

## New RuO<sub>2</sub> and carbon–RuO<sub>2</sub> composite diffusion layer for use in direct methanol fuel cells

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### Abstract

A RuO<sub>2</sub> diffusion layer is examined for use in direct methanol fuel cells (DMFC) by comparison with acetylene black and Vulcan XC-72R. In the test with a DMFC unit cell, the RuO<sub>2</sub> diffusion layer is superior to the other two materials. The difference in performance is interpreted in terms of structural and electrical properties which are evaluated by porosity, scanning electron microscopy and resistance measurements. The RuO<sub>2</sub> diffusion layer displays different behaviors at the anode and cathode sides. These characteristics can be attributed to a reduced loss of catalyst in the active catalyst layer, which leads to increased methanol diffusion at the anode and prevention of water flooding in the cathode. The effect of the RuO<sub>2</sub> diffusion layer on cell performance becomes more pronounced at lower temperatures and during operation in the presence of air. Finally, a carbon–RuO<sub>2</sub> composite is evaluated as a diffusion layer material for a DMFC. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Direct methanol fuel cell; Diffusion layer; RuO<sub>2</sub>; Carbon–RuO<sub>2</sub> composite

### 1. Introduction

The direct methanol fuel cell (DMFC) utilizes methanol, in the form of a vapor or liquid, as a fuel and is based on a solid polymer electrolyte (SPE) as the proton conducting membrane [1–6]. It is operated at relatively low temperatures, i.e. below 100 °C, and has a structure which is a composite of two porous electrocatalytically active electrodes on each side of the SPE membrane. The DMFC is a promising electrochemical power source for use in portable electronic devices. Nevertheless, improvements in the performance of the DMFC are required before a practical application can be realized.

The membrane–electrode assembly (MEA) structure consists of a membrane, an electrode and a (backing) diffusion layer which serves to reduce mass-transport limitations. The diffusion layer in a DMFC consists of carbon black mixed with polytetrafluoroethylene (PTFE) that is deposited on a macro-porous carbon paper and provides a physical micro-porous support for the catalyst layer. This arrangement allows liquid or gas transport to or from the catalyst layer. It is clear that optimization of the diffusion layer can lead to

substantial improvements in the performance of the cell. From this point of view, several studies have been reported on improvements in the characteristics of the diffusion layer in terms of composition, thickness and the material used.

Paganin et al. [7] investigated the performance of a polymer electrolyte membrane fuel cell (PEMFC) with varying PTFE content (10, 15, 20, 30 and 40 wt.%) and diffusion layer thickness using Vulcan XC-72R carbon black. It was found that, the effect of the diffusion layer on cell performance was small and that a diffusion layer containing 15 wt.% PTFE gave the best performance. Giorgi et al. [8] proposed that the PTFE content affected the porosity of the diffusion layer, namely, increase in the PTFE content led to a decrease in the diffusion layer porosity. The diffusion layer thickness had a much greater influence on cell performance, and a thickness of 50 μm was found to give the best performance. These workers concluded that the effect of the diffusion layer thickness could be attributed to a decrease in the electrical resistance of the electrode with increasing thickness. The decrease in the performance for a 65 μm diffusion layer was attributed to a long gas diffusion path or to flooding problems. Recently, Jordan et al. [9] investigated the effect of carbon morphology and the amount of carbon loading in a PEMFC. It was found that acetylene black carbon, which has a lower porosity, gave an improve-

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ment in maximum power density of nearly 15% compared with Vulcan XC-72R. The increase in performance was attributed to acetylene black, being better able to remove water from the cell, which would result in a reduction in cathode flooding. To date, most studies on the diffusion layer have focused on the structural control of conventional carbon materials such as Vulcan XC-72 or acetylene black.

In this paper, an investigation is made of the effect of RuO<sub>2</sub> on the performance of DMFC as both the anode and cathode diffusion layers. Composites of carbon–RuO<sub>2</sub>, as a diffusion layer in a DMFC, are also fabricated by the sol–gel method and are characterized by electrochemical tests and unit-cell measurements.

## 2. Experimental

For structural analyses of diffusion layer materials, such as carbon powder (Vulcan XC-72R and acetylene black) and RuO<sub>2</sub>, the surface area, mesopore area, micro-pore ratio and average pore radius were measured using a porosimeter (Quantachrome Autosorb-1). The resistance of the diffusion layer was measured vertically or horizontally in each side of the MEA, and the indicated values represent averages. Carbon powders (Vulcan XC-72R and acetylene black) and a RuO<sub>2</sub> (Aldrich) ink solution for the formation of diffusion layer were prepared by using 40 wt.% PTFE and isopropyl alcohol. The diffusion layer was fabricated by pasting the carbon and RuO<sub>2</sub> on a teflonized carbon paper (TGPH-090) substrate using the aforementioned ink solution. After a brushing step, the diffusion layer was heat-treated in air at 350 °C for 1 h to induce the formation of a porous structure. The catalyst layer was then pasted on the diffusion layer with 5 wt.% Nafion<sup>®</sup> solution as a binder. The anode (PtRu black, Johnson–Matthey Co.) and cathode (Pt black, Johnson–Matthey Co.) catalysts contained 15 and 7 wt.% Nafion<sup>®</sup>, respectively. In order to prevent discrepancies in performance as a function of the amount of catalyst, the catalyst loadings at both sides were controlled to a constant value of 5 mg cm<sup>-2</sup>.

