

Short communication

## Membrane electrode assembly for passive direct methanol fuel cells

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### Abstract

A novel structure of membrane electrode assembly (MEA) for a passive direct methanol fuel cell (DMFC) was proposed to achieve high performances. Composite membrane with low methanol cross-over and diffusion layers with hydrophilic nano-particles developed in this study were used for a novel MEA structure. The membrane and the diffusion layers were investigated for water back diffusion effects and performances in a passive DMFC. The proposed electrodes were proven to be two times more effective in water back diffusion than conventional electrodes, and their MEAs showed higher performances than conventional MEA. The novel MEA with composite membrane showed power density of  $48 \text{ mW cm}^{-2}$  at 0.3 V, which is 1.5 times higher than a conventional MEA with Nafion<sup>®</sup> membrane.

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**Keywords:** DMFC; Composite membrane; Diffusion layer; Water recycle; Passive DMFC

### 1. Introduction

The direct methanol fuel cell (DMFC) is an attractive candidate for mobile energy sources because of its advantageous properties such as easy fuel storage, low operating temperature, and simple design applicability. For applications in small electronic devices, high energy density is especially critical as a portable DMFC system. High energy density can be achieved by using highly concentrated fuel while the size of fuel reservoir (tank or cartridge) in a DMFC system is reduced. It should, however, be noted that a high concentration of fuel (methanol) could cause an increase in the amount of methanol cross-over, which often poisons the cathode catalyst [1].

In order to ensure an effective fuel cell operation, water management should be considered in the design of the membrane electrode assembly (MEA) structure because it could figure out several issues simultaneously. First, while several approaches, such as methanol-tolerant catalysts and cross-over minimized membrane, have been proposed [2–18], water management approach has been demonstrated to effectively resolve

the issues in the methanol concentration, the power density, and the fuel efficiency in a DMFC system [19–21]. This water management basically utilizes water at the cathode side to dilute the anode fuel and thus achieve high energy density and long-term stability. Also, by recycling water from cathode to anode, one can prevent possible water flooding at the cathode side of the fuel cell, which often causes blocking of air flow to cathode catalyst layers. Such water flooding can decrease power and stability of DMFC system. To reduce the water flooding and increase the performance, the diffusion layers, which are also called micro-porous layers, in DMFCs have been improved by controlling the hydrophilicity of substrate and other components, and they have been optimized according to the operation conditions of DMFCs such as temperature, amount and concentration of fuels [22–25]. However, those approaches should be more innovative in passive DMFC systems because there is no active component that can prevent water flooding.

Efficient water recycling can be achieved through either an internal or external path. However, the internal method through the membrane has been generally preferred over the external method in a passive DMFC system because of its design simplicity and has been adopted in many of recent works [20,26,27]. Blum et al. [27] proposed a water neutral micro-DMFC consists of porous membrane made of PVDF and SiO<sub>2</sub>, and liquid–water leak-proof system that has several sub layers placed on both sides of the cathode current collector. They reported a long oper-

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ation time of 900 h and a high fuel efficiency of 92%, but the power density was lower than  $15 \text{ mW cm}^{-2}$  with 1M methanol as anode fuel. Nanoporous electrolyte used in their study, which has 50% porosity, is permeable with methanol and water, therefore methanol cross-over issue still exists when highly concentrated methanol is used as fuel for high energy density. The concept of water back diffusion was proven by Ren et al. [20] who made a hydrophobic microporous layer with carbon particles and/or PTFE. Their system operated at  $30 \text{ mW cm}^{-2}$  for 30 h with fuel efficiency of over 50%. They still used Nafion<sup>®</sup> membrane as electrolyte, in which the degradation of cell due to methanol cross-over can hardly be eliminated.

Here, we propose a new MEA structure to effectively reduce the methanol cross-over by adopting a composite membrane. The structure was carefully designed to enhance water back diffusion through the membrane by using diffusion layers made of custom-designed porous materials developed in our institute, Samsung Advanced Institute of Technology (SAIT). Both our novel MEA structure and the conventional structure were built and tested, and the test results were compared to check the effectiveness of the new structure. The water back diffusion efficiency was measured in a passive hydrogen/air test, and our novel MEA showed an impressive improvement compared with the conventional structure, which in turn can realize a high power density of the fuel cells.

