Oxygen reduction characteristics of IrO_2 covered Pt electrode

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Introduction

The polymer electrolyte fuel cells (PEFCs) are under developing for the electric vehicles and the co-generation systems, because of the high power density and the low operation temperature. For the practical applications of the PEFCs, the high performance and low cost are required. In order to obtain the high performance of PEFCs, the large cathode overpotential should be reduced.

The purpose of this paper is the development of the high-activated cathode using the interaction between Pt and second materials. Iridium oxide was chosen as the second material. It is active for oxygen evolution in aqueous solutions and it was reported that the theoretical equilibrium potential of the oxygen electrode reaction at IrO_2 covered Pt electrode was observed1). However, the effect of the interaction between Pt and IrO_2 on the oxygen reduction reaction is not clear.

Experimental

Pt plate (10mm×10×0.2, R.F.: 1.5) was immersed in the Ir plating liquid (Iridex 100: Japan Electroplating Eng. Co.Ltd.), and Ir was deposited for t seconds at 85℃ with reduction current of 2.5 mA cm^{-2}. The electrode of t =10 and 20 was defined Pt/IrO_2-1 and Pt/IrO_2-2, respectively. The covering quantity of iridium on those electrodes was 25 and 50mC cm^{-2}, respectively. Afterwards, IrO_2 film was grown by repeating scan of potential within 0.05-1.5V(vs. RHE) in 1 mol dm^{-3} H_2SO_4 with N_2 bubbling at 298K. Slow scan cyclic voltammetry (1mV s^{-1}) was performed within 0.4-1.2V in 0.1 mol dm^{-3} under oxygen atmosphere at 298K in order to examine the catalytic activity of oxygen reduction. The current was affected by the scanning direction, although the scanning rate was slow (1 mV/s). In this experiment, the current value observed in the cathodic direction was adopted. Furthermore, the cycle number affected the reduction current. The steady state was reached after 5 or 6 cycles, and the steady state value was adopted. Reversible hydrogen electrode (RHE) was used as reference electrode. The current density was shown per geometry area.

Results and Discussion

Figure 1 shows the cyclic voltammogram of Pt, Pt/IrO_2-1 and Pt/IrO_2-2 with the scanning rate of 50mV/sec. The reversible peaks in IrO_2 covered Pt electrodes near 0.9V was observed. These peaks are based on the change of the stoichiometry of the Ir oxide2). In Pt/IrO_2-1, reduction peak (near 0.8V) of the Pt oxide film was also observed. This suggested that the iridium oxide film was porous and the platinum did not covered completely. In Pt/IrO_2-2, since the quantity of deposited Ir was large, the peaks that corresponded to Pt oxide was not observed.

Figure 2 shows the Tafel plot for oxygen reduction reaction on Pt and IrO_2 covered Pt electrodes in 0.1 mol dm^{-3} H_2SO_4. Since Tafel slope of the electrodes was almost the same (60mV/decade), it was thought that the mechanism of the oxygen reduction did not change. The catalytic activity of oxygen reduction on Pt/IrO_2-2 electrode is lower than that of platinum, since the active site of the platinum surface was covered with iridium oxide. On the other hand, oxygen reduction current of the PtIrO_2-1 electrode at 0.85V was 1.38 times larger than that of platinum. High catalytic activity of Pt/IrO_2-1 seemed to appear by the interaction between Pt and IrO_2.

Conclusion

In order to develop the high-activated cathode for PEFC, oxygen reduction catalytic activity of the IrO_2 covered Pt electrode was examined. Two Pt electrodes (Pt/IrO_2 1 and 2) were electrochemically covered with IrO_2. Iridium covering quantity of those electrodes was 25 and 50mC cm^{-2}, respectively. In 0.4-1.2V potential range, the oxygen reduction current was measured by 1mV s^{-1} slow scan cyclic voltammetry. The steady oxygen reduction current of the Pt/IrO_2 1 at 0.85V vs. RHE became 1.38 times larger than that of Pt in the cathodic sweep.

References

1) R. Notoya et al. US Patent No.4917972 (1990).
2) D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, 55, 375-381 (1974).

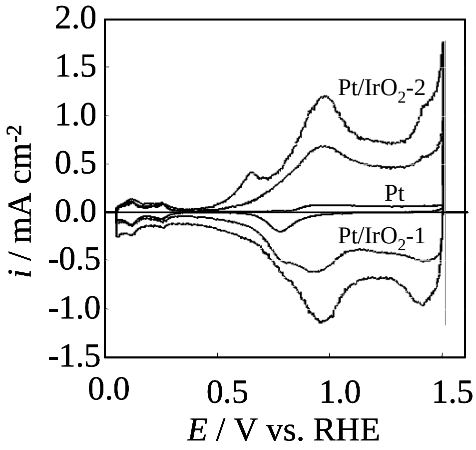

Fig.1. Cyclic voltammogram of Pt and IrO_2 Covered Pt electrode in 1M H_2SO_4.
Triangular sweeps at 50mV/s, 0.05-1.5V
N_2, 298K.

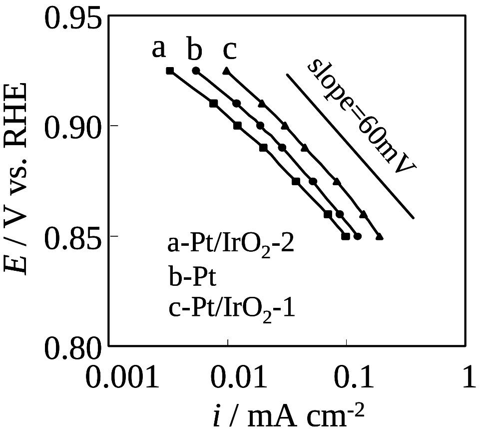

Fig.2. Comparison of Tafel plots for oxygen reduction on Pt and IrO_2 covered Pt electrodes in 0.1M H_2SO_4.
1mV/s, 0.4V-1.2V, cathodic sweep, O_2, 298K.