

## Short communication

Development of a PEFC under low humidified conditions<sup>☆</sup>S. Yoshioka<sup>\*</sup>, A. Yoshimura, H. Fukumoto, O. Hiroi, H. Yoshiyasu*Advanced Technology R&D Center Mitsubishi Electric Corporation, Amagasaki, Hyogo 661-8661, Japan*

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**Abstract**

The life performance must be improved in order to commercialize polymer electrolyte fuel cells (PEFC). A decline of the cell voltage has been found to result from deterioration of the materials and a localization of reaction in the cell. We investigated the localization phenomenon, measuring the current density in the cell. The distribution of current density was measured by divided and isolated electrodes for a long period of operation. At the beginning of generation of electricity, a high current region is observed in the lower gas channel which is relatively humid. However, the high current region gradually moves to the upper dry channel in proportion to the voltage drop, which is remarkable under conditions of low humidity operation. This reaction seems to be reversible, since the PEFC can mostly recover the initial performance, once it is restarted. Improving the MEA and gas separators for low humidified conditions on the basis of this internal analysis, we operated a 20 cells PEFC stack of 0.4 kW for 5000 h and the stack showed  $-1.5$  mV/1000 h of average voltage degradation.

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**Keywords:** Polymer electrolyte fuel cells; Low humidity; Current density distribution**1. Introduction**

The polymer electrolyte fuel cell (PEFC) is of high interest in energy research due to the potential for direct conversion of chemical energy into electrical energy with high efficiency, high power density, low pollution and low operation temperature [1,2]. The PEFC is, therefore, considered to be an attractive power source for stationary co-generation units as well as for automotive applications. However, the PEFC has to overcome some engineering and economic problems for commercial success.

At present, the most severe problem of the PEFC is a low life performance as well as high material costs. Cost effectiveness can be obtained by using alternative electrode materials, cheaper and thinner membranes and also by reducing the need for peripheral equipment, such as a gas humidification section. Excess humidification is especially accompa-

nied by energy loss. Hence, an operation under low humidified conditions is of great advantage for energy conversion efficiency. Moreover the low humidified conditions hardly induce the problem that too much water will cause flooding of the cathode region and not allow the reactant gases to reach the catalyst layers. It is, however, considered that low humidified gas conditions accelerate the decay of the electrolyte membrane which is a key material for the PEFC. The stability of the membrane is determined by its water content. Proper hydration of the membrane is critical for maintaining membrane conductivity and mechanical stability [3,4]. In fact, the upper limit of operating temperature of conventional PEFCs using perfluorinated ionomers is dictated by the need to maintain membrane water content. Therefore, relative humidity of fuel and oxidant gases influences voltage performance and stability.

In order to evaluate the practical life, the reason for degradation has to be analyzed in detail. The decline of cell voltage is partly caused by irreversible chemical degradation of materials and partly caused by reversible resistance changes by the water content of membrane and both catalyst layers. Many studies have examined various aspects of PEFC performance

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as a function of operating conditions [5–8]. To achieve optimum voltage and life performance under low humidified gas conditions, the homogeneous electrochemical reaction over the electrode area is required. Since the excellent life performance probably requires highly humidified conditions, it is necessary to keep the homogeneous water content in the membrane under even low humidified conditions. The gas diffusion layers (GDL), electrodes, the separators and the humidifier were the targets of modifications. For example, the GDL has both hydrophilic and hydrophobic regions in itself though a conventional GDL is prepared by an almost completely hydrophobic treatment. Information on the current distribution change in long-term operation is essential for the development of cell design and membrane electrode assemblies (MEA). The demonstrated approaches to acquiring this knowledge are through the use of a segmented cell [9–11]. It is, however, important to evaluate the distribution for practically designed cells for commercial use. This paper is concerned with the current distribution dependent on the humidity conditions and operating time using an internally developed measurement system.

