

Development of a high-performance PEFC module operated by reformed gas

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Abstract

Improvements in the CO tolerance of the anode has been studied with the objective of developing PEFC modules operated with reformed gas. The CO tolerance of the Pt–Ru alloy anode was improved by reducing its thickness from 40 μm to 20 μm . Maintaining a saturated steam pressure of the fuel cell anode gas outlet is expected to decrease the influence of CO poisoning. When keeping sufficient water content in the feed fuel, it was established that the cell performance was stable over a wide range of air-humidification conditions. Successful operation was achieved with a 1 kW class system utilizing the improved CO-tolerant anode and fuel processor. An output power of 1.1 kW (average cell voltage: 0.62 V) was achieved at the current density of 0.3 A/cm². © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polymer electrolyte fuel cell; CO poisoning; Anode

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are expected to have use in residential applications. In a previous stage of work on residential use, a 1 kW class PEFC portable power unit using pure hydrogen as fuel had been test marketed since 1998 [1].

In the present stage, several-kilowatt class PEFC power systems using town gas have been developed under the Phase 2 of the NEDO program. In order to feed town gas to the system, a fuel processor is required for reforming town gas to hydrogen. However, reformed gas contain 10–100 ppm CO. Therefore, improvements of CO tolerance and durability of modules operated with reformed gas are important issues for residential use.

The present objective is to improve CO tolerance and demonstrate a 1 kW class system under actual operating condition. In Section 3.1, the effect of the anode on overpotential is investigated. The relationship between the humidification condition of the processed gas and CO tolerance is also investigated. In Section 3.2, the module is tested while adopting an improved anode and reformer [2].

2. Experimental

2.1. Investigation for improving CO tolerance of anodes

The polarization of anodes as a function of anode thickness was simulated and the simulation results were verified by cell tests of a single cell with an active electrode area of 25 cm². Pt–Ru/C, with the ratio of Pt to Ru at 1:1, was used as the anode catalyst, and the catalyst loading was 0.3 mg-Pt/cm² for both 20 μm and 40 μm thick catalyst layers. Pt/C was used as the cathode catalyst, and the catalyst loading was 0.6 mg-Pt/cm². Perfluorosulfonic acid polymer membrane thickness of 20 μm and 50 μm were used as the polymer electrolyte. The cell tests were run at a cell temperature of 80°C and fuel utilization (U_f)/oxidant utilization (U_{ox}) = 50%/20%. The current density was constant at 0.5 A/cm². Pure hydrogen or CO-containing hydrogen (10–100 ppm CO/H₂ bal.) was used as fuel. Air was used as the oxidant. A single cell with an active electrode area of 100 cm² was tested under the condition of U_f/U_{ox} = 70%/40% to confirm the influence of up-scaling.

Moreover, the effect of the humidification condition of the processed gas on cell performance was also confirmed. The water content of the inlet gas was calculated from the humidification temperature of the humidifier. The outlet

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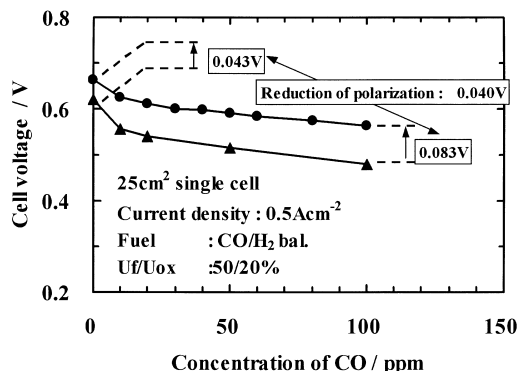


Fig. 1. Results of CO-tolerance characteristics of anodes with thicknesses of 20 μm and 40 μm using a single cell of 25 cm^2 : ● Anode thickness of 20 μm , ▲ Anode thickness of 40 μm .

gas was cooled with the condenser, and the water content was calculated from the quantity of condensed water. In this test, pure hydrogen or 100 ppm CO/H₂ was used as fuel.

2.2. Operation of the modules

The cell tests of a 1 kW class module (100 $\text{cm}^2 \times 60$ cells) and a two-cell module (100 $\text{cm}^2 \times 2$ cells) were carried out while using an improved anode. Life-time characteristics were confirmed by the two-cell module tests operating with simulated reformed gas (10 ppm CO/20% CO₂/H₂ bal.) of a realistic composition as fuel. The module was run at a cell temperature of 80°C, $U_f/U_{ox} = 70\%/40\%$ and atmospheric pressure. The current density was constant at 0.3 A/cm². The initial performance was confirmed by tests of the 1 kW-class module.

