluoroethylene (PTFE) dispersion (ZhongHao, 60 wt%, China) for 5 min, followed by drying in air for 15 min and heat-treating in oven at 350 °C for 30 min. The PTFE loading was about 30 wt%.

To prepare the GMPL, carbon powder (Vulcan XC-72, Cabot Co.) was mixed with an appropriate amount of distilled water and PTFE dispersion in a supersonic mixer for 60 min. NH_4Cl was added as pore-former to the suspension and stirred for another 60 min to form MPL slurry.

The GMPL was prepared by three steps. First, a wet-proofed carbon paper was screen printed with a MPL slurry with 50 wt% NH_4Cl pore-former, labeled as L-1. This was followed by a second coating with a MPL slurry with 30 wt% NH_4Cl pore-former (referred to L-2) and a third coating with a MPL slurry with 10 wt% NH_4Cl pore-former (referred to L-3). As-prepared GMPL was sintered in oven at 350 °C for 30 min. The carbon loading of each layer in the GMPL was about 0.8 mg cm^{-2} and total carbon loading was about 2.4 mg cm^{-2} . The PTFE content was about 30 wt%.

For the purpose of comparison, conventional homogeneous MPL samples were also fabricated by the screen-printing of a MPL slurry with NH_4Cl pore former content of 10 and 50 wt% on the wet-proof carbon paper.

Catalyst coated membrane (CCM) with Nafion 112 membrane and Pt loading of 0.4 mg cm^{-2} for both anode and cathode side was used to investigate the single cell performance of the GDE samples. The CCM was fabricated as follows. First, 1 g Pt/C catalysts (40 wt% Pt/C, Johnson Mathey) were mixed with 10 mL deionized water under vigorous stirring. Then 24 mL

Nafion DE 520 solutions (5 wt%, EW 1000, Du pont) was added to the mixture, followed by ultrasonic treatment for 30 min and high-speed homogenizer (20,000 rpm) for 1 h to form catalyst slurry. The catalyst slurry was sprayed to a PTFE sheet with Pt loading of 0.4 mg cm^{-2} . Then the catalyst layer was transferred to Nafion 112 membrane to form CCM. Fig. 1 shows schematically the preparation procedures of the membrane-electrode-assembly based on the GMPL.

2.2. Characterization

The surface and the cross-section of GMPL were observed using scanning electron microscopy (SEM, JSM-5600). The sample for the cross section analysis was prepared by freezing the sample in liquid nitrogen and cutting it with a blade.

The porosity distribution of GMPL and MPL was measured by a mercury-intrusion porosimetry (PM-33, Quantachrome Instruments). During the test, the sample was immersed in hydrargyrum, filling both hydrophilic and hydrophobic pores in the GDL and MPL.

The performance of the single cell was measured with H_2 as fuel gas and air as oxidant at 60 °C without back pressure in a fuel cell test station (ElectroChem. Co.). The external humidification temperature of both H_2 and air was kept constant at 60 °C. H_2 and air flow rates were 300 and 2000 sccm, respectively. Prior to record the performance curve, cells were activated by polarization at a constant current till stable performance was obtained.

3. Results and discussion

3.1. Microstructure of MPL

The surface micrographs of micro-porous layers, L-1, L-2, and L-3 are shown in Fig. 2. Fig. 3 shows the cross-section of a GMPL sample with three micro-porous layers of L-1, L-2, and L-3. The surface of MPL becomes coarse and more porous from L-3 to L-1. It appears that both pore size and porosity decrease from L-1, L-2 to L-3. As shown in Fig. 3, the contact between various micro-porous layers is good. From L-1 to L-3, MPL become denser, and size of pores also decreases. This indicates that a graded porous structure is formed in the MPL.