MEAs for unit-cell tests were prepared by pressing an as-formed anode and cathode on to each side of a pre-treated Nafion<sup>®</sup> 117 electrolyte membrane at 110 °C and 800 psi

for 3 min. Pre-treatment of the membrane involved boiling the membrane for 1 h in 3 wt.% H<sub>2</sub>O<sub>2</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively.

The carbon–RuO<sub>2</sub> composite was prepared as described in the literature [10]. RuCl<sub>3</sub>·xH<sub>2</sub>O was dissolved in deionized water and then mixed with the carbon material. The pH of the mixed solution was adjusted to about 7.0. The precipitate was washed, filtered, and annealed in air at a high temperature. Cyclic voltammograms (CVs) in 0.5 M H<sub>2</sub>SO<sub>4</sub> and X-ray diffraction (XRD) patterns of the composites were obtained in order to confirm the structure of the composite.

Cell performance was evaluated in a DMFC unit cell with a 2 cm<sup>2</sup> cross-sectional area, and measured with a potentiometer (WMPG-1000) which recorded the cell potential from the circuit voltage under a constant current. Both fuel and oxidant flow paths were machined into graphite block end plates, which also served as current-collectors. The cell temperature was maintained by means of heating lines embedded into each cell housing. A 2 M methanol solution with a flow rate of 1 cm<sup>3</sup> min<sup>-1</sup> was supplied by a Maxterflex liquid micro-pump and the dry O<sub>2</sub> (or air) flow was regulated at 500 cm<sup>3</sup> min<sup>-1</sup> by means of a flow meter.

## 3. Results and discussion

### 3.1. Structural analysis of diffusion layer

The physical and electrical properties of the diffusion layer materials are shown in Table 1. From porosimetry data, the multi-point BET surface area (m<sup>2</sup> g<sup>-1</sup>), mesopore area (m<sup>2</sup> g<sup>-1</sup>), micro-pore ratio (%) and average pore radius (nm) for each component was investigated. The morphologies of the diffusion layer materials were different in terms of surface area and pore-size distribution. Acetylene black has a smaller surface area of 127.9 m<sup>2</sup> g<sup>-1</sup> and a larger pore radius of 9.0 nm than Vulcan XC-72R, which has a surface area of 229.3 m<sup>2</sup> g<sup>-1</sup> and a pore radius of 7.0 nm. Moreover, Vulcan XC-72R has a large micro-pore (smaller than 2 nm) ratio of 47%, while acetylene black and RuO<sub>2</sub> have no micropores. RuO<sub>2</sub> has a very small surface area of 15.4 m<sup>2</sup> g<sup>-1</sup> and the largest average pore radius of 15.5 nm. Due to the high content of PTFE (40 wt.%), the resistance of the diffusion

Table 1  
Physical and electrical properties of diffusion-layer materials

	Vulcan XC-72R	Acetylene black	RuO <sub>2</sub>	No diffusion layer
Porosity				
Surface area (m <sup>2</sup> g <sup>-1</sup> )	229.3	127.9	15.4	
Mesopore area (m <sup>2</sup> g <sup>-1</sup> )	121.5	127.9	15.4	
Micro-pore ratio (%)	47.1	0	0	
Average pore radius (nm)	7.0	9.0	15.5	
Resistance				
Vertical (Ω cm <sup>-1</sup> )	6.0–9.5	4.5–6.0	1.4–1.8	1.7–2.1
Horizontal (Ω cm <sup>-1</sup> )	6.9–8.7	5.9–6.3	1.1–1.3	3.1–4.0

layers is relatively high compared with metals. Acetylene black has a lower resistance than Vulcan XC-72R.  $\text{RuO}_2$  has, however, the lowest resistance along the horizontal and vertical directions compared with the other materials. The thickness of the diffusion layer composed of various materials was roughly similar, 50  $\mu\text{m}$ .

### 3.2. Comparison of DMFC unit-cell performance

The effect of the diffusion layer on DMFC unit-cell performance was investigated. Current density–cell voltage plots for a DMFC unit cell, with or without a diffusion layer, are shown in Fig. 1(a). The current densities at 0.45 V are 320 (no diffusion layer), 250 (Vulcan XC-72R), 430 (acetylene black), and 430 ( $\text{RuO}_2$ )  $\text{mA cm}^{-2}$ , respectively. The cell performances, tested by using acetylene black, and the  $\text{RuO}_2$  diffusion layer are much better than in the other cases. Although there is little difference in open-circuit voltage (OCV), apparent different features are shown in the ohmic polarization region. The maximum power densities of each