## 2. Experiments

### 2.1. Materials and MEA preparation

PtRu (HIGHSPEC 6000) and Pt (HIGHSPEC 1000) were purchased from Johnson Matthey<sup>®</sup> with surface area of  $80 \text{ m}^2 \text{ g}^{-1}$  for PtRu black and  $20 \text{ m}^2 \text{ g}^{-1}$  for Pt black. Polymer membrane was fabricated in SAIT by solution casting method [28] to have thickness of  $50 \text{ }\mu\text{m}$ . Nano-silica of 4–5 nm and ordered mesoporous silica (OMS) of 300 nm in size with 10–20 nm pore were used as constituents of diffusion layers [29]. Nafion<sup>®</sup> ionomer solution from Dupont<sup>®</sup> and polyvinylidene fluoride (PVDF) from Aldrich<sup>®</sup> were used as binder in the formation of catalyst layers and diffusion layers. Carbon papers from Toray<sup>®</sup> & SGL<sup>®</sup> were used to support the catalysts and the diffusion layers. Gold-coated nickel mesh was used as current collector.

The catalyst layers were prepared by squeezing method. PtRu black and Pt black were used as catalysts for the anode and cathode, respectively. Catalysts were first mixed with deionized (DI) water, followed by addition of isopropanol (IPA), and ionomer solution (5 wt.% Nafion<sup>®</sup> solution). After mechanical stirring, the slurry was sonicated for 120 min. Then the slurry was coated on the catalyst support layer made of Toray 030 plain paper. Loadings of PtRu and Pt in the anode and cathode catalyst layers were  $8 \text{ mg cm}^{-2}$ . The anode diffusion layer was sprayed on carbon backing layer with nano-silica particles and PVDF mixture whose weight ratio was 7:3. For the cathode diffusion layer, mixture of carbon particles (Vulcan XG 72) and polytetrafluoroethylene (PTFE) was first sprayed on the carbon backing layer with the loading of  $2 \text{ mg cm}^{-2}$  carbon base. Then, mixture of the

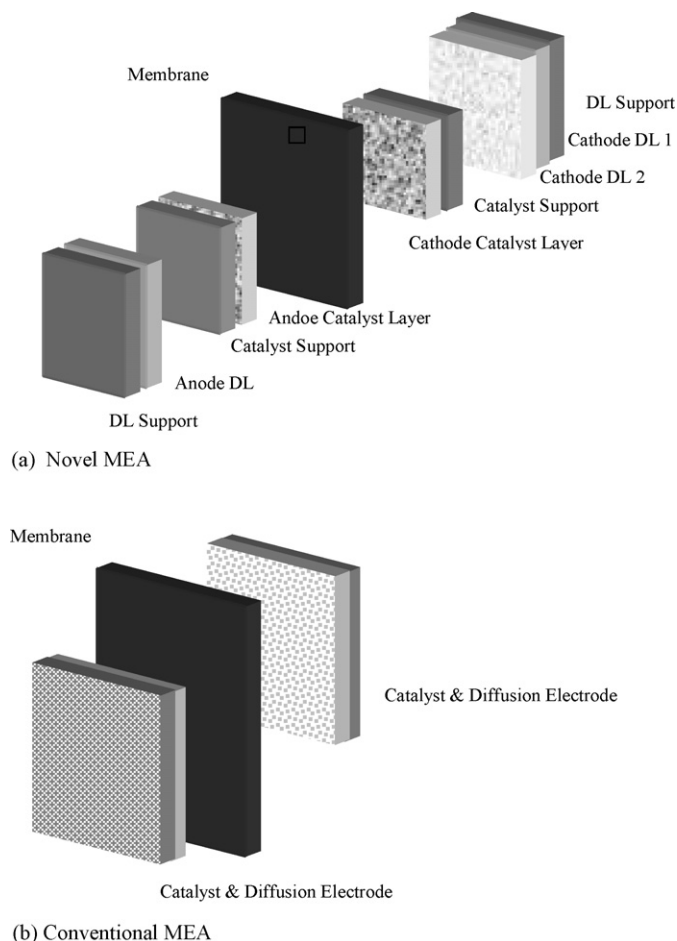


Fig. 1. Schematic diagrams of (a) novel MEA and (b) conventional MEA.