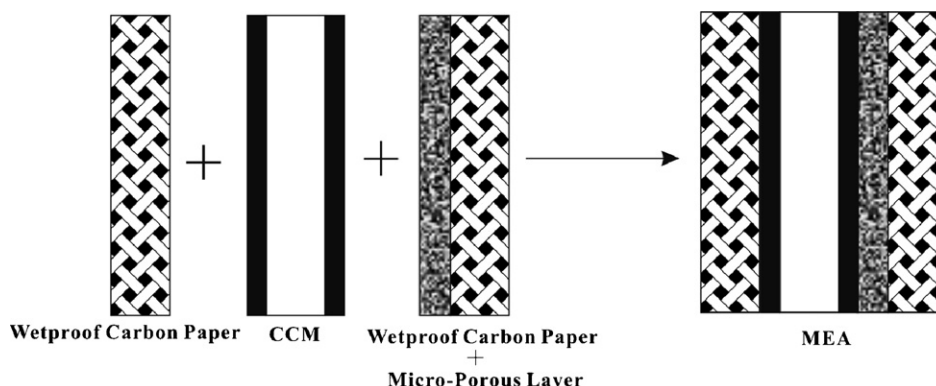


Fig. 1. Preparation procedure of membrane-electrode-assembly using porosity-graded micro-porous layer.

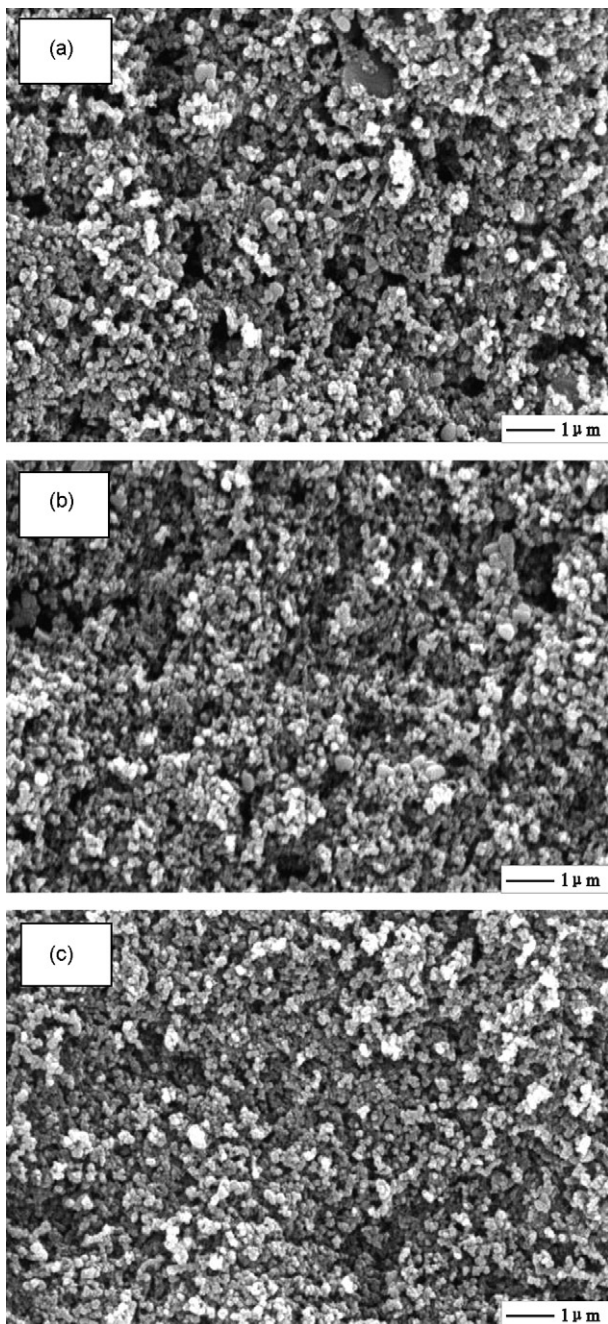


Fig. 2. Surface micrographs of different micro-porous layers in the GMPL: (a) L-1 with 50 wt% NH₄Cl pore-former; (b) L-2 with 30 wt% NH₄Cl pore-former; (c) L-3, 10 wt% NH₄Cl pore-former.