diffusion layer were 187 (no diffusion layer), 172 (Vulcan XC-72R), 206 (acetylene black), and 227 ( $\text{RuO}_2$ )  $\text{mW cm}^{-2}$ , respectively (see Fig. 1(b)). The pore size of the diffusion layer is known to affect the cell performance through the control of fuel and oxidant (methanol and oxygen) and the flow of products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) [11]. A significant difference in performance is seen in the diffusion-controlled region at high-current density. Acetylene black and  $\text{RuO}_2$ , with a large pore size compared with Vulcan XC-72R, give better performance in the diffusion-limited region where maximum power density is obtained. It is also noteworthy from Fig. 1(a) that, the polarization slope of the cell using a  $\text{RuO}_2$  diffusion layer in the ohmic-controlled region is relatively flat. It is concluded that, this results from the low resistance of the  $\text{RuO}_2$  diffusion layer [12]. Due to low ohmic polarization, as the result of the low resistance of  $\text{RuO}_2$ ,  $\text{RuO}_2$  was further identified as a good diffusion layer material in DMFC.

Cell performance at a low temperature, 30 °C, is shown in Fig. 2(a) and (b). Because of the low electrocatalytic activity

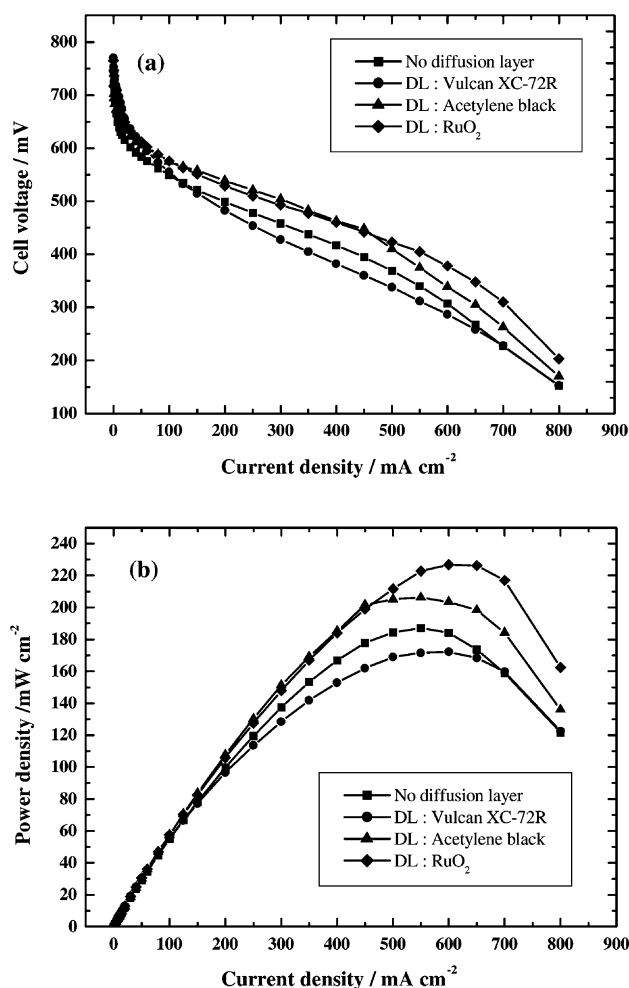


Fig. 1. DMFC performance comparison with Vulcan XC-72R, acetylene black and  $\text{RuO}_2$ : (a) current density–cell voltage polarization curve, and (b) current density–power density curve. Cell temperature is 70 °C, and 2 M methanol solution and dry  $\text{O}_2$  are supplied at anode and cathode, respectively.

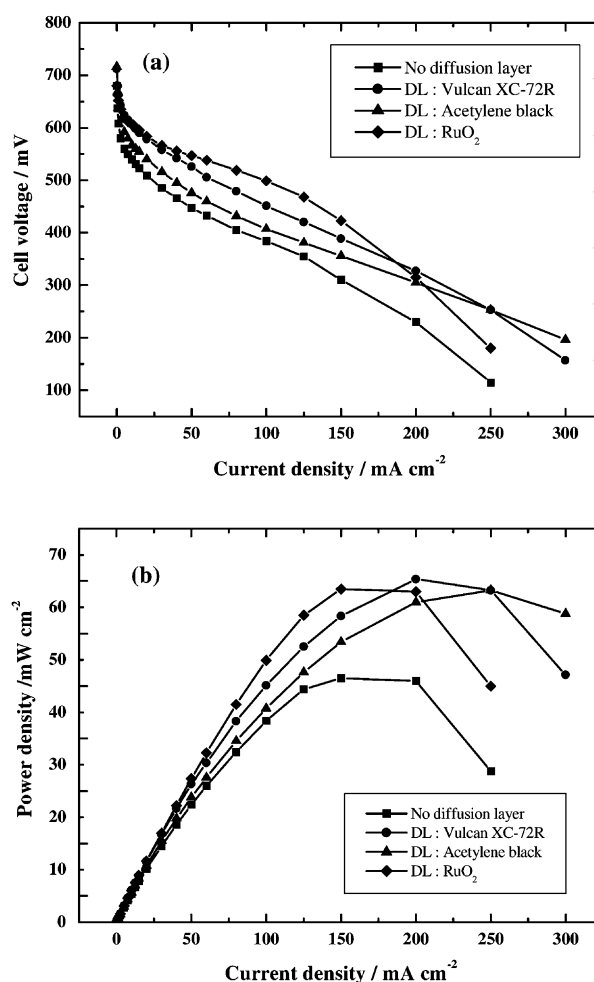


Fig. 2. DMFC performance comparison with Vulcan XC-72R, acetylene black and  $\text{RuO}_2$ : (a) current density–cell voltage polarization curve, and (b) current density–power density curve. Cell temperature is 30 °C, and 2 M methanol solution and dry  $\text{O}_2$  are supplied at anode and cathode, respectively.

