RRDE Studies on Oxygen Reduction and Hydrogen Oxidation Reactions of Pd Single Crystal Electrodes

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INTRDUCTION

Although platinum (Pt) material has been mainly used as a catalyst of the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR), which are a cathode and anode reactions, respectively, of polymer electrolyte fuel cell (PEFC), electrocatalytic activity of Pt is still inefficient for practical use for PEFC and Pt is so expensive. Many research groups are finding new catalyst having a higher catalytic activity and cheaper than Pt. Palladium (Pd) has similar chemical properties because Pd is in the same group as Pt in the periodic table and Pd has hydrogen absorption property, and therefore, Pd is expected to be employed as a new catalyst material both for ORR and HOR. Some groups have already measured the ORR activity of Pd single crystal electrodes using rotating disk electrode (RDE) technique [1,2].

A rotating ring-disk electrode (RRDE) measurement is one of the most useful electrochemical techniques to investigate electrochemical reactions including both kinetics and energetics, such as kinetic current density, the number of electrons, and half-wave potential. Moreover, RRDE leads us to the intermediate reaction although information about it is not obtained from the similar technique such as the RDE measurement.

In this study, the electrocatalytic activity for ORR and HOR using the rotating Pd single crystal disk - polycrystalline Pt ring electrode system was investigated and compared with the data of the Pt single crystal electrodes.

EXPERIMENTAL SECTION

Pd and Pt single crystal disks (Pd(100), Pd(110), Pt(111), Pt(100) and Pt(110)) were mechanically processed to connect our RRDE system, were mechanically polished with a diamond paste, and then were annealed by using an induction heater under ultrapure Ar and mixed gas (Ar:H_2) atmosphere, respectively, at 1300 °C and 1600 °C, respectively, for 1 h. After that, they were quenched in ultrapure water under the same atmosphere. The annealed/quenched electrode was set with the RRDE holder with an ultrapure water droplet for protection. The single crystal disk electrode in the RRDE holder was dipped at 0.50 V (vs. RHE) in an oxygen-saturated 0.1 M $HClO_4$ and then a linear sweep voltammogram (LSV) was measured at several rotation rates for the ORR measurements. The potential was scanned from 0.20 V to the positive direction up to 1.00 V at a scan rate of 10 mV s^{-1}. In order to examine whether hydrogen peroxide was produced on the disk electrode or not, the potential of the ring electrode was kept at 1.30 V, which is more positive than the oxidation potential of hydrogen peroxide. From the Koutecky-Levich plots of the data at several potentials, kinetic current density, $\boldsymbol{J_k}$, and the number of electrons used for ORR were obtained.

RESULTS AND DISCUSSION

Figure 1 shows a typical example of the set of LSVs of the Pd(100) disk - polyPt ring electrode. These LSVs have the following two characteristic regions similar to those of the literatures [1,2]; the diffusion-limiting currents ($\boldsymbol{J_d}$) region between 0.3 - 0.7 V and the mixed diffusion and kinetic control region between 0.7 - 1.0 V. Since no oxidation current flows at the ring electrode in the potential range between 0.3 - 1.0 V, ORR is proceeding with four electrons, indicating no production of hydrogen peroxide.

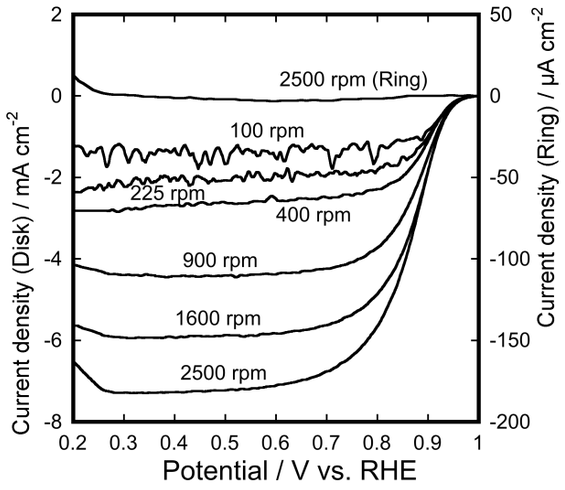

Figure 1. LSVs for ORR of the Pd(100) disk - polyPt ring electrode measured in the oxygen-saturated 0.1 M $HClO_4$ at a scan rate of 10 mV s^{-1} with several rotation rates. Ring electrode potential was kept at 1.30 V.

From the Koutecky-Levich plot at several electrode potentials, the number of electrons for ORR was 3.93 and 3.96 at the Pd(100) and the Pd(110) electrode, respectively, also suggesting that four electron reactions ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) are dominant at the potential range between 0.30 V and 1.00 V. The kinetic current density of the Pd(100), $\boldsymbol{J_k}$, was 2.14 mA cm^{-2} at 0.90 V, which is best value for ORR observed for other single crystal electrodes.

REFERENCES

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[2] S. Kondo et al., *J. Phys. Chem. Lett.*, 113 (2009) 12625.