## 2. Experimental

We have designed and constructed a cell current measuring distribution system for analysis of PEFC performance. The cell was made up by an MEA with an active electrode area of  $110\text{ cm}^2$ , a cathode molded separator, an anode molded separator and a cooling plate made of carbon. These plates were 2 mm in thickness and attached on both sides of a MEA as shown in Fig. 1. Current collectors were divided into 15 segments and placed at intervals of 1 cm. A shunt resistor was attached to the individual current collector which had a

$2.2\text{ cm} \times 1.7\text{ cm}$  area each. Local current was measured by the voltage drop of the shunt resistor. The cell was precisely controlled at constant temperature by hot water through a cooling plate. Cell temperature are controlled at  $75 \pm 1^\circ\text{C}$  by water coolant. In usual measurements, an average current density was set at  $0.25\text{ A cm}^{-2}$ . Fig. 2 shows a schematic cross-section of the measuring cell, and Fig. 3 a photo of the current collectors and the insulation plate. The MEA was prepared using a thin-film technique developed in our laboratory. The catalyst layers of anode and cathode were cast from inks onto each carbon paper as gas diffusion layers. The carbon papers and a polymer electrolyte membrane were hot-pressed to form the MEA. The MEA was interposed by anode and cathode gas separators, which had flow channels on the MEA side. In addition, a cooling plate was placed on this separator and current collectors were placed on the cooling plate. Insulation plates made of polycarbonate sandwiched the cell. To improve the contact resistance of the cell components and to prevent leakage of the fuel cell hardware, this cell was compressed by springs and terminal metal plates. To diminish the contact resistant of the components, porous carbon paper was inserted between the insulation plate and the current collector as well as the individual current collector plates which were made of gold plated copper. The electric lead wires connected to the current collectors were kept as short as possible to keep ohmic losses to a minimum. Shunt resistance had to be lower than other cell resistances which contain activation, diffusion and ohmic polarization components. The sum of resistance can be calculated to be  $1.37\text{ mohm}$  at  $27.5\text{ A}$  ( $0.25\text{ A cm}^{-2}$ ) by the voltage drop from the open circuit voltage and the current operated. If the shunt resistance is equivalent to or higher than the cell resistance, local current measured is influenced by voltage drops across the shunt resistors. Since the average cell resistance of the divided individual cell was calculated to be  $20.6\text{ mohm}$  ( $1.37\text{ mohm} \times 15$ ), we employed a shunt resistance of  $1.00\text{ mohm}$ . This resulted in a higher measurement accuracy.

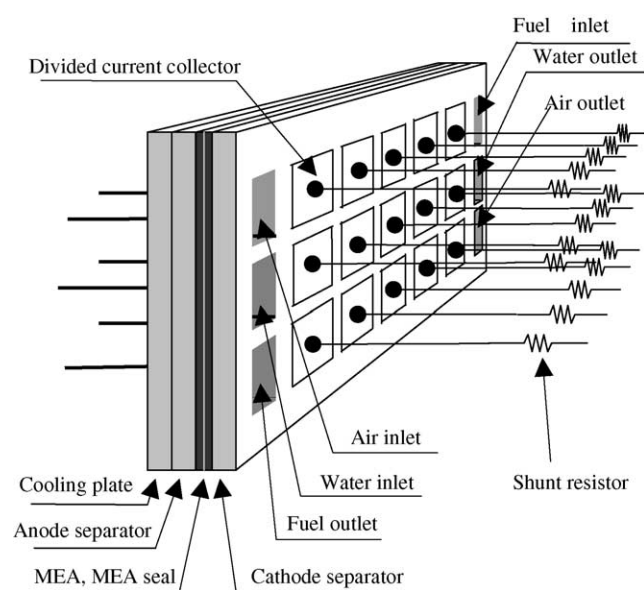


Fig. 1. Schematic of local current measurement system with  $3 \times 5$  divided current collectors.

## 3. Results and discussions

### 3.1. Analysis for voltage degradation

The cell voltage at an initial stage of the continuous operation was often observed to drop gradually, especially, under low humidified conditions in the case of our conventional cells as shown in Fig. 4. It is, however, possible to restore the voltage by a shut down and a start up procedure. To elucidate the reason of the recovery, it is necessary to improve the cell performance. We analyzed the reaction distribution in the cell by using the local current measurement system.