OMS and PVDF was loaded by spraying. SGL plain paper was used as the anode backing layer and Toray 090 (40 wt.% PTFE) as the cathode backing layer. Schematic diagram of novel MEA configuration is described in Fig. 1(a). All the layers were hot-pressed at 1 ton for 1 min and then at 2.2 tonnes for 3 min at  $125 \text{ }^\circ\text{C}$ .

In case of conventional MEA, the diffusion layers composed of Vulcan XG 72 particles and PTFE were formed on carbon backing layer (SGL paper). The anode and cathode catalyst layers were formed onto the diffusion layers with PtRu and Pt black at  $8 \text{ mg cm}^{-2}$  loading, respectively. The active area of MEA in this work was  $10 \text{ cm}^2$ . Fig. 1(b) shows the schematic diagram of conventional MEA. Four types of MEA were prepared for experiments and their components and configuration are summarized in Table 1.

### 2.2. Characterizations

Hydrogen/air test was performed to measure the amount of water diffused back from the cathode to the anode through the membrane. Dry hydrogen flowed into the anode with  $200 \text{ ml min}^{-1}$  and air was supplied by natural convection. Outlet flow at the anode was condensed to collect the water by cooling in an ice water bath. As the water at the cathode is a function of electrical current and electro-osmosis, water back

Table 1  
MEA configuration used in the experiments

	Membrane	Anode DL	Cathode DL	MEA Configuration
CON-N112	Nafion112	Carbon:PTFE	Carbon:PTFE	Conventional
CON-N115	Nafion115	Carbon:PTFE	Carbon:PTFE	Conventional
NOV-N112	Nafion112	Nano-sized silica:binder	Carbon:PTFE, OMS:binder	Novel
NOV-C050	SAIT composite membrane	Nano-sized silica:binder	Carbon:PTFE, OMS:binder	Novel

diffusion efficiency can be calculated from the ratio of the water diffused back, the water condensed at anode outlet, to the water accumulated at cathode side, the water produced and dragged by electro-osmosis. Constant current of 0.5 A was applied for all four types of MEA for 4 or 6 h with continuous hydrogen feeding. For investigation of fuel cell performances, 5 ml of 3 M methanol solution was applied and air was supplied by natural convection. After injecting methanol fuel, open circuit voltage (OCV) was observed for 30 min. The polarization performances were measured and compared.

### 3. Results and discussion

One should approach effective water management first by considering water balance between the cathode and the anode through the membrane. Theoretically, water flux to the cathode arises from three contributions of diffusion, electro-osmosis, and hydraulic permeation, as expressed by following equation:

$$j_m = -D \frac{\Delta C_{c-a}}{\delta_m} + n_d \frac{I}{F} - \frac{K}{\mu_l} \Delta p_{c-a} \frac{\rho}{M_{H_2O}} \quad (1)$$