Moreover, the 1 kW system with the improved module and the improved fuel processor was demonstrated under actual operating conditions.

3. Results and discussion

3.1. Investigation for improving CO tolerance of anodes

The anode polarization was simulated with a model equation based on the parameters obtained from actual

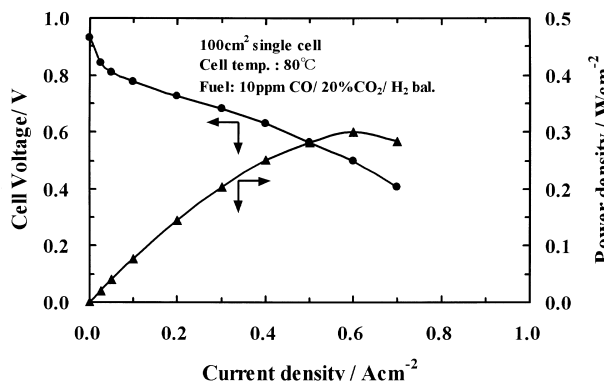


Fig. 2. Current–voltage curves of a single cell with an active electrode area of 100 cm^2 .

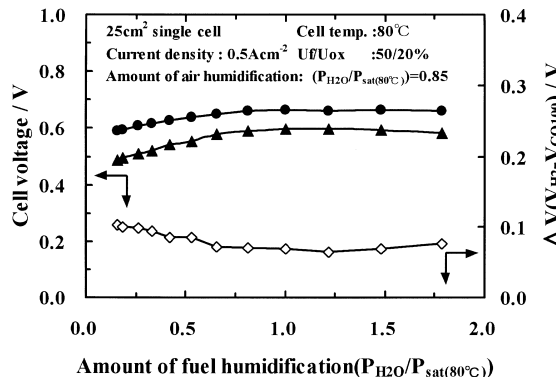


Fig. 3. Influence of fuel humidification on cell voltage at a current density of 0.5 A/cm² and a cathode-humidified condition of 0.85 ($P_{H_2O}/P_{sat(80)}$): ● Cell voltage using H₂ as fuel, ▲ Cell voltage using 100 ppm CO/H₂ balance as fuel, ◇ Cell voltage difference between H₂ fuel and 100 ppm CO/H₂ fuel.

measurements of anode polarization in a single cell. The results indicate that a thin catalyst layer performed well when using reformed gas as fuel. Fig. 1 shows the test results of CO-tolerance characteristics of anodes with thicknesses of 20 μm and 40 μm using a single cell with an active electrode area of 25 cm^2 . The cell voltage difference at a fuel composition of pure H₂ was 43 mV, and the difference at a fuel condition of 100 ppm CO-containing H₂ was 83 mV. These results show that the thickness of the catalyst layer has a significant effect on anode polarization. Polarization reduction of 40 mV was observed when changing the anode thickness from 40 to 20 μm . Based on this data, a cell test with an active electrode area of 100 cm^2 was undertaken. The current–voltage curve of the cell is shown in Fig. 2. The output power density of 0.204 W/cm² was obtained at a current density of 0.3 A/cm² while using simulated reformed gas (10 ppm CO/20% CO₂/H₂ bal.) as fuel. The maximum output power density was over 0.30 W/cm². Little difference was observed between the performance with 25 cm^2

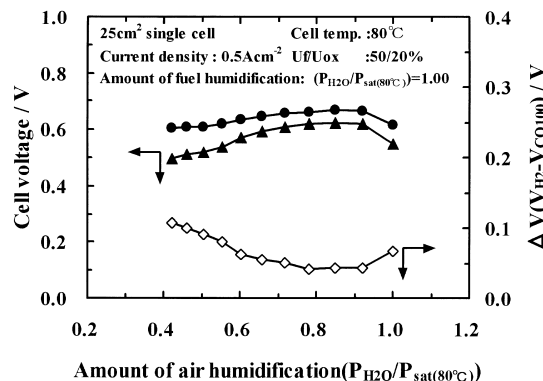


Fig. 4. Influence of the amount of air humidification on cell voltage at a current density of 0.5 A/cm² and fuel-humidity of 1.00 ($P_{H_2O}/P_{sat(80)}$): ● Cell voltage using H₂ as fuel, ▲ Cell voltage using 100 ppm CO/H₂ balance as fuel, ◇ Cell voltage difference between H₂ fuel and 100 ppm CO/H₂ fuel.