at low temperatures, the ohmic characteristics of the diffusion layer become much more important. Overall, the cell performance with Vulcan XC-72R, acetylene black and  $\text{RuO}_2$  as the diffusion layer, respectively, is much better than that for a cell without a diffusion layer. In particular, the cell performance using  $\text{RuO}_2$  is good in the practical voltage region, i.e. at voltages lower than 0.35 V. The current density and power density at 0.4 V is  $160 \text{ mA cm}^{-2}$  and  $64 \text{ mW cm}^{-2}$ , respectively.

### 3.3. Effect of $\text{RuO}_2$ diffusion layer at anode and cathode

With respect to the diffusion layer properties that affect cell performance, the effect of the diffusion layer at the anode and cathode was investigated using a unit-cell test. For these studies,  $\text{RuO}_2$  was used as the diffusion layer. Current density–cell voltage plots at  $70^\circ\text{C}$  under flowing oxygen are presented in Fig. 3(a) and (b). The current densities at 0.45 V are 320 (no diffusion layer), 347 (anode only), 430 (cathode

only), and 430 (both sides)  $\text{mA cm}^{-2}$ , respectively. The origin of the low cell performance without a diffusion layer is the infiltration of catalysts into the carbon paper. This results in substantial loss of catalysts and, especially in the high-current region, a limitation of diffusion caused by the obstruction of methanol flow due to the permeation of PtRu nanoparticles into the macro-pores of the carbon paper. Therefore, the role of the anode diffusion layer becomes important in the high-current density region, that is, the  $\text{RuO}_2$  diffusion layer, in part, supplies methanol and facilitates the flow of methanol to the anode catalyst layer. Finally, the concentration polarization is reduced. The cells with a  $\text{RuO}_2$  diffusion layer at only the cathode give better cell performance than the cell without a diffusion layer. It is likely that water flooding phenomena of the cathode catalyst is diminished by the hydrophobic diffusion layer which facilitates water removal from the catalyst layer.

Cell performance under an air flux is shown in Fig. 4(a) and (b). In this case, the role of the diffusion layer is more

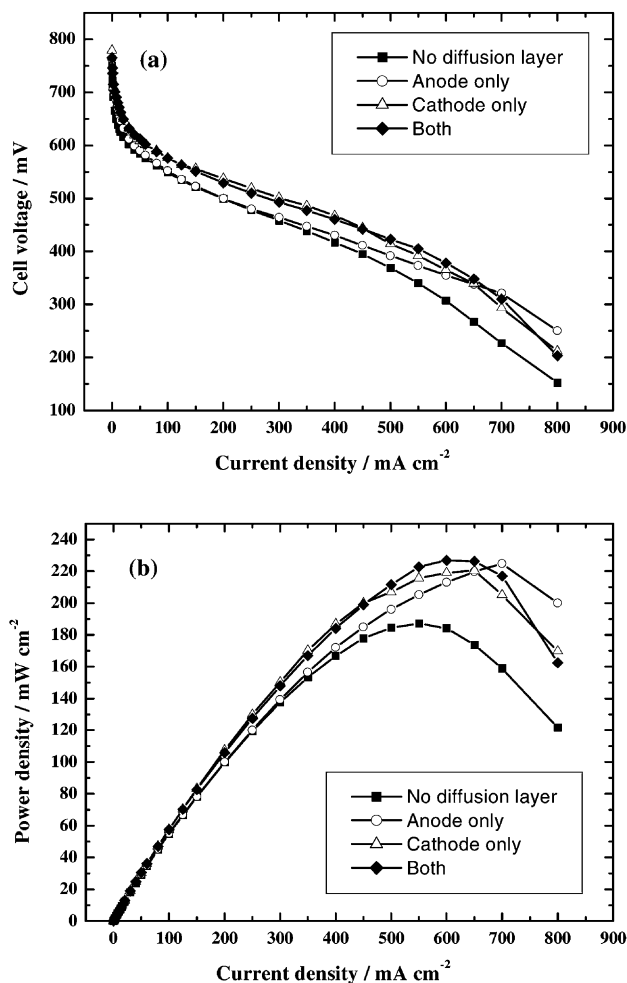


Fig. 3. DMFC performance comparison of  $\text{RuO}_2$  as anode/cathode diffusion layers: (a) current density–cell voltage polarization curve, and (b) current density–power density curve. Cell temperature is  $70^\circ\text{C}$ , and 2 M methanol solution and dry  $\text{O}_2$  are supplied at anode and cathode, respectively.

