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Author(s)	Shudo, Toshio; Suzuki, Kensuke
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Performance improvement in direct methanol fuel cells using a highly porous corrosion-resisting stainless steel flow field

*Toshio Shudo

Division of Energy and Environmental Systems, Hokkaido University

N13 W8, Sapporo, 060-8628 Japan

Email: shudo@eng.hokudai.ac.jp

Tel/Fax: +81-11-706-6402

Kensuke Suzuki

Division of Energy and Environmental Systems, Hokkaido University

Abstract

Power generation with direct methanol fuel cell (DMFC) systems require only simple equipment, and has the important advantages of using a liquid fuel with higher energy density and easier handling characteristics than hydrogen. However, the power output of DMFC is lower than hydrogen fuel cells. To improve the power output of DMFC it is very important to reduce diffusion polarization at higher current density conditions. This research used a corrosion-resisting type porous stainless steel developed based on the technology for metal-hydride battery electrodes in the separator flow fields for reactants and products in a single cell DMFC and analyzed its influence on performance characteristics.

Keywords: Direct Methanol Fuel Cell, Flow Field, Porous Stainless Steel, Diffusion Polarization

1. Introduction

Fuel cell technology has advanced greatly in the last decade, and hydrogen fuel cells are expected to become a sustainable power source in the environmentally friendly society of the future. However, hydrogen has the disadvantage of very much lower energy density per unit volume than conventional liquid fuels, the handling of hydrogen is also more difficult than liquid fuels [1]. Because of this, direct methanol type fuel cells (DMFC) fed with liquid methanol appear more advantageous than hydrogen fuel cells. A DMFC system is simpler than hydrogen fuel cell systems and is suited for many applications such as small portable power sources [2]. In spite of the advantages, DMFC also has the downside that the power output and efficiency are substantially lower than hydrogen fuel cells [2]-[3]. This makes it very important to improve the efficiency and output power of DMFC. The efficiency characteristics of the proton exchange membrane (PEM) type fuel cells are influenced by the activation polarization, the ohmic polarization, and the diffusion polarization [4]. Diffusion polarization limits the performance at higher current density conditions, and reducing the diffusion polarization is crucial to improve the performance of DMFC [5]-[6]. This research applied a corrosion-resisting type porous stainless steel (porosity around 90%) developed based on the technology for Ni-MH battery electrodes [7] to the separator flow fields for reactants and products in a single cell DMFC and used experiments to analyze its influence on efficiency and power output with different cell temperatures.

2. Experiments

The experiments used a single cell with different kinds of flow fields, 5wt% methanol in water solution was fed to the anode at preset flow rates through a diaphragm type electromagnetic pump (ProMinet GVLA1000). The cathode was fed with oxygen from a high pressure cylinder through a pressure regulator. The cathode gas flow rate was controlled with a needle valve and measured with a mass flow meter (Yamatake CMS0005). Fuel cell output power was measured with a fuel cell load unit coupled with a frequency response analyzer unit for impedance measurement (Kikusui KFM2030). Cell temperature and anode feed temperature were controlled with a constant temperature vessel (Azone DOV-450P). Specifications of the tested membrane electrode assembly (MEA) are shown in **Table 1**. The catalyst loading on the anode was $1\text{mg}/\text{cm}^2$ (Pt-Ru), while that on cathode was $1\text{mg}/\text{cm}^2$ (Pt). The catalysts are with carbon support. Percentages of Pt-Ru and Pt to carbon powder were 50wt%. A Nafion 117 polymer electrolysis membrane was sandwiched between the electrodes. Carbon paper with 0.28mm thickness was used as gas diffusion layer (GDL) on both sides of the MEA. Setup of the tested fuel cell is schematically shown in **Figure 1**.