Current distributions were measured from the voltage drop of resistors when the cell was operated at a constant temperature of  $75^\circ\text{C}$  and at a constant average current density of  $0.25\text{ A cm}^{-2}$ . Fuel and oxidant were supplied at 75 and 40% of gas utilization, respectively. The temperatures of the hu-

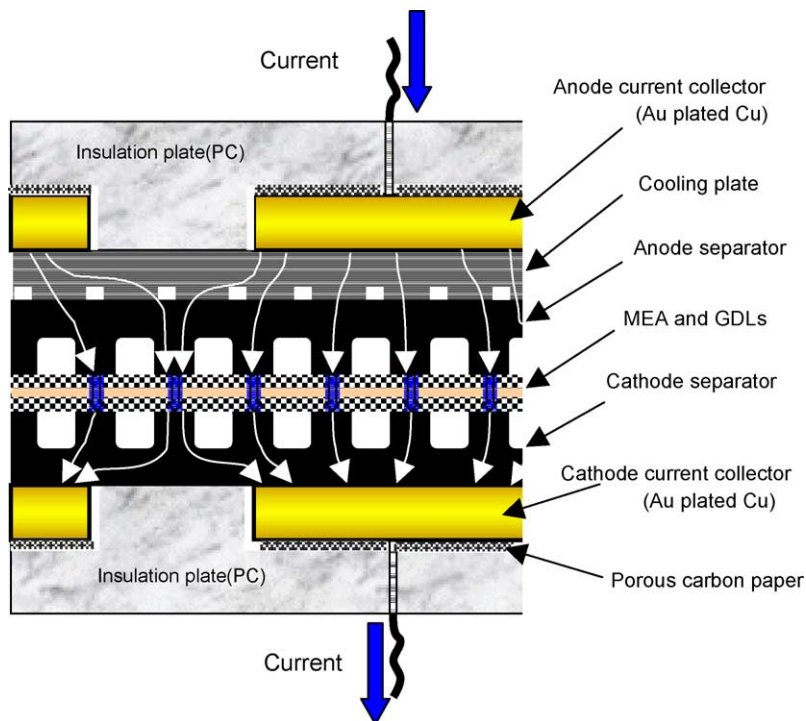


Fig. 2. Schematic image of the cross-section of the measuring cell.

modifiers for the anode and the cathode were set at (A) 55 °C, (B) 65 °C, (C) 75 °C. The current distributions depended on the dew-point of gases. At an extreme low humidity condition of (A) in Fig. 5, there was a difference of about 17% between a maximum and minimum current. And the region of maximum current was localized near the air outlet where the membrane had a higher water content relatively. The membrane near the air inlet was considered to dry up even if water is formed by the cell reaction in the MEA. Since the evaporation rate is faster than the reaction for our conventional cell structure, the water content of the membrane near the

air inlet is in equilibrium with the relative humidity which is calculated to be about 40 RH% from the composition of the cathode gas. Therefore, local cell resistance near the air inlet is higher than near the air outlet. Equally the evaporation is caused by fuel flow. However, the fuel channel pattern hardly depends on the reaction distribution on the basis of the evaporation of water in the membrane. This is because the flow rate of the fuel is lower than that of air in the present condition of gas utilization. On the other hand, the current distribution at the (C) temperature was more homogeneous than that at (A) and (B). This tendency was responsible for the homogeneous water content of the membrane through the



Fig. 3. Photo of insulation plate made of poly carbonate and current collectors.

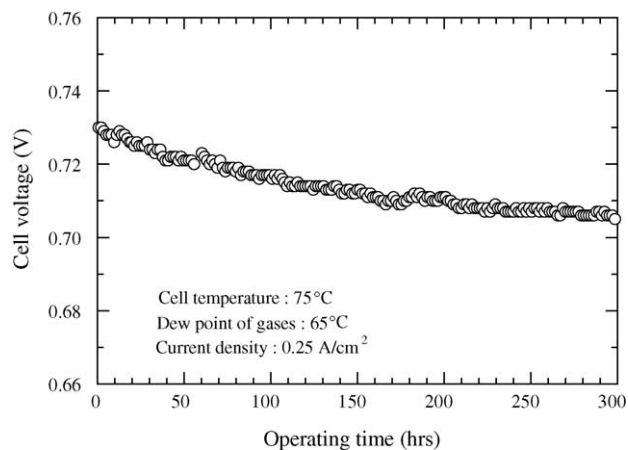


Fig. 4. The voltage change of a conventional cells for a continuous operation under low humidified gas conditions.