Fig. 4 shows pore-size distribution of GMPL measured by Hg-intrusion porosimetry. Fig. 5 is the corresponding cumulative pore size distribution. For the purpose of comparison, data of conventional MPLs with pore former content of 10 and 50 wt% are also displayed. The result shown that the pore size distribution of GMPL is between 0.01 and 10 μm (also see in Table 1). There are also two main types of pores in the GMPL. Type-I is between 0.01 and 0.08 μm, and type-II is between 0.08 and 10 μm. The pore volume of type-II pores is higher than that of type-I. It is notable that the type-II pore had a relatively large pore

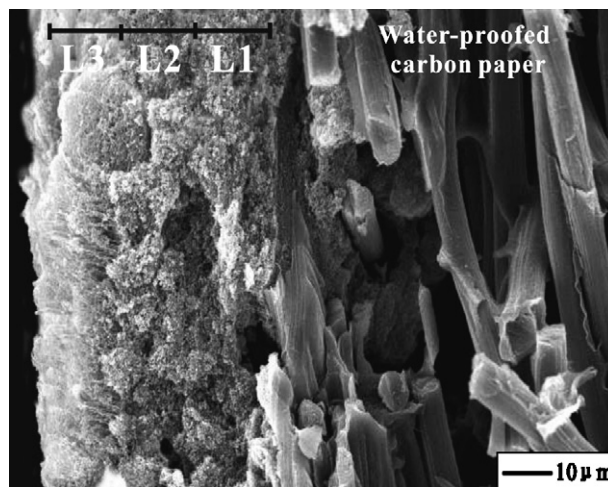


Fig. 3. Cross-section micrographs of a GMPL on a wet-proofed carbon paper.

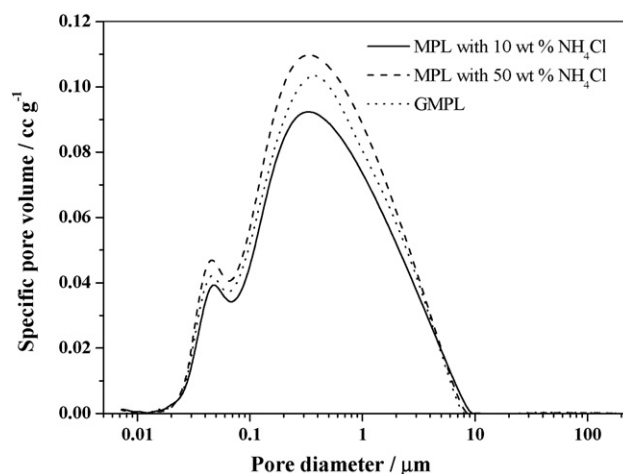


Fig. 4. Specific pore-size distribution of different MPL of conventional homogeneous MPL with 10 wt% NH₄Cl (solid line), conventional homogeneous MPL with 50% NH₄Cl (dashed line) and GMPL (dotted line).

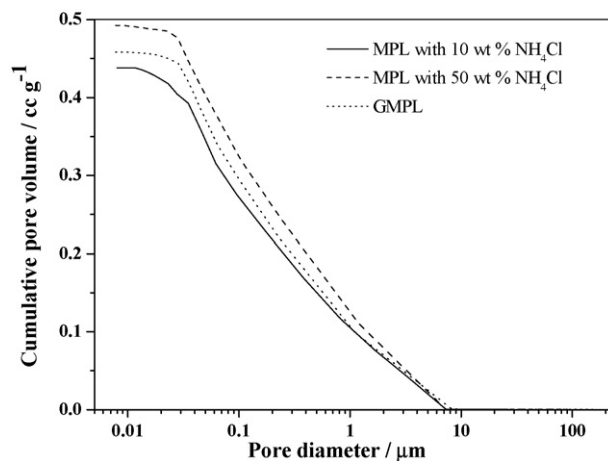


Fig. 5. Cumulative pore-size distribution of different MPL of conventional homogeneous MPL with 10 wt% NH₄Cl (solid line), conventional homogeneous MPL with 50% NH₄Cl (dashed line) and GMPL (dotted line).