where  $I$  is the current density,  $\rho$  the density of water,  $\delta_m$  the membrane thickness,  $F$  the Faraday constant,  $K$  the hydraulic permeability,  $n_d$  the electro-osmotic drag coefficient of water,  $\mu_l$  the liquid water viscosity,  $D$  the diffusion coefficient,  $M_{H_2O}$  the molecular weight of water, and  $C_{c-a}$  and  $p_{c-a}$  are the difference of water concentration and hydraulic pressure across the membrane from the cathode to the anode [26]. Eq. (1) signifies that water flux to cathode can be controlled by modifying  $\Delta C_{c-a}$ ,  $\Delta p_{c-a}$ ,  $\delta_m$ , and current without changing  $K$  and  $n_d$ , which are the properties of the membrane. The water flux to cathode is mainly generated by electro-osmosis and hydraulic pressure difference. And electro-osmosis depends on the electro-osmotic drag coefficient, which is the characteristic of the membrane, and the hydraulic pressure difference depends on whole MEA structure. Reducing  $\Delta C_{c-a}$ , or  $\Delta p_{c-a}$  leads to the decrease of water flux to cathode, that is, the increase of water flux from the cathode to the membrane or to the anode. Its concepts are similar with self-humidified MEA, in which water produced at cathode is used for humidifying membrane or MEA, reducing resistance and then increasing fuel cell performances. Also, water flux should be favorable with thinner membrane. Such water back diffusion is significantly useful in preventing methanol cross-over since this back diffusion could lower the concentration of the anode fuel.

The new MEA structure, proposed in this study, was designed to enhance the water back diffusion by controlling  $\Delta C_{c-a}$  and  $\Delta p_{c-a}$ . This was enabled by adopting new materials and struc-

ture for diffusion layers in our novel MEA structure. Shown in Fig. 1 is a schematic diagram, which compares the structure of our novel MEA and the conventional MEA. For the conventional MEA, diffusion layers, a mixture of Vulcan XG 72 (carbon) particles and PTFE, were formed on carbon backing layer (carbon paper SGL paper or Toray Paper). Anode and cathode catalyst layers were formed on diffusion layers with PtRu and Pt black loadings of  $8 \text{ mg cm}^{-2}$ , respectively. In the novel structure, the anode diffusion layer, a porous structure of nano-sized silica particles and binder is expected to help an even distribution of methanol and water due to its hydrophilicity, and also an effective removal of  $\text{CO}_2$ . To enhance water back diffusion through membrane,  $\Delta p_{c-a}$  can be decreased by using hydrophilic anode diffusion layer and hydrophobic cathode diffusion layer. The water concentration difference,  $\Delta C_{c-a}$  can be decreased by making cathode diffusion layer hydrophilic. Therefore, the cathode diffusion layer should possess hydrophilicity and hydrophobicity at the same time for water back diffusion to take place. In this study the cathode diffusion layers had two sub-layers for solving this conflict. The first layer is hydrophobic and so is expected to decrease hydraulic pressure difference,  $\Delta p_{c-a}$ , through membrane. Also the second layer, which is hydrophilic, would decrease water concentration difference,  $\Delta C_{c-a}$ , while holding back water vaporization. SEM images, shown in Fig. 2, exhibit the surface morphologies of the diffusion layers. The cathode diffusion layer has less porous structure than the anode diffusion layer because larger particles of ordered mesoporous materials were used.

In order to examine the effect of the designed diffusion layer, we carried out a passive hydrogen/air test, in which dry hydrogen was allowed to flow into the anode at  $200 \text{ ml min}^{-1}$  and air was supplied by natural convection, and the water (produced at the cathode and diffused back to the anode through the membrane) was condensed in an ice water bath placed at the anode outlet. The amount of the condensed water was measured to calculate water back diffusion efficiency,  $E_{BD} = m_{H_2O,ano}/m_{H_2O,cat}$ , from the ratio of the water diffused back and the water accumulated at the cathode side. The latter can be obtained from the amount of applied current, the operation time, and electro-osmotic drag coefficient of Nafion<sup>®</sup> membrane. First, the water produced by reduction at cathode,  $m_{H_2O,rxn}$ , was calculated from current and operation time (Eq. (2)):

$$m_{H_2O,rxn} = \frac{I}{2F} M_{H_2O} T \quad (2)$$

where  $M_{H_2O}$  is the molecular weight of water, and  $T$  the operation time. Then, the amount of water accumulated at the cathode,