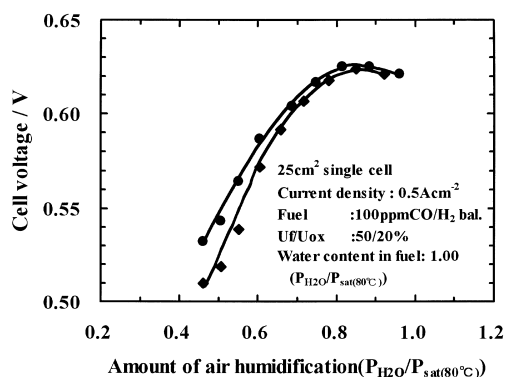


Fig. 5. Relationship between cell voltage and the amount of air humidification with two electrolyte membrane thicknesses: ● 20 μm, ◆ 50 μm.

and 100 cm². This result indicates that the gas distribution and temperature distribution were acceptable in spite of up-scaling to 100 cm². The optimization of thickness was confirmed to be successful in achieving high power density. Moreover, no significant decline was observed in fuel utilization tests that used simulated reformed gas as fuel.

In order to understand the factors influencing CO poisoning of the anode, the influence of the humidification condition on the performance of cells was investigated. Fig. 3 shows the influence of fuel humidification on cell voltage at 0.5 A/cm² current density and a cathode-humidification condition of 0.85 (P_{H₂O}/P_{sat(80°C)}). P_{H₂O} is the dew point of water in fuel, and P_{sat(80°C)} is the saturated steam pressure at 80°C. The cell voltage difference (ΔV) between H₂ fuel and 100 ppm CO/H₂ fuel was also plotted. For both H₂ fuel and 100 ppm CO/H₂ fuel, the cell voltages were found to decrease under fuel humidification of ca. 1.0. Moreover, the cell voltage differences (ΔV) showed a tendency to increase under fuel humidification of ca. 1.0. It was also found that CO poisoning increased with a reduction in fuel humidification. Accordingly, we concluded that the anode-humidified condition has a major influence on the resistance of anodes to CO poisoning.

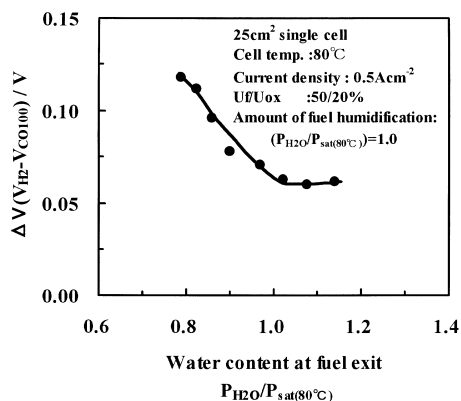


Fig. 6. Relationship between cell voltage drop by CO poisoning and water content in the outlet gas of the anode.

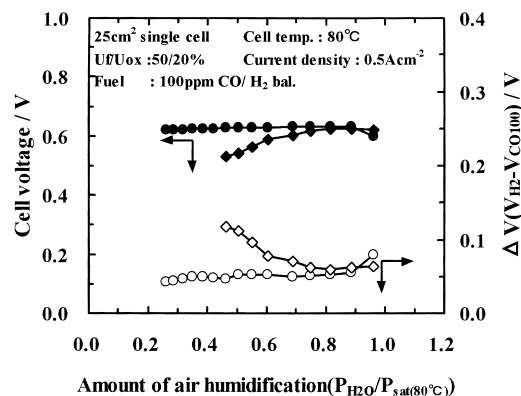


Fig. 7. Relationship between the amount of air humidification and cell voltage under two conditions of fuel humidification: ●, ○ P_{H₂O}/P_{sat(80°C)} 1.48, ◆, ◇ P_{H₂O}/P_{sat(80°C)} = 1.00.

Fig. 4 shows the influence of the amount of air humidification on cell voltage at 0.5 A/cm² current density and fuel humidity of 1.00 (P_{H₂O}/P_{sat(80°C)}). The cell voltage difference (ΔV) between H₂ fuel and 100 ppm CO/H₂ fuel was also plotted. For both H₂ fuel and 100 ppm CO/H₂ fuel, the cell voltages showed a maximum at air humidification of about 0.8–0.9. Similarly, the cell voltage difference (ΔV) showed a minimum at air humidification of about 0.8–0.9. This result shows that CO poisoning increases with a reduction in the amount of air humidification below 0.8–0.9. The flux of water passing through the membrane from anode to cathode was increased by reducing the amount of air humidification. Accordingly, there was a drying of the anode. This suggests that CO poisoning is dependent on the drying of the anode by reduced air humidification. It was also assumed that drying of the polymer electrolyte in the anode was due to the drying of the anode side. Consequently, as the reaction sites decrease, the CO poisoning increases.