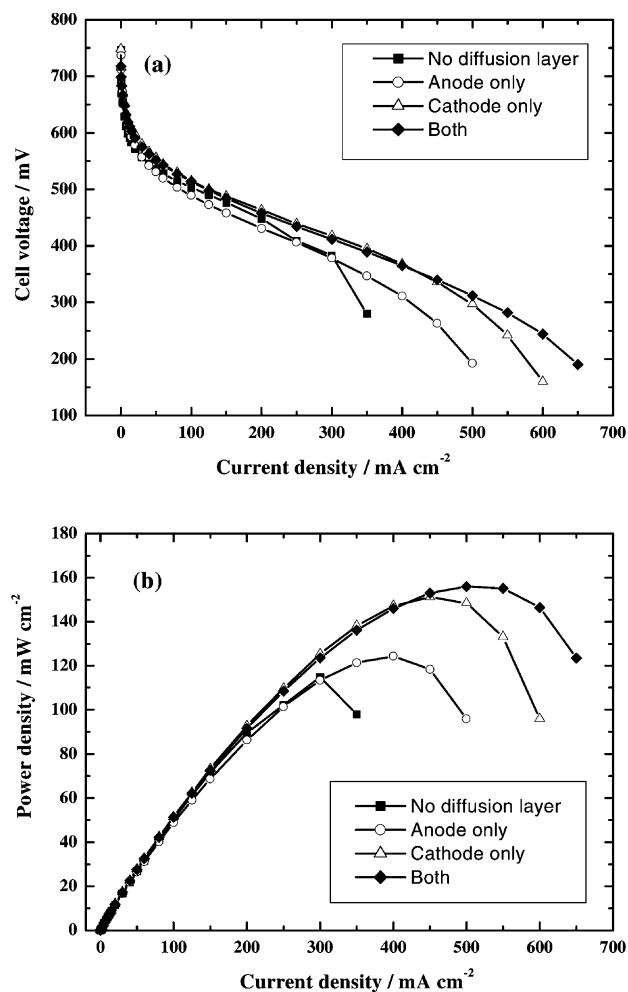


Fig. 4. DMFC performance comparison of  $\text{RuO}_2$  as anode/cathode diffusion layers: (a) current density–cell voltage polarization curve, and (b) current density–power density curve. Cell temperature is  $70^\circ\text{C}$ , and 2 M methanol solution and dry air are supplied at anode and cathode, respectively.

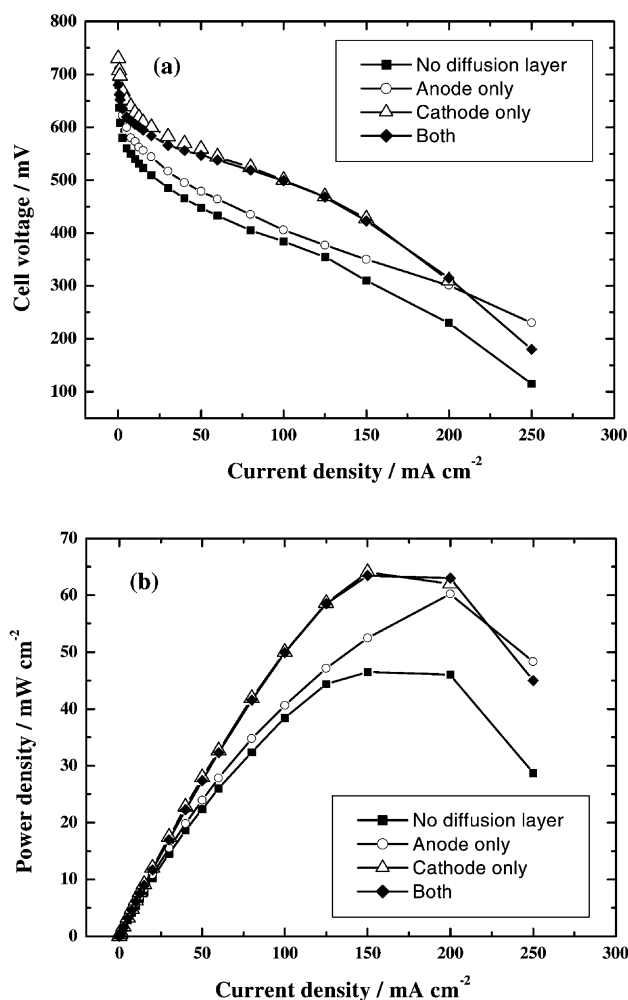


Fig. 5. DMFC performance comparison of RuO<sub>2</sub> as anode/cathode diffusion layers: (a) current density–cell voltage polarization curve, and (b) current density–power density curve. Cell temperature is 30 °C, and 2 M methanol solution and dry O<sub>2</sub> are supplied at anode and cathode, respectively.

obvious. The difference between oxygen and air is related to the lower partial pressure of oxygen in air and the diffusive blanketing effect of nitrogen in air [9,13]. Thereby, the diffusion layer in the cathode side could become more important than that in the anode side. Thus, in Fig. 4, the contribution of the cathode diffusion layer to cell performance is much larger than that of the anode, and a combined effect in cell performance with diffusion layers at both electrodes is observed. The diffusion layers at the anode and cathode sides provide good methanol diffusion and easier water removal, respectively. It is observed that the maximum power densities under an air flux are 106 (no diffusion layer), 124 (anode only), 151 (cathode only), and 156 (both sides) mW cm<sup>-2</sup>, respectively.