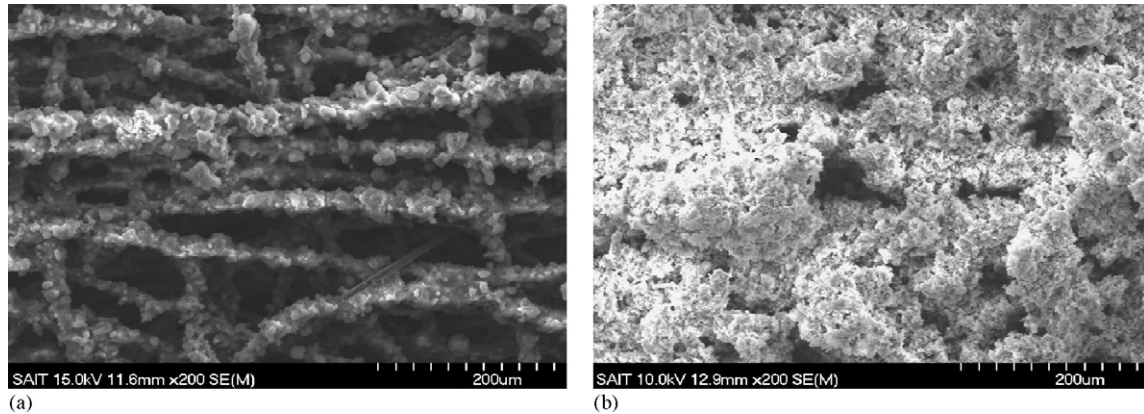


Fig. 2. SEM images of diffusion layers in novel MEA (a) surface of anode diffusion and (b) surface of cathode diffusion.

Table 2  
Efficiency of water back diffusion under hydrogen feeding

MEA	$I$ (A)	$T$ (h)	$m_{\text{H}_2\text{O,rxn}}$ (g)	$m_{\text{H}_2\text{O,cat}}$ (g)	$m_{\text{H}_2\text{O,ano}}$ (g)	$E_{\text{BD}}$ (%)
CON-N112	0.5	4	0.6716	4.7012	0.60	12.76
CON-N115	0.5	6	1.0074	7.0518	0.50	7.09
NOV-N112	0.5	6	1.0074	7.0518	1.55	21.98
NOV-C050	0.5	6	1.0074	3.0222	0.70	23.16

$m_{\text{H}_2\text{O,rxn}}$  is the amount of water produced by the reduction at the cathode,  $m_{\text{H}_2\text{O,cat}}$  is the amount of water accumulated at the cathode by reduction and water transferred by electro-osmotic drag, and  $m_{\text{H}_2\text{O,ano}}$  is the water condensed in the ice water bath placed at the anode outlet.

$m_{\text{H}_2\text{O,cat}}$ , was calculated as the sum of water produced by electrochemical reduction and water transferred by electro-osmotic drag:

$$m_{\text{H}_2\text{O,cat}} = \left( n_d + \frac{1}{2} \right) \frac{I}{F} M_{\text{H}_2\text{O}} T \quad (3)$$

The electro-osmotic drag coefficient of Nafion<sup>®</sup> membrane was assumed to be 3 at the operating temperature and that of SAIT composite membrane was assumed to be 1 because water swelling and water cross-over of composite membrane was proven to be one-third to one-fourth less than Nafion<sup>®</sup> membrane at DMFC operation [27,28]. In this test, the constant current of 0.5 A was applied for all four types of MEA for 4 or 6 h with continuous hydrogen feeding. The current of 0.5 A is applied with considering the current of DMFCs. The amount of the water collected at anode outlet was measured and compared for four MEAs.