The relationship between cell voltage and the amount of air humidification with two differing electrolyte membrane thicknesses (50 μm and 20 μm) is shown in Fig. 5. The

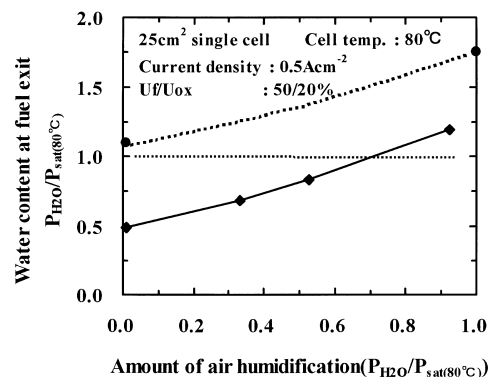


Fig. 8. Relationship between amount of air humidification and water content at fuel exit: ● P_{H₂O}/P_{sat(80°C)} = 1.48, ◆ P_{H₂O}/P_{sat(80°C)} = 1.00.

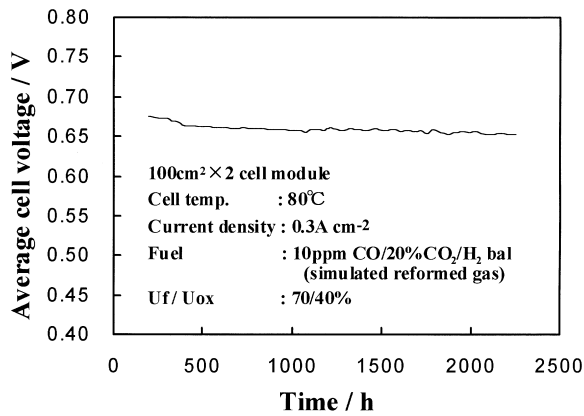


Fig. 9. Life characteristics of a two-cell module with simulated reformed gas.

cell voltage when using a membrane thickness of 20 μm was higher, especially under low air humidification. This result suggests that thinner membranes have higher back diffusion of water from the cathode, and thus drying of the anode is prevented even under a low air-humidification condition. Fig. 6 shows the relationship between cell voltage drop by CO poisoning and water content in the outlet gas of the anode. The water content in the outlet gas of the anode was varied with the amount of air humidification. In the non-saturated condition region, that is the region of $P_{\text{H}_2\text{O}}/P_{\text{sat}}(80^\circ\text{C}) = 0.8\text{--}1.0$, the cell voltage drop was decreased by increasing the water content. In the saturated condition region, that is the region of the $P_{\text{H}_2\text{O}}/P_{\text{sat}}(80^\circ\text{C}) = 1.0\text{--}1.2$, cell voltage was nearly stable. Fig. 7 shows the relationship between the amount of air humidification and cell voltage under two conditions of fuel humidification. When the amount of fuel humidification was 1.0 $P_{\text{H}_2\text{O}}/P_{\text{sat}}(80^\circ\text{C})$, the cell performance was not stable. In particular, the cell voltage drop increased under the condition of low air humidification. On the other hand, when the amount of fuel humidification was 1.48 $P_{\text{H}_2\text{O}}/P_{\text{sat}}(80^\circ\text{C})$, cell performance was stable over a wide range of air-humidification conditions.

Fig. 8 shows the relationship between air humidification and water content at the fuel exit when the amounts of fuel

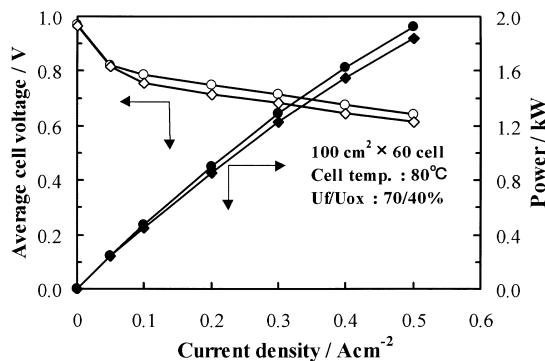


Fig. 10. Current–voltage curves of a 1 kW-class module: \circ \bullet H_2 , \diamond , \blacklozenge 10 ppm CO/20% CO_2/H_2 bal.