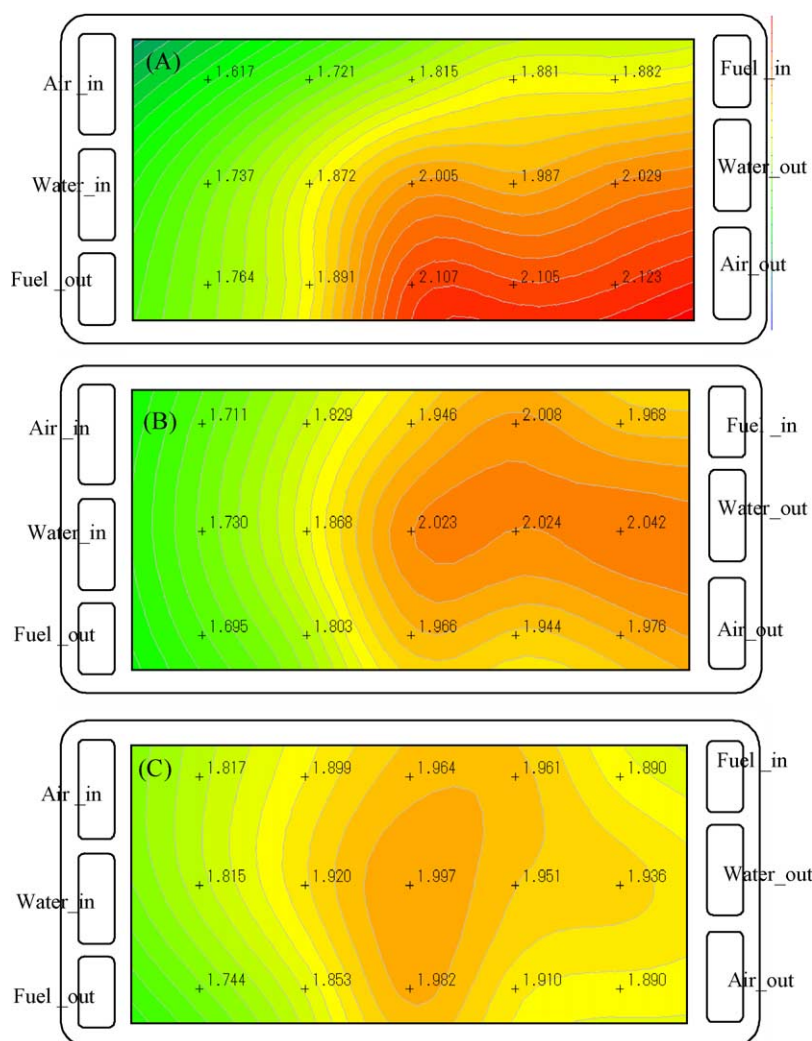


Fig. 5. Comparison of the reaction current distributions at an average current density of  $0.25 \text{ A cm}^{-2}$  and at a cell temperature of  $75^\circ\text{C}$ . Oxidant and fuel gases are fed at a dew-point temperatures of (A)  $55^\circ\text{C}$ , (B)  $65^\circ\text{C}$ , (C)  $75^\circ\text{C}$ .

reaction area of the cell at a high humidity condition since the whole of membrane is equilibrium with the gases of 100% relative humidity in the condition (C).

The reaction distribution varies with operating time gradually. Fig. 6 shows the change of current density profile along the gas channels at a dew-point temperature of  $65^\circ\text{C}$ . The cell was operated at a temperature of  $75^\circ\text{C}$  and at a constant average current density of  $0.25 \text{ A cm}^{-2}$ . The current density near the gas outlet and the gas inlet decreased after 250 h operation. The decrease in the current density near the gas outlet is considered to be responsible for an excess accumulation of reaction water and osmotic water drag from the anode even if it is operated under a low humidified condition. And a gradual dry-up of the membrane caused a decrease of current density. In the middle region of the cell, on the other hand, a current density increases relatively. The current distribution change corresponded to a voltage drop. The cell voltage recovered to the initial value when the cell shut down temporarily or the

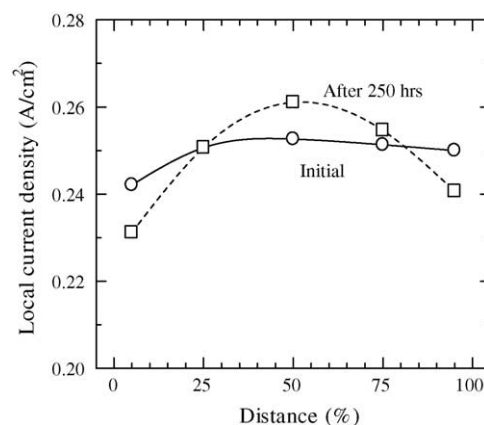


Fig. 6. Distributions of measured local current density along the gas channel at the initial stage of operation and after 250 h.



