Investigation into Electrocatalysts for Long-term Endurance test Using Micro-electrode Technique

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1. Introduction

A long-term operation test of PEFCs was conducted for single cells having an effective area of 25 cm^2. In order to clarify the cause of the voltage decay, materials composing membrane electrode assembly (MEA) were analyzed by disassembling a cell every 3000 hours. After the long-term operation, changes of materials, such as particle size change of Pt-Co cathode catalyst, loss of ionomer layers on Pt-Co/C, decrease in thickness of the polymer electrolyte membrane, and pore size changes of the cathode, were observed [1]. The micro-electrode technique was applied to investigate the electrochemical properties of the cathode electrode catalyst [2]. O_2 reduction voltammograms of the electrode catalysts were measured after the long-term operation.

2. Experimental

A perfluorosulfonic acid membrane with thickness of approximately 50 μm. The membrane was supplied by Asahi Kasei E-materials Corporation. Pt-Ru/C (54 wt%) and Pt-Co/C (52 wt%) supplied by Tanaka Kikinzoku Kogyo Co., Ltd were used for the anode and cathode catalyst, respectively. Single cells having an operating electrode area of 25 cm^2 were fabricated. The loading amount of Pt was 0.5 mg cm^{-2} for both the anode and the cathode. The long-term durability test of the test cells was conducted at 80 °C under a constant current density of 200 mA cm^{-2}, and 100% relative humidity (RH) for the anode and 66% RH for the cathode [3].

Small particle of electrode catalyst (50~100μm) was put on the Au electrode (φ50μm) as a working electrode. O_2 reduction voltammograms of the electrode catalysts was observed in 0.5 mol dm^{-3} H_2SO_4 at a scan rate of 1 mV s^{-1}.

3. Results and discussion

Figure 1 shows the terminal voltage of a test cell during a continuous 12000 h operation. The decay rate of the cell voltage was relatively large in the beginning, but was decreased to about 4 μV h^{-1} in a period from 3000 to 6000 h. In the later stage of the test from 9000 to 12000 h, this cell showed somewhat larger decay rate of about 7 μV h^{-1}.

In Fig. 2 (a) and (b), the catalyst particles before and after operating 9000 h, respectively, are presented. The outer ionomer layer, which is indicated by a broken line, became much thinner after 9000 h operation. And it is assumed that the outer ionomer layer was gradually decomposed during long-term operation [4], [5].

Micro-electrode technique was applied for the evaluation of the electrode catalyst. Figure 3 shows oxygen reduction reaction (ORR) characteristics of the 0 hour operation (a) and 9000 hours operation (b). According to the figure, the onset potential for O_2 reduction varies with the operation times. In addition, the magnitude of the diffusion-limited current density decreases with increasing operating time of the single cell.

Acknowledgement

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References

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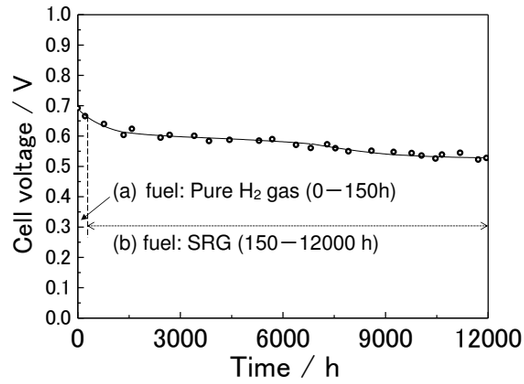

Fig. 1 Transition of cell voltage of a test cell during a continuous operation for 12000 h. Current density: 200 mA cm^{-2}, Temperature: 80 °C, Humidity: 100% RH for anode and 66% RH for cathode.

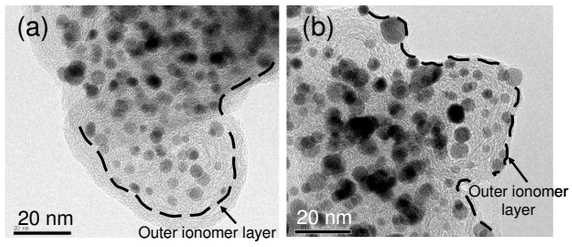

Fig. 2 TEM images of catalyst particles of cathode: (a) Initial stage, (b) After operation for 9000 h. The broken lines indicate outer ionomer layers of Pt-Co/C particles.

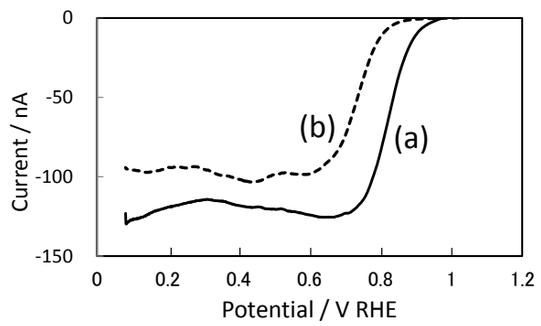

Fig. 3 i-E curves of ORR in O_2 satulated 0.5 mol dm^{-3} H_2SO_4 solution. (a): a catalyst of beginning operation, (b): a catalyst of 9000 hours operation. Scan rate of 1mVs^{-1}.