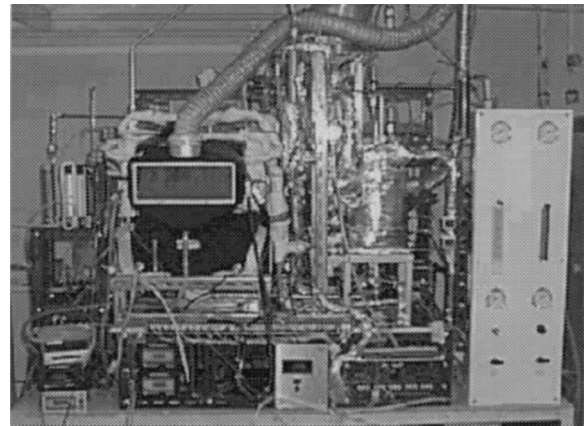


Fig. 11. Test situation of a 1 kW class system using a fuel processor and a module.

humidification are 1.0 and 1.48, under the same conditions as shown in Fig. 6. When the amount of fuel humidification was 1.0, if the amount of air humidification became 0.7 or less, the water content at the fuel exit became 1.0 or less, and the anode was found to be dry. This value is in agreement with the conditions under which the CO tolerance of the anode falls abruptly in Fig. 6. On the other hand, when the amount of fuel humidification was 1.48, if the amount of air humidification was low, the moisture of the anode was always maintained. These results indicate that maintaining a saturated steam pressure of the fuel cell anode gas outlet can decrease the influence of CO poisoning.

3.2. Operation of the modules

Fig. 9 shows the lifetime characteristics of the two-cell module with simulated reformed gas (10 ppm CO/20%

Table 1
Operation percent conditions of 1 kW class module

Items	Operation conditions
Fuel	Methane
Operation pressure	Atmospheric pressure
Reformer	S/C ratio Reaction temperature GHSV
	2.5 700°C 700 h ⁻¹
CO shift converter (two step series)	Burner fuel Reaction temperature GHSV
	Methane 220°C 900 h ⁻¹
CO removal reactor	Reaction temperature O ₂ /CO GHSV
	140–200°C 1.2 12,000 h ⁻¹
PEFC module (100 cm ² × 60 cells)	Fuel Oxidant Utilization
	Reformed gas Air U _f : 60%, U _{ox} : 40% at 300 mA/cm ²

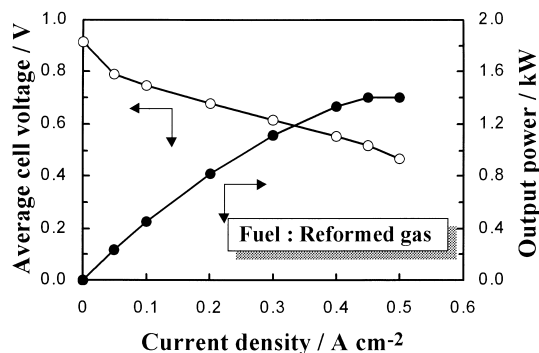


Fig. 12. Current–voltage curves of a 1 kW-class system.

CO₂/H₂ bal.) of a realistic composition as fuel. The test was run at a temperature of 80°C and a current density of 0.3 A/cm² under a gas condition of $U_f/U_{ox} = 70\%/40\%$. The rate of cell voltage drop was confirmed as 10 mV/1000 h. The stability of the anode developed in Section 2.1 was confirmed for at least 2000 h. Fig. 10 shows the current–voltage curve of the 1 kW class module. An output power of 1.2 kW (average cell voltage: 0.68 V) was achieved at a current density of 0.3 A/cm². There was no significant difference between the experiment with H₂ and 10 ppm CO/20% CO₂/H₂ bal. as fuel. These data indicate that the advanced anode has possibilities for both acceptable life-time characteristics and high initial performance. The testing of a 1 kW class system using our original fuel processor and module is shown in Fig. 11. The operation of conditions is shown in Table 1. Fig. 12 shows the current–voltage curve of the test. An output power of 1.1 kW (average cell voltage: 0.62 V) was achieved at a current density of 0.3 A/cm² under the condition of $U_f/U_{ox} = 60\%/30\%$.

4. Conclusions

The CO tolerance of the Pt–Ru alloy anode was improved by reducing its thickness from 40 μm to 20 μm. Maintaining a saturated steam pressure of the fuel cell anode gas outlet can decrease the influence of CO poisoning. When the amount of fuel humidification was 1.48 $P_{H_2O}/P_{sat(80°C)}$, cell performance was stable over a wide range of cathode-humidification conditions. A 1 kW class system with the improved CO-tolerant anode and our original fuel processor was successfully operated. An output power of 1.1 kW (average cell voltage: 0.62 V) was achieved at the current density of 0.3 A/cm².

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