Table 1
Porosity of micro-porous layer with different pore shape

MPL	Total porosity (%)	Pore size (μm)			
		Local porosity (%)			
		<0.01	0.01–0.08	0.08–10	>10
MPL with 10 wt% NH_4Cl	49.7	0.05	16.39	31.68	0.08
MPL with 50 wt% NH_4Cl	52.0	0.66	18.15	33.69	0.22
GMPL	51.5	0.56	17.75	32.72	0.06

size distribution. It may be attributed to the introduced NH_4Cl pore former in the sub-layer. The NH_4Cl would be recrystallized when the carbon/PTFE/ NH_4Cl suspension are dried on the GDL, resulting in formation of NH_4Cl particles in the sub-layer. The NH_4Cl would decompose, forming relatively large pores. At the same time, the as-produced NH_3/HCl gas would escape from the GDL and the escape of the gas would influence the pore size distribution.

The pore volume of types-I and -II pores and the cumulative pore volume (Fig. 5) for GMPL are between that of conventional homogeneous MPL with 10 wt% NH_4Cl and 50 wt% NH_4Cl . As shown in [10,11], the small pores (type-I) are in charge of transferring gas, the large pores (type-II) are in charge of expelling water during the cell operation. Therefore the bimodal distribution of porosity of the GMPL is beneficial for the transportation of both reactant gas and water in the GDL.

3.2. Performance of the single cell

Fig. 6 shows the $V-I$ performance of the single cells with GMPL and conventional homogeneous MPLs. The performance of single cells with GMPL is higher than that with MPL (10% or 50% NH_4Cl content), especially at the high current densities ($>700 \text{ mA cm}^{-2}$). Considering that the GMPL did not have the highest porosity both in small and large pore region, the high

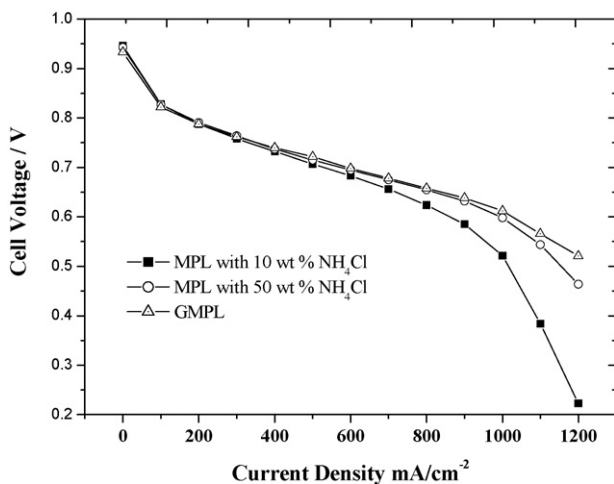


Fig. 6. The $V-I$ curve of single PEM fuel cells with different MPL of conventional homogeneous MPL with 10 wt% NH_4Cl (■), conventional homogeneous MPL with 50% NH_4Cl (○), and GMPL (△). Anode and cathode Pt loading: 0.4 mg cm^{-2} ; cell temperature: 60°C ; back pressure: 0 psi.

performance of the cell with the GMPL is most likely due to the right pore distribution. In the porosity-graded MPLs, the porosity and pore size decreased from the inner layer of the MPLs (in contact with catalyst layer) to the outer layer of the MPLs (in contact with the carbon paper), thus the inner layer of the MPLs has better water expelling ability than the outer layer. Hence the water can be removed efficiently, leading to the high cell performance particularly at high currents.

3.3. Discussions of the results

Due to the existence of PTFE, water in the pores of MPL is non-wetting phase, and the gas is wetting phase. The pressure difference between the wetting and non-wetting phase is given by the capillary pressure p_c as:

$$p_c = p_{nw} - p_w = p_{\text{H}_2\text{O}} - p_g = \frac{2\sigma}{r} \quad (1)$$

where p_c is the capillary force, σ the surface tension, and r is the curvature radius of liquid/gas interface.

Fig. 7 shows the state of water in different water saturation s which is the volume ratio of water in pore to the pore volume. It can be concluded that when:

$$S_1 < S_2, \quad \text{Then: } r_1 > r_2$$

According to Eq. (1):

$$p_{c1} < p_{c2}$$

It can also be concluded that the capillary force increases as the water saturation increases. Water flow in hydrophobic porous

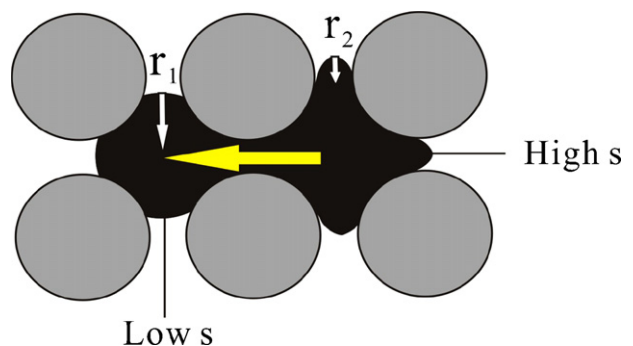


Fig. 7. Model of different saturated water in the MPL pores.