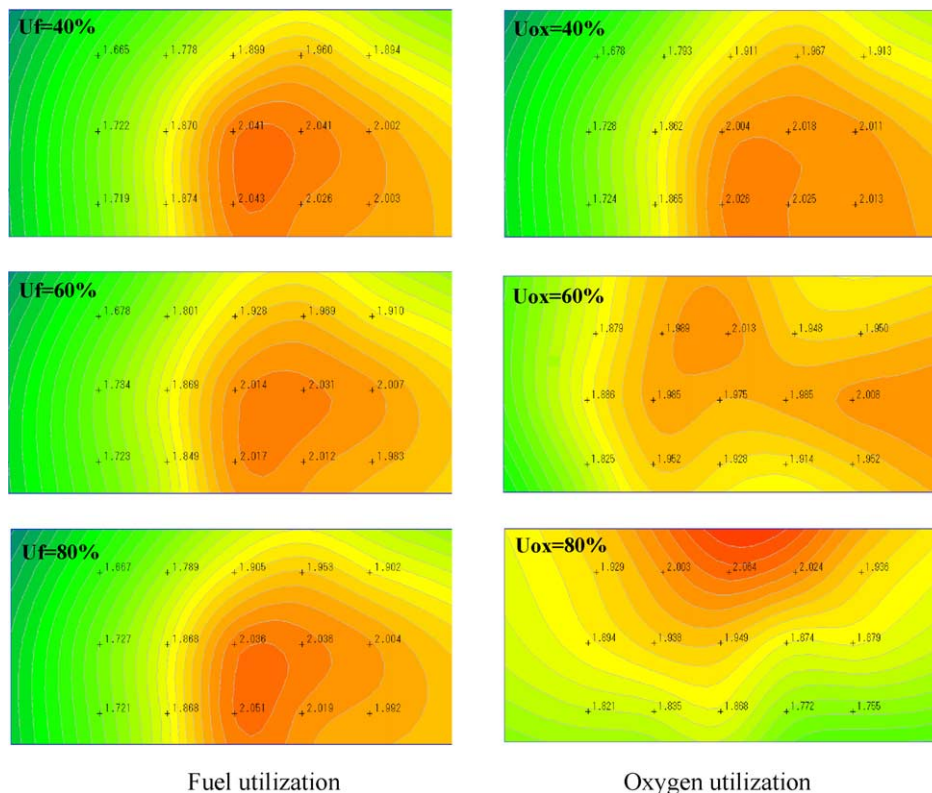


Fig. 7. Current distributions at some gas utilization. Left figures—the influence of fuel utilization at a constant oxygen utilization of 40%. Right figures—the influence of oxygen utilization at a constant fuel utilization of 75%. Average current density is set at  $0.25 \text{ A cm}^{-2}$ . Inlet and outlet manifolds of gases and coolant are placed at the same position in Fig. 5. The temperatures are kept at a constant of  $75^\circ\text{C}$  by circulation of coolant. Dew points of gases are kept at a constant of  $65^\circ\text{C}$ .

operation conditions changed to high humidity. This result indicates that homogeneous reaction distribution is advantageous to the stable performance in long-term operation. The current density depends not on fuel utilization but oxygen under low humidified conditions as shown in Fig. 7. The difference of utilization corresponds to that of gas flow rate. Since water transfers from anode to cathode in PEFCs, the anode is in a dry condition, while the cathode is in a high humidity condition. The low flow rate in the cathode induces stagnation of water which floods the cathode as shown at the oxygen utilization of 80%. Moreover, near the air outlet, the cathode near the gas outlet shows high reaction resistance because of the low oxygen partial pressure. In any event, this failure can be avoided by redesign of the gas flow channel.

### 3.2. Endurance test of a PEFC stack

We have been developing PEFC stacks focusing on the stability of the cell voltage for long-term operation under low humidified conditions. It is likely that most of the gradual voltage degradation is caused by the decrease of water content in the membrane near the gas inlet, and by flooding especially in a cathode near the gas outlet. The advanced cell has been developed from the viewpoints of both maintaining the water content of membrane and im-

proving the drainage of reaction water. The water content of MEAs that were used in the advanced stack were controlled by the originally designed electrode which has both hydrophobic and hydrophilic region in catalytic layers and GDLs. The gas flow channels were also improved on the basis of the depression of evaporation near the air inlet.

