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Electrochemical Behavior of Pt-modified Cobalt Oxide Electrodes in NaOH Solutions under Oxygen Atmosphere

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Pt-modified cobalt oxides (Pt + Co_3O_4) were prepared from H_2PtCl_6 and $Co(NO_3)_2$ by pyrolysis. The deposited Pt species were in highly oxidized states. Glassy carbon-supported Pt + Co_3O_4 electrodes of ca. 10 mol%-Pt exhibited the equilibrium oxygen electrode potential and electrocatalytic activity toward the O_2 reduction in O_2-saturated 1 mol dm^{-3} NaOH solutions.

Kinetics of oxygen electrode reaction and design of highly active oxygen electrodes are important subjects in the development of fuel cells, oxygen sensors, water-based electrochemical energy conversion systems, and so on. Platinum electrodes reduce O_2 to H_2O_2 or to H_2O, depending on the electrode potential, and the latter reaction takes place at rather low potentials. Recently, spinel-type metal oxides such as Co_3O_4 were found to be promising electrocatalysts for the O_2 cathodes.[1-4] Since metal oxide such as Co_3O_4 is active toward catalytic decomposition of H_2O_2 to H_2O,[1-5] combination of Pt and Co_3O_4 may be expected to enhance the complete reduction of O_2 to H_2O. We have investigated this synergistic effect for Pt + Co_3O_4 binary electrocatalysts in NaOH solutions under O_2 atmosphere.

Co_3O_4 oxide was prepared by hydroxide precipitation from aqueous Co(Ⅱ) salts.[4] A solution containing 1.4 mol dm^{-3} of Co^{2+} ions was prepared from $Co(NO_3)_2 6H_2O$ (Wako Pure Chemicals Ind., 99.5% in purity) using deionized water, and after N_2 bubbling and cooling in an ice water bath, deoxygenated 5 mol dm^{-3} NaOH solution was added dropwise to obtain pink-colored precipi-

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tate of $Co(OH)_2$. After adding 30 % H_2O_2, the precipitate was separated from the solution by centrifuge, dried at 80 ℃ in an oven and heated at 600℃ in an electric furnace for 5 h. Both bulk and surface composition of this oxide was assigned to be Co_3O_4[6] by XRD and XPS (Shimazu Corp., ESCA-750).

To prepare Pt-modified Co_3O_4 (Pt + Co_3O_4) electrodes, aqueous H_2PtCl_6 solutions were added to a suspension of Co_3O_4 at a required mole ratio. The mixtures then dried at 80 ℃ and calcined at 300 ℃ for 1 h to yield Co_3O_4 + Pt composits. These oxides were suspended in deionized water, painted on GC (glassy carbon) rods (Tokai Carbon Co. Ltd., GC-20S, 5 mm$^{\phi}$), dried at 80 ℃ and calcined at 300℃ for 1 h. Electrochemical experiments were carried out in a three-compartment cell.

Figure 1 shows cyclic voltammograms of GC-supported electrodes of Co_3O_4 and Pt + Co_3O_4 in a N_2- and an O_2-saturated 1 mol dm^{-3} NaOH solutions (pH = 14), together with those of a smooth Pt electrode. In the case of the GC-supported Co_3O_4 electrode under N_2 atmosphere (dotted curve 1), oxidation and reduction current waves were seen at potentials higher than 1.1 V (vs. RHE). At the lower potentials only a double-layer charging current was observed. In the O_2-saturated solution (solid curve 1), reduction currents appeared at $E < 0.8$ V in the negative- and positive-going sweeps. They monotonously increased with a decrease of the electrode potential. In the N_2 saturated solution, the Pt + Co_3O_4 electrode of 11 mol%-Pt showed a similar feature in the