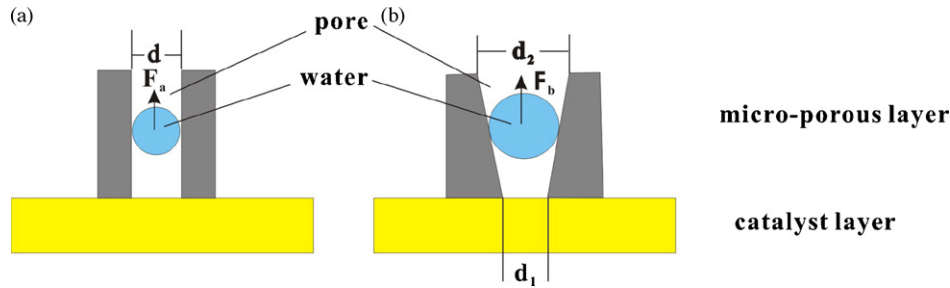


Fig. 8. Two different pore structures of micro-porous layer. (a) Straight pore shape; (b) graded pore structure.

media can be expressed as [24]:

$$\dot{m}_{1,\text{H}_2\text{O}} = -\frac{\rho K K_{rl}}{\mu_1} \nabla p_{1,\text{H}_2\text{O}} = -\frac{\rho K K_{rl}}{\mu_1} \left(\frac{dp_c}{ds} \right) \nabla s \quad (2)$$

where $\dot{m}_{1,\text{H}_2\text{O}}$ is the water flow, ρ the water density, K the absolute permeability, K_{rl} the relative permeability, μ_1 the water viscosity, p_c the capillary force, and s is the water saturation volume. Because p_c increase with s , thus $(dp_c/ds) > 0$. The water saturation s decreases ($\nabla s < 0$) through gas diffusion layer from catalyst layer to bipolar plate. According to Eq. (2), $\dot{m}_{1,\text{H}_2\text{O}} > 0$. Water flow direction is from the catalyst layer to the gas diffusion layer, driven by the differential capillary force. The sketch of water flow is illustrated in Fig. 7.

The water states in the GMPL and MPL with straight pore (SMPL) are shown in Fig. 8. The pore diameter of SMPL is d ; the pore diameter of GMPL is from d_1 and d_2 , respectively ($d_1 < d_2$). F is the driving force of water expelling. According to capillarity equation:

$$2r \cos \theta = d$$

Then,

$$p_c = \frac{4\sigma \cos \theta}{d} \quad (3)$$

where p_c is the capillary force, σ the surface tension, r the curvature radius of liquid/gas interface, θ the contact angle, and d is the diameter of capillary.

As shown in Fig. 8(a), it can be drawn from above analysis that the driving force for water transportation or flow is $F_a = \nabla p_c$

Based on the Fig. 8(b), the force of water droplet is analyzed. Due to the difference of pore size ($d_1 < d_2$), according to Eq. (3), there is a difference of capillary force ($p_{c1} > p_{c2}$) because of the difference of pore shape. The driving force for water flow in the GMPL is $F_b = \nabla p_c + (p_{c1} - p_{c2})$.

Comparing with MPL with SP, GMPL has an additional driving force due to the graded porous structure ($F_b > F_a$), the gradient direction in porosity is from catalyst layer to carbon paper. Such graded porosity is advantageous in expelling water more effectively. Thus the performance of single cell using GMPL is improved, especially at high current density ($>700 \text{ mA cm}^{-2}$), as compared to that of the fuel cells with conventional homogeneous MPL, as shown in the present study.