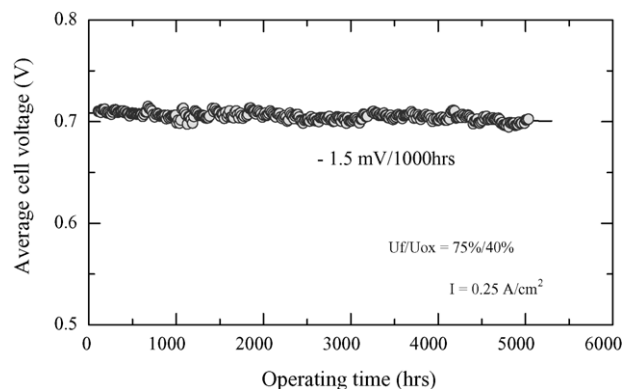


Fig. 8. Long-term endurance operation test of an advanced PEFC stack of 20 cells (0.4 kW) under 74% relative humidity in cathode gas and 57% relative humidity in anode gas that contains 25%  $\text{CO}_2$ , 75%  $\text{H}_2$  and 10 ppm  $\text{CO}$ . Coolant operating temperature at stack outlet was kept at  $75^\circ\text{C}$ .

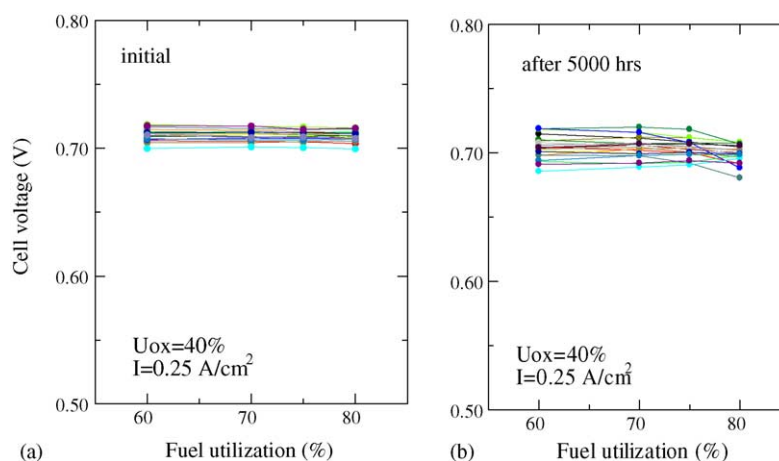


Fig. 9. Cell voltage change of the 20 cell stack from (a) initial to (b) 5000 h operation. Plots show each cell voltage depending on fuel utilization.

For an endurance continuous operation, advanced 20 cells stack of approximately 0.4 kW was constructed. The number of cells was decided by the ease of a long operation and by the validity of the test. The operating temperature were controlled at  $75 \pm 0.5^\circ\text{C}$  by the water coolant. Gas conditions were set at 74% relative humidity in cathode (dew point:  $68^\circ\text{C}$ ) and 57% relative humidity in anode (dew point:  $62^\circ\text{C}$ ). The anode gas contained 25%  $\text{CO}_2$ , 75%  $\text{H}_2$  and 10 ppm  $\text{CO}$ , while ambient air was supplied to the cathode. The utilization of fuel and oxygen was set at 75, 40%, respectively. An average degradation rate of 1.5 mV/1000 h was achieved as shown in Fig. 8. As a result, the advanced PEFC stack has sustained a prominent voltage stability under low humidified conditions. On the other hand, some insights for a longer operation have been revealed. Fig. 9 shows the voltage change of each cell. The whole cell voltage varied from 0.70 to 0.72 V in initial operation. The difference between the maximum and minimum voltage increased from 20 to 45 mV after 5000 h operation.

#### 4. Conclusions

We were able to determine the current distribution in a practical operating cell by a measurement system using divided current collectors. The effect of low humidified conditions on current distribution is presented. It has become apparent that the reaction current concentrates near the gas outlet where the humidity is relatively high. Moreover, a high current region gradually moves to the upper area for long-term operation, which was found to be reversible since the current was recovered to the initial distribution when the cell was stopped and restarted. Lifetime can be extended through the improvement of cells, based on the analysis of humidity de-

pendence. Significant progress in maintaining the water content of the membrane homogeneously, has been conducted to achieve good durability. The average voltage degradation rate of 1.5 mV/1000 h has been achieved for the PEFC under low humidified conditions.

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