Table 2 shows the specifications of the tested porous stainless steel. To achieve good corrosion-resisting properties, the composition has been adjusted to Fe with 30wt% Cr, 2wt% Ni, and 4wt% Mo. The corrosion characteristics of an ordinary stainless steel (JIS SUS316L; Fe-19Cr-12Ni-2Mo) and the tested corrosion-resisting type stainless steel (Fe-30Cr-2Ni-4Mo) are shown in **Figure 2** [7]. The figures show the elution characteristics of Fe and Cr from the two kinds of steel into sulfuric acid. Test pieces of $10\times 10\times 0.2\text{mm}$ made of the two kinds of steels (non-porous, machined samples) were soaked in 1N sulfuric acid at 353K. The elution of Fe and Cr from the corrosion-resisting stainless steel

is substantially lower order of magnitude than that from the ordinary stainless steel especially at longer soak times, over 90 hours. This good corrosion-resisting performance would enable the compound to be used in polymer electrolysis fuel cells. The current research tested a separator flow field made of the corrosion-resisting stainless steel in a highly porous structure as shown in **Figure 3**. It has a porosity of around 90% and a pore size of 0.3-0.4mm. The images in **Figure 3** were obtained with a laser scanning microscope (Keyence VK-9700).

The porous stainless steel flow fields were placed in the cell separators shown in **Figure 4 (a)**. For comparison, solid stainless steel separators with a straight-channel (groove) type flow field as shown in **Figure 4 (b)** were also used. The depth of the porous flow field was 2 mm which is the same as the depth of the groove type flow field. The flow field volume is 5cc for the porous and 2.9cc for the channel type. Experiments with four combinations: porous-porous, porous-channel, channel-porous, and channel-channel type flow fields on the anode-cathode are compared.

3. Results and Discussions

3.1. Effect of the porous stainless steel flow field on cell performance

Figure 5 shows cell voltage and power versus current density at 353K cell temperature with the porous flow field on both electrodes and the straight-channel (groove) type flow field on both electrodes. The anode feed was 10cc/min and the cathode feed 1000cc/min. These flow fields give similar performance under a $0.1\text{A}/\text{cm}^2$ current density. However the porous flow field enables the cell to operate with higher voltage at current densities higher than $0.1\text{A}/\text{cm}^2$. This results in higher output power especially at higher current density conditions where diffusion polarization usually lowers the cell performance. To investigate this effect, the AC impedance of the cell was measured at $0.3\text{A}/\text{cm}^2$ current density for both flow field types, the condition for the highest power output with the porous flow field. The impedance spectra were obtained at frequencies from 3kHz to 1Hz. **Figure 6** shows the imaginary part jX and real part R of the measured complex impedance Z .

$$Z = R + jX \quad (1)$$

The results indicate that the arc diameter for the porous case is smaller than that for the groove case. The arc mostly corresponds to reaction resistance which includes activation resistance and diffusion resistance. This result signifies that the porous flow field improves diffusion of reactants and products, and that an even supply of fuel and oxygen to the electrodes and smooth removal of CO_2 from the anode and H_2O from the cathode were achieved. The effective electrode area is also increased by the porous flow field because it has no ribs which may act as an obstacle to the reactant supply and product removal with the groove flow field.

The influence of cathode and anode feed rates on the cell performance are shown in **Figures 7 and 8** respectively. In both cases, the porous flow field maintains higher performance than the groove type at any feed rate. The differences between porous and groove flow field results increase with decreases in the feed rates.