The results from this test clearly demonstrate that the design changes in the diffusion layers have produced a significant impact on the water back diffusion. Summarized in Table 2 is experimental data obtained from the test. The two samples (NOV-N112 and NOV-C050) that adopted the novel diffusion layer structure are several times better in the water back diffusion coefficient than those (CON-N112 and CON-N115) using the conventional structure. This result implies that the modifications made to the materials and structure of the diffusion layers reduced significantly the concentration gradient and pressure gradient, which might, in turn, lead to a substantially increased water back diffusion. A close look at the data in Table 2 also reveals that the thinner membrane produced water back diffusion more than the thicker one. Nafion112 and Nafion115 have

the same conventional structure and differ only in the membrane thickness. Water back diffusion efficiency for Nafion112 which is a thinner membrane (70  $\mu\text{m}$ ) is 12.76% while Nafion115 of a thicker membrane (175  $\mu\text{m}$ ) has the water back diffusion efficiency of 7.09%. This result seems reasonable since water will diffuse through a thin membrane more easily than through a thick one. In addition, the sample with the SAIT membrane displayed water back diffusion larger than that with the Nafion<sup>®</sup> membrane. Nevertheless, it should also be pointed out that the membrane thickness of the SAIT membrane is slightly thinner than that of the Nafion<sup>®</sup> membrane. At this point, it is difficult to separate the two effects, thickness and membrane's characteristic. The improvement in the water back diffusion enabled a higher power density for our novel structure. Shown in Fig. 3

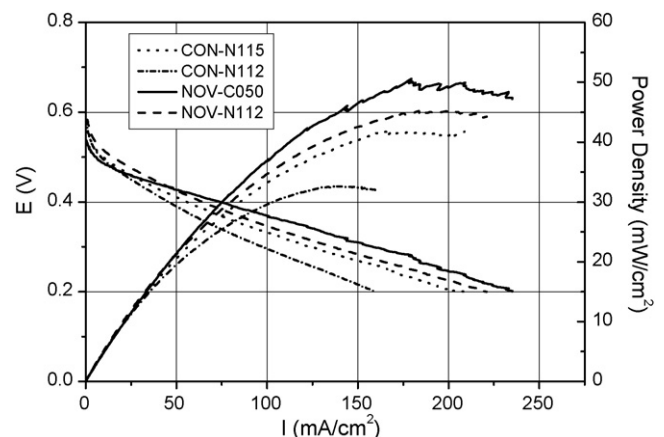


Fig. 3. Polarization curves for single cell: passive condition.



are polarization curves taken from passive single cell measurements, where 5 ml of 3 M methanol solution and air breathing were applied at ambient temperature after open circuit voltage (OCV) was monitored for 30 min. The curves for the novel structure, NOV-C050 and NOV-N112, are positioned much higher than those for the conventional structures, CON-N115 and CON-N112. The power density curves also lie significantly higher than those for the conventional structures. These results indicate that there is no mass transport limit with the change of diffusion layer. Such higher power density in NOV-C050 is due to the lower cross-over of methanol by using SAIT composite membrane compared with NOV-N112 and less water flooding by employing novel diffusion layers which results in higher water back diffusion. Conventional MEA with Nafion115, CON-N115, showed higher performance than that with Nafion112, CON-N112, due to lower methanol cross-over under the conditions of air breathing and 3 M methanol. Liu et al. [30] discussed that cell performances in a passive system comprised with mixed potential and temperature increase from methanol cross-over. In this study, complication from membrane thickness was not addressed. It means our MEAs showed discrete performance with membrane and diffusion layers. However, proposed MEA with composite membrane and new materials in diffusion layers evidently showed the effectiveness of water management in passive systems.

#### 4. Conclusions

A novel structure of membrane electrode assembly (MEA) was proposed for a passive direct methanol fuel cell (DMFC) system which exhibits a higher power density for a mobile energy source. In this novel structure, modifications of the materials and the structure in diffusion layers have been made to improve water back diffusion efficiency and lower methanol cross-over, which in turn make higher energy density possible. The design breakthrough of membrane and diffusion layer produced high water back diffusion efficiency and lower methanol cross-over, hence higher power and energy density than conventional MEA were achieved. Experiments results proved that water back diffusion efficiency increased several times higher for our novel structure than that for the conventional structure. These improvements were found to produce a direct impact on the single cell performance. In the polarization test, the power density was found to be significantly larger for the novel structure. Such higher power density in NOV-C050 comes from the lower cross-over of methanol with SAIT composite membrane

and less water flooding with novel diffusion layers due to higher water back diffusion.