Cell performance at 30 °C under an oxygen and an air flux is shown in Figs. 5 and 6, respectively. The prevention of catalyst loss by the diffusion layer results in a dramatic increase in cell performance and the power density shows a 34–36% improvement at 30 °C. The increment of power

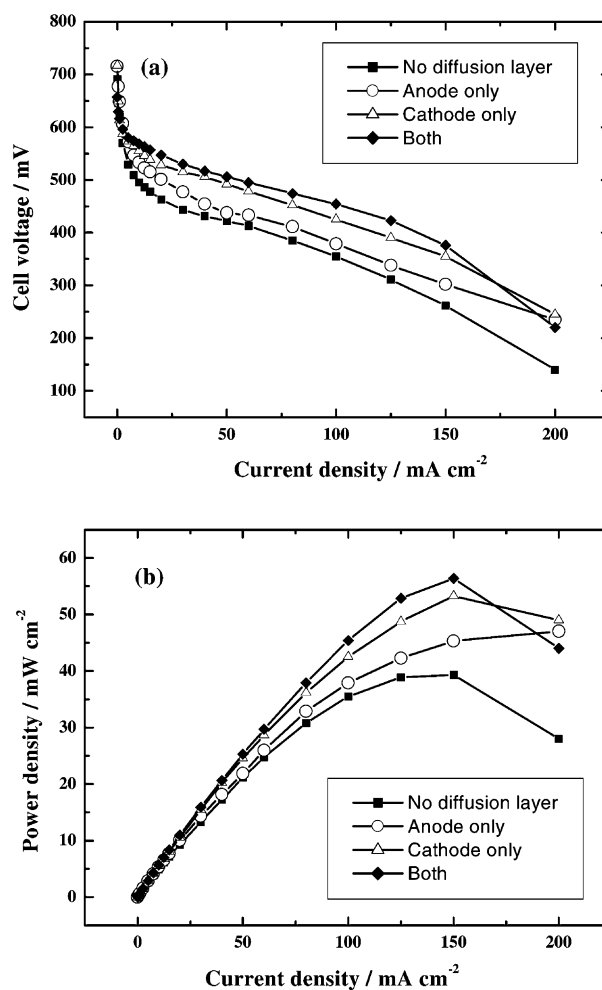


Fig. 6. DMFC performance comparison of RuO<sub>2</sub> as anode/cathode diffusion layers: (a) current density–cell voltage polarization curve and (b) current density–power density curve. Cell temperature is 30 °C, and 2 M methanol solution and dry air are supplied at anode and cathode, respectively.

density at 70 °C under an oxygen flow is approximately 14–22%. Consequently, the diffusion layer plays an important role in cell performance at low temperatures and is extremely efficient under an air flux.

### 3.4. Carbon–RuO<sub>2</sub> composite as diffusion layer

CVs for a carbon (acetylene black)–RuO<sub>2</sub> composite in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mV s<sup>-1</sup> as a function of the amount of RuO<sub>2</sub>, are shown in Fig. 7. As the amount of RuO<sub>2</sub> in the composite is increased, the current (A g<sup>-1</sup>) and double-layer thickness of the CV are increased. The CV for acetylene black is thinner compared with that for a carbon (acetylene black)–RuO<sub>2</sub> composite. It is well known that carbon–RuO<sub>2</sub> composites serve as a thick double-layer in the CV, as a result of OH adsorption by the RuO<sub>2</sub>. This suggests that, as the amount of RuO<sub>2</sub> in the composites is increased, the physical structure of the composite, i.e. hydrophilic properties, as well as the porosity of carbon material, is modified.