3.2 Each effect of porous flow field on anode and cathode

This section attempts to separate the effects of the porous flow field on anode and cathode. **Figure 9** shows the results. Triangular symbols are with the conventional groove flow field on the anode and the porous flow field on the cathode. Solid circular symbols are with the porous flow field on the anode and the groove flow field on the cathode. Results with the groove flow fields on both electrodes are also shown with open circular symbol for comparison. The anode feed rate was 10cc/min and the cathode feed rate 1000cc/min. In both experiments, the porous flow field achieves higher output power than the groove flow field especially at higher current densities. The effect to improve the cell performance is higher at the cathode than at the anode. This suggests that the water removal from the cathode by the porous medium is more effective to improve cell performance than the CO_2 removal from the anode by the porous medium. On the cathode, there is cross-over water from the anode through the membrane in addition to the water generated by the cathode reaction of protons, electrons, and oxygen. This makes efficient removal of water is very important in DMFC. On the anode, theoretically 0.3cc/s of CO_2 is produced at $0.3\text{A}/\text{cm}^2$ current density, this CO_2 production rate is higher than the fuel supply rate of 0.16cc/s . The flow field volume of the porous type is 1.6 times that of the groove type, showing that CO_2 removal is easier with the porous flow field than with the groove type.

3.3 Influence of cell temperature

The effect of the porous flow field was investigated at different cell temperatures. **Figure 10** shows the results at 313K and 333K cell temperature. The anode feed was 10cc/min, and the cathode feed 1000cc/min. Cell performance with the porous flow field exceeds that with the groove type at all cell temperatures. Output with the porous type at 40 degree C is higher than that with the groove type at 333K. **Figure 11** shows the voltage at $0.2\text{A}/\text{cm}^2$ versus cell temperature. The performance difference between the porous and groove flow field experiments increases with decreasing cell temperature. The saturated vapor pressure at 313K is around 1/5 of that at 353K, and more water condenses in the flow field at the lower temperature. The capillary effect of the small pores in the porous medium may play a role to suck in water adjacent to the electrode. Better heat transfer between cell and oxygen by the porous medium may also be a reason for the better cell performance at lower temperatures, because the cathode feed of oxygen was at room temperature, without heating.

4. Conclusions

- (1) By employing a corrosion-resisting porous stainless steel with around 90% porosity as the flow field in separators, performance of a direct methanol fuel cell is improved, compared to operation with conventional channel type flow fields.
- (2) The improved cell performance by the porous flow field is better at the cathode than at the anode. The porous medium would improve the reactant supply to and product removal from electrodes. Because of this, diffusion polarization decreases and cell performance is improved especially at higher current densities.
- (3) The improved performance is also attributed to the increased effective electrode area by the porous flow field because it has no ribs which may act as an obstacle to the reactant supply and product removal with conventional groove flow fields.
- (4) The improvement in cell performance is maintained at lower temperatures. The performance difference between porous and channel flow fields increases at lower cell temperatures where more water condenses.

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Table1 MEA specification and feed conditions

Polymer membrane	Nafion117 (175 μ m)
Reaction area	25 cm ² (5 x 5 cm)
Anode catalyst	Pt-Ru 1.0 mg/cm ²
Cathode catalyst	Pt 1.0 mg/cm ²
Anode feed	5w% MeOH solution
Cathode feed	dry O ₂ ,

Table 2 Specification of the tested porous stainless steel

Composition	Fe-30Cr-2Ni-4Mo
Pore size	0.3 - 0.4 mm
Pore ratio	90 $\pm$ 2 %

Fig.1 Setup of tested fuel cell

(a) JIS SUS316L stainless steel (Fe-19Cr-12Ni-2Mo)

(b) Corrosion-resisting stainless steel (Fe-30Cr-4Mo-2Ni)

Fig.2 Corrosion characteristics of ordinary and corrosion-resisting stainless steels [7]

Fig.3 Surface of the tested porous stainless steel

(a) Porous stainless steel flow field

(b) Solid stainless steel with a groove type flow field
Fig.4 Separators with different flow fields used here

Fig.5 Cell performance with porous and groove flow fields

Fig.6 Impedance plots for porous and groove flow fields

Fig.7 Influence of cathode feed rate on cell performance

Fig.8 Influence of anode feed rate on cell performance

Fig.9 Effect of porous flow field on each electrode

Fig.10 Effect of porous flow field at (a) 333K and (b) 313K cell temperatures

Fig.11 Influence of cell temperature on cell voltage at 0.2A/cm² current density