4. Conclusions

Micro-porous layer (MPL) with graded porosity (GMPL) was prepared experimentally and used as gas diffuse sub layer between the catalyst layer and gas diffusion layer. The morphology and porosity of the GMPLs were characterized and the performance of the cell with GMPLs was compared with those having conventional homogeneous MPLs. The result demonstrates that the fuel cells consisting of GMPL have better performance than those consisting of conventional homogeneous MPLs, especially at high current densities. Micro-porous layer with graded porosity is beneficial for the electrode process of fuel cell reaction probably by facilitating the liquid water transportation through large pores and gas diffusion via small pores in the GMPLs. The reason could be due to increased capillary force of the graded porosity in MPL; hence increasing the water expelled capacity of the electrode.

References

- [1] M. Williams, J. Strakey, W. Surdoval, J. Power Sources 143 (2005) 191–196.
- [2] M. Perry, T. Fuller, J. Electrochem. Soc. 149 (2002) S59–S67.
- [3] M. Pan, H.L. Tang, S. Mu, R. Yuan, J. Mater. Res. 19 (2004) 2279–2284.
- [4] M. Pan, H.L. Tang, S.P. Jiang, Z. Liu, J. Electrochem. Soc. 152 (2005) A1081–A1088.
- [5] Z. Liu, S.P. Jiang, J. Power Sources 159 (2006) 55–58.
- [6] Z.Q. Tian, X.L. Wang, H.M. Zhang, B.L. Yi, S.P. Jiang, Electrochem. Commun. 8 (2006) 1158–1162.
- [7] Z.Q. Tian, S.P. Jiang, Y.M. Liang, P.K. Shen, J. Phys. Chem. B 110 (2006) 5343–5350.
- [8] U. Pasaogullari, C. Wang, Electrochim. Acta 49 (2004) 4359–4369.
- [9] W. Sun, B. Peppley, K. Karan, J. Power Sources 144 (2005) 42–53.
- [10] C. Lim, C. Wang, Electrochim. Acta 49 (2004) 4149–4156.
- [11] X. Wang, H. Zhang, J. Zhang, H. Xu, Z. Tian, J. Chen, H. Zhong, Y. Liang, B. Yi, Electrochim. Acta 51 (2006) 4909–4915.
- [12] J. Moreira, A.L. Ocampo, P.J. Sebastian, A. Mascha, M.D. Smit, P. Salazar, J.A. del Angel, R. Montoya, L. Pérez, Martínez, Int. J. Hydrogen Energy 28 (6) (2003) 625–627.
- [13] E. Antolini, R.R. Passos, E.A. Ticianelli, J. Power Sources 109 (2002) 477–482.
- [14] L. Giorgi, E. Antolini, A. Pozio, E. Passalacqua, Electrochim. Acta 24 (1998) 3675–3680.
- [15] L.R. Jordan, A.K. Shukla, T. Behrsing, N.R. Avery, B.C. Muddle, M. Forsyth, J. Power Sources 86 (2000) 250–254.
- [16] Z. Qi, A. Kaufman, J. Power Sources 109 (2002) 38–46.
- [17] C. Kong, D. Kim, H. Lee, Y. Shul, T. Lee, J. Power Sources 108 (2002) 185–191.
- [18] D. Wilkinson, J. St-Pierre, J. Power Sources 113 (2003) 101–108.

- [19] J. Nam, M. Kaviany, *Int. J. Heat Mass Transfer* 46 (2003) 4595–4611.
- [20] H. Chu, C. Yeh, F. Chen, *J. Power Sources* 123 (2003) 1–9.
- [21] R. Roshandel, B. Farhanieha, E. Saievar-Iranizad, *Renewable Energy* 30 (2005) 1557–1572.
- [22] T. Hottinen, O. Himanen, S. Karvonen, I. Nitta, doi:[10.1016/j.jpowsour.2006.10.076](https://doi.org/10.1016/j.jpowsour.2006.10.076).
- [23] Z.G. Zhan, J.S. Xiao, D.Y. Li, M. Pan, R. Yuan, *J. Power Sources* 160 (2006) 1041–1048.
- [24] M. Kaviany, *Principles of Heat Transfer in Porous Media*, 2nd ed., Springer, New York, 1999.