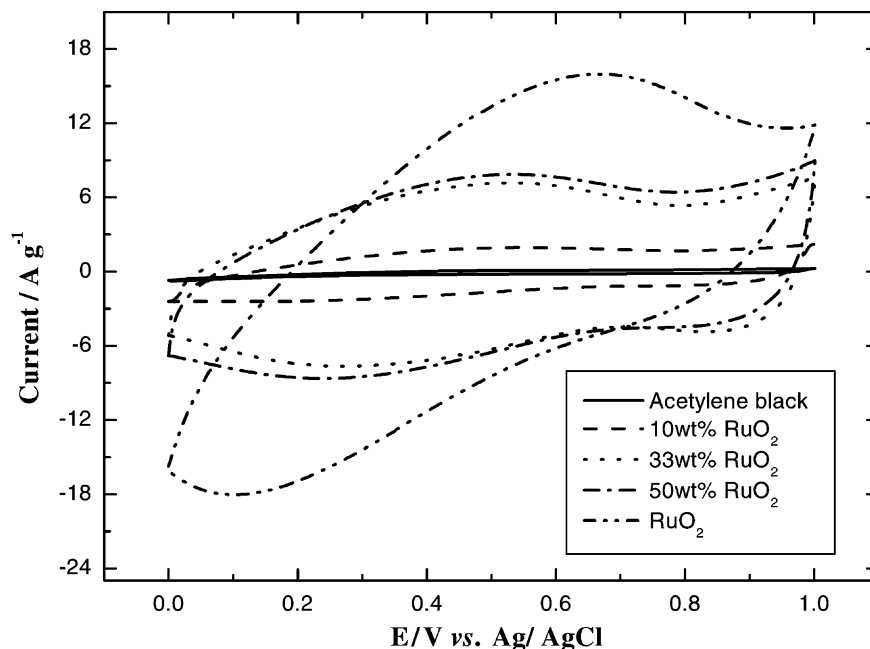


Fig. 7. Cyclic voltammograms for carbon–RuO<sub>2</sub> composites according to content of RuO<sub>2</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mV s<sup>-1</sup>.

The XRD patterns of a 33 wt.% RuO<sub>2</sub> composite, which is annealed at various temperatures in air is shown in Fig. 8. At high annealing temperatures, amorphous RuO<sub>2</sub> is converted into a crystalline structure. It has also been reported that the resistivity of as-prepared RuO<sub>2</sub> is relatively higher than that of RuO<sub>2</sub> annealed at a temperature of over 100 °C [14]. At temperatures above 100 °C, the resistivity is less dependent on the annealing temperature. A comparison of the DMFC performance of a carbon–RuO<sub>2</sub> composite with only an acetylene black diffusion layer is shown in Fig. 9. Carbon–RuO<sub>2</sub> composites were used for both the anode and the

cathode diffusion layer materials. The diffusion layer with the as-prepared carbon–RuO<sub>2</sub> composite has a relatively low performance for the DMFC. Due to the lower resistivity and the proper pore structure of the annealed carbon–RuO<sub>2</sub> composite, however, the carbon–RuO<sub>2</sub> composite diffusion layer, after annealing at 150 and 400 °C, displays a much improved power density, which is comparable to that obtained with acetylene black diffusion layers. This suggests that a carbon–RuO<sub>2</sub> composite could be modified into an advantageous structure for the diffusion of fuel or oxidant and by-products. Additional experiments are currently underway

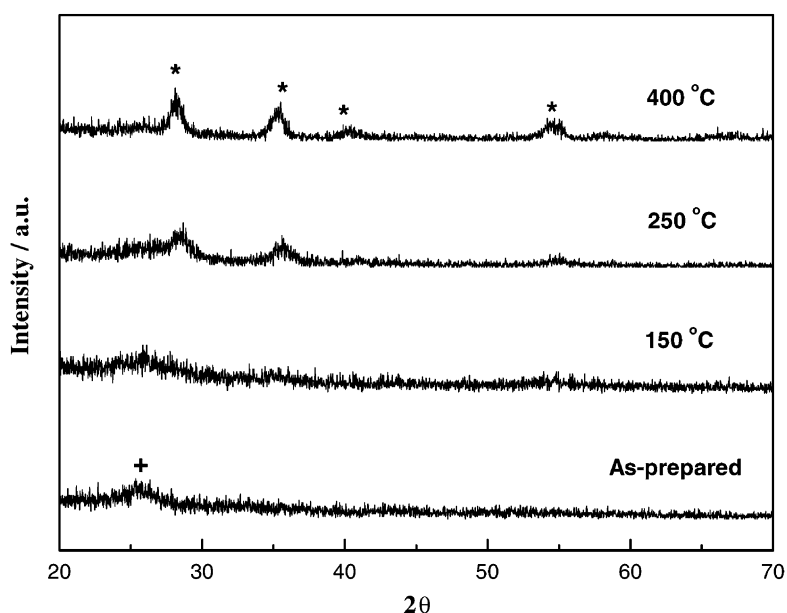


Fig. 8. X-ray diffraction patterns of carbon–RuO<sub>2</sub> composite (33 wt.% RuO<sub>2</sub>) with annealing temperature in air.