#### References

- [1] R. Dillon, S. Srinivasan, A.S. Arico, V. Antonucci, J. Power Sources 127 (2004) 112.
- [2] J.H. Kim, H.Y. Ha, I.H. Oh, S.A. Hong, H.I. Lee, J. Power Sources 135 (2004) 29–35.
- [3] H.N. Dinh, X. Ren, F.H. Garzon, P. Zelenay, S. Gottesfeld, J. Electroanal. Chem. 491 (2000) 222.
- [4] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, Science 280 (1735).
- [5] M. Watanabe, M.K. Ravikuma, S. Saegusa, P. Stonehart, J. Electroanal. Chem. 271 (1989) 213.
- [6] W.A. Chrzanowski, A. Wieckowski, Langmuir 14 (1967).
- [7] P.S. Kaurenan, E. Skou, J. Electroanal. Chem. 408 (1996) 189.
- [8] M.K. Ravikuma, A.K. Shukla, J. Electrochem. Soc. 143 (1996) 2601.
- [9] S. Gupta, D. Tryk, S.K. Zecevic, W. Aldred, D. Guo, R.F. Savinell, J. Appl. Electrochem. 28 (1998) 673.
- [10] R.Z. Jiang, D. Chu, J. Electrochem. Soc. 147 (2000) 4605.
- [11] A. Heinzl, V.M. Barragan, J. Power Sources 84 (1999) 70.
- [12] M.K. Walker, K.M. Baumgartner, M. Kaiser, J. Kerres, A. Ullrich, E. Rauchle, J. Appl. Polym. Sci. 74 (1999) 67.
- [13] J. Cruickshank, K. Scott, J. Power Sources 70 (1998) 40.
- [14] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 1111.
- [15] A.S. Arico, P. Creti, V. Baglio, E. Modica, V. Antonucci, J. Power Sources 91 (2000) 202.
- [16] J. Wang, S. Wasmus, R.F. Savinell, J. Electrochem. Soc. 142 (1995) 4218.
- [17] D. Weng, J.S. Wainright, U. Landau, R.F. Savinell, J. Electrochem. Soc. 143 (1996) 1260.
- [18] H. Kim, C. Lim, H. Chang, 199 Electrochemical Society Conference Proceeding, Washington, DC, USA, 2001.
- [19] S. Yao, X. Tang, C.C. Hsieh, Y. Alyousef, M. Vladimer, G. Fedder, C.H. Amon, Energy 31 (2006) 636–649.
- [20] X. Ren, J.J. Becerra, R.S. Hirsch, S. Gottesfeld, F.W. Kovacs, K.J. Shufon, US Patent 0,209,136 A1 (2004).
- [21] C. Xie, J. Bostaph, J. Pavio, J. Power Sources 55 (2004) 136.
- [22] M. Neergat, A.K. Shukla, J. Power Sources 104 (2002) 289–294.
- [23] H. Dohle, R. Jung, N. Kimiaie, J. Mergel, M. Müller, J. Power Sources 124 (2) (2003) 3771–4384.
- [24] K.W. Park, B.K. Kwon, J.H. Choi, J.S. Park, Y.M. Kim, Y.E. Sung, J. Power Sources 109 (2) (2002) 439–445.
- [25] C.Y. Chen, C.S. Tsao, Int. J. Hydrogen Energy (2006) 391–398.
- [26] G.Q. Lu, F.Q. Liu, C.Y. Wang, Electrochem. Solid-State Lett. 8 (1) (2005) A1.
- [27] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, J. Power Sources 117 (2003) 22.
- [28] C.H. Rhee, H.K. Kim, H. Chang, J.S. Lee, Chem. Mater. 17 (7) (2005) 1691.
- [29] S.S. Kim, T.R. Pauly, T.J. Pinnavaia, Chem. Commun. (2000) 1661.
- [30] J.G. Liu, T.S. Zhao, Z.X. Liang, R. Chen, J. Power Sources 153 (2006) 61–67.