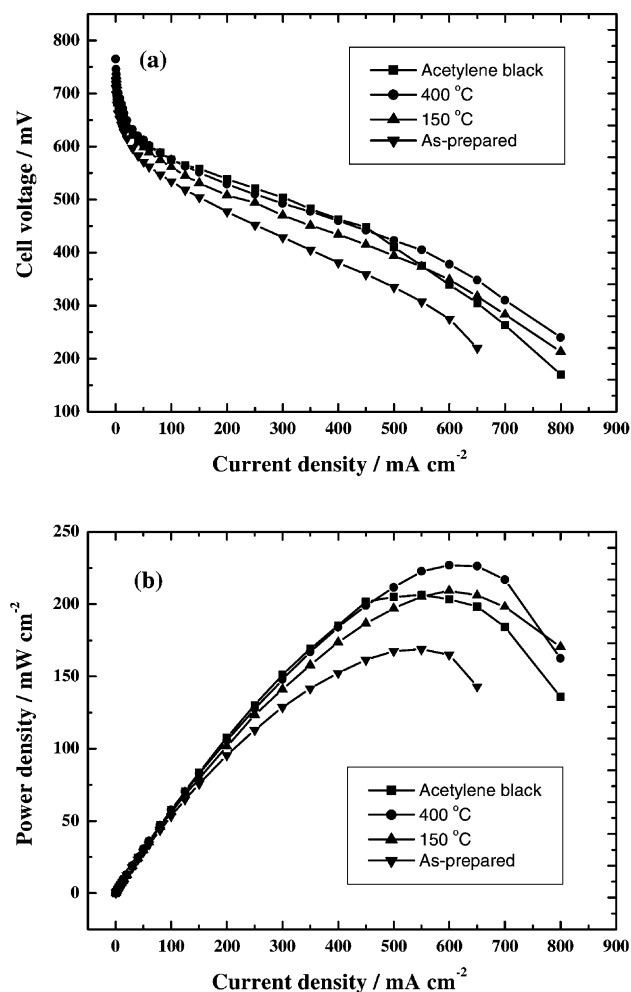


Fig. 9. Comparison of DMFC performance at 70 °C, using acetylene black and carbon (acetylene black)–RuO<sub>2</sub> composites: (a) current density–cell voltage polarization curve, and (b) current density–power density curve. dry O<sub>2</sub> and 2 M methanol solution are supplied at cathode and anode, respectively.

to evaluate the long-term stability of these materials and their practical implications to DMFC.

#### 4. Conclusions

The diffusion layer in the liquid feed of a DMFC is the flow channel for fuels (methanol and oxygen) and products (CO<sub>2</sub> and H<sub>2</sub>O). The optimum diffusion layer in a MEA leads to a reduction in the loss of catalyst in the active catalyst layer, caused by the formation of a dense layer between the carbon paper and the catalyst layer. In addition, the hydrophobic diffusion layer prevents the cathode catalyst from water flooding by the vigorous venting of H<sub>2</sub>O. With respect to the polarization curve of the DMFC, a distinct difference, as a diffusion layer material, is found in the diffusion-controlled region. Acetylene black and

RuO<sub>2</sub>, with a large pore size and low porosity compared with Vulcan XC-72R, gives better performance caused by the ease of diffusion of methanol and the removal of water. In particular, a DMFC unit cell with the RuO<sub>2</sub> diffusion layer of the lowest resistance produces the highest cell power density in the low ohmic polarization region.

RuO<sub>2</sub>, as a diffusion layer material, shows different behavior in the anode and cathode compartments. When it is used as an anode diffusion layer, cell performance is increased due to minimal loss of catalyst and the facile diffusion of methanol. As a result, the role of the anode diffusion layer is important in the high-current-density region, which is the diffusion-limited region. When it is used in the cathode diffusion layer, cell performance increases dramatically due to a reduction in water flooding from the cathode catalysts. These properties are obvious under an air flux because of the relatively low oxygen partial pressure. In addition, the effect of the diffusion layer on cell performance becomes dominant at low temperatures, especially for operation in air. Finally, the effect of a carbon–RuO<sub>2</sub> composite, as a diffusion-layer material on DMFC performance is examined. The composites are found to perform very well. Further work is required to evaluate such materials in detail for fuel cell applications, and such investigations are currently in progress.

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#### References

- [1] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466.
- [2] A. Kuver, W. Vielstich, J. Power Sources 74 (1998) 211.
- [3] A. Heinzel, V.M. Barragan, J. Power Sources 84 (1999) 70.
- [4] V. Tricoli, N. Carretta, M. Bartolozzi, J. Electrochem. Soc. 147 (2000) 1286.
- [5] X. Ren, T.E. Springer, S. Gottefeld, J. Electrochem. Soc. 147 (2000) 92.
- [6] X. Ren, S. Gottefeld, J. Electrochem. Soc. 148 (2001) 87.
- [7] V.A. Paganin, E.A. Ticianelli, E.R. Gonzalez, J. Appl. Electrochem. 26 (1996) 297.
- [8] L. Giorgi, E. Antolini, A. Pozio, E. Passalacqua, Electrochim. Acta 43 (1998) 3675.
- [9] L.R. Jordan, A.K. Shukla, T. Behrsing, N.R. Avery, B.C. Muddle, M. Forsyth, J. Power Sources 86 (2000) 250.
- [10] J.P. Zheng, Electrochem. Solid-State Lett. 2 (1999) 359.
- [11] A. Fisher, J. Jindra, H. Wendt, J. Appl. Electrochem. 28 (1998) 277.
- [12] G.J.K. Acres, G.A. Hards, Phil. Trans. R. Soc. 354 (1996) 1671.
- [13] M. Baldauf, W. Preidel, J. Power Sources 84 (1999) 161.
- [14] J.P. Zheng, P.J. Cygan, T.R. Jow, J. Electrochem. Soc. 142 (1995) 2699.