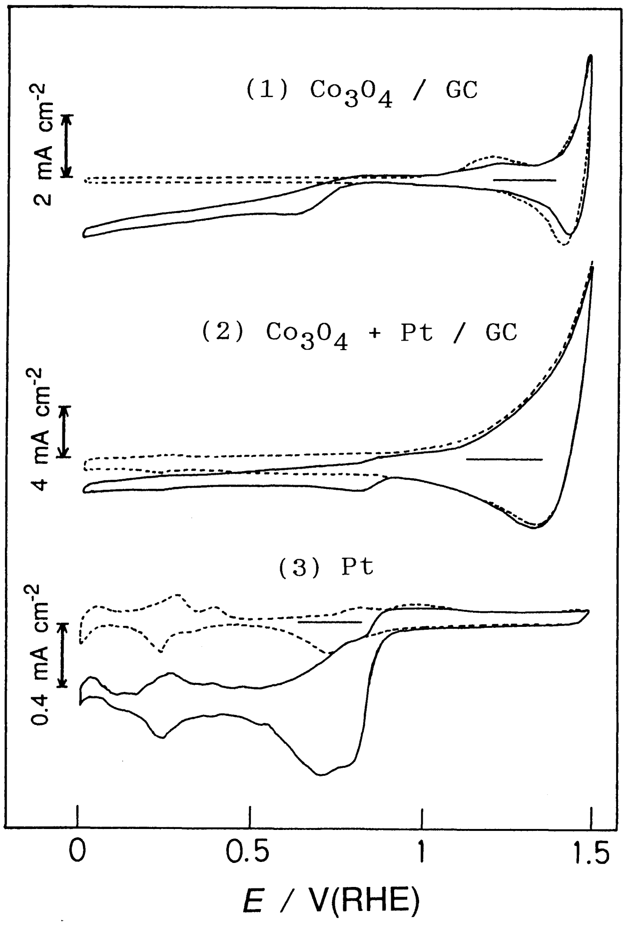

Fig.1. Cyclic voltammograms of glassy carbon-supported electrodes of (1) Co_3O_4 and (2) Pt + Co_3O_4 in 1 mol dm^{-3} NaOH, together with those of a smooth Pt electrode. (---); 1 atm N_2, (——); 1 atm O_2. Sweep rate; 100 mV s^{-1}. Surface areas of the glassy carbon substrates (ca. 0.6 cm^{-2}) were used as apparent surface areas of the electrodes of (1) and (2).

voltammogram (dotted curve 2) as the Co_3O_4 electrode, but after introduction of O_2 into the solution, O_2 reduction took place at $E < 0.9$ V in both the negative- and positive-going sweeps. Thus, Pt modification enhanced the O_2 reduction.

A typical cyclic voltammogram of a smooth Pt electrode in the O_2-free NaOH solution was shown as the dotted curve 3. In the O_2-saturated solution (solid curve 3), currents of O_2 reduction appeared at potentials below 0.9 - 1 V. In the negative-going sweep the reduction current wave showed a complex structure. A peak around 0.8 V involves the reduction current of Pt oxide layer. In the hydrogen region, $E < 0.4$ V, the hydrogen wave was still observable.

Rest potentials of the Pt + Co_3O_4 electrodes were measured in the N_2- and O_2-saturated 1 mol dm^{-3} NaOH solutions. Under N_2 atmosphere, Co_3O_4 electrodes modified and unmodified with Pt showed rest potentials around 0.9 V. Similarly, the rest potential of the polycrystalline Pt electrode was 0.9 - 1 V. Under O_2 atmosphere the rest potentials of all the electrodes studied increased. As presented in Fig.2, the highest rest potential was obtained at the Pt + Co_3O_4 electrodes of ca. 10 mol%-Pt. The value was 1.22 V, which is practically in agreement with the thermodynamic equilibrium potential of O_2 / H_2O (1.23 V vs. RHE). The Pt + Co_3O_4 electrodes of other composition, as well as the pure Pt metal electrode (shown at the right-hand side ordinate) showed significantly lower rest potentials. The synergistic effect observed for the Pt + Co_3O_4 composits is notable.

In the case of the Pt + Co_3O_4 system, Co_3O_4 particles may affect chemical states of the deposited Pt species. XPS spectra of Co2p and O1s of the

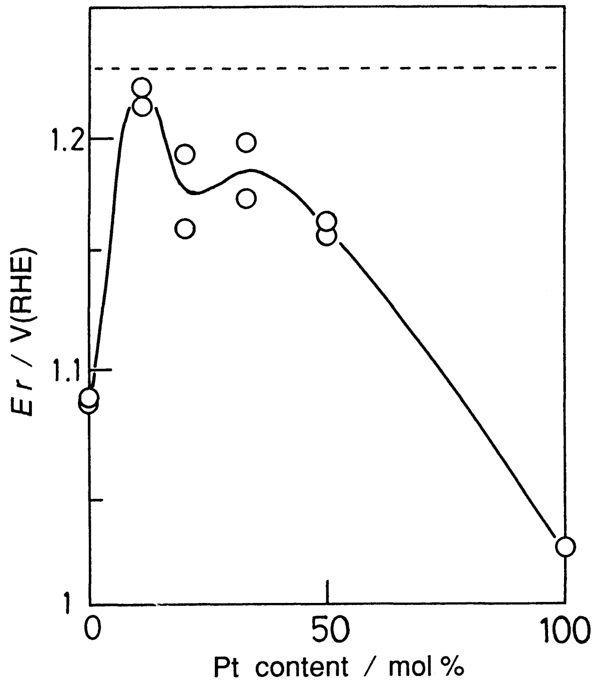

Fig.2. Relationship between mol%-Pt and the rest potential of glassy carbon-supported Pt + Co_3O_4 electrodes obtained in 1 mol dm^{-3} NaOH under 1 atm O_2 atmosphere. The result obtained on a smooth polycrystalline Pt electrode is given at the right-hand side ordinate. The broken line indicates the equilibrium potential of O_2 / H_2O (1.23 V vs. RHE).

Pt-modified Co_3O_4 (11 mol%-Pt) specimen, shown in Fig.3, exhibit similar spectroscopic features as those of the Co_3O_4 specimen. Pt4f spectrum shows that $4f_{7/2}$ and $4f_{5/2}$ peaks are located at rather high energy positions, i.e., 75 and 77 eV as compared with those of Pt metal (70.7 and 74.0 eV, respectively [7]). This result suggests that Pt atoms or small cluster particles deposited on Co_3O_4 oxide particles are at a highly oxidized state, Pt(Ⅳ).

The synergism in the Pt-modified Co_3O_4 electrodes (Fig.2) may be attributed to; (1) Pt atoms in particular chemical states which act as active sites for the O_2 redox reaction, (2) Co_3O_4 particles enhance the decomposition of H_2O_2 produced at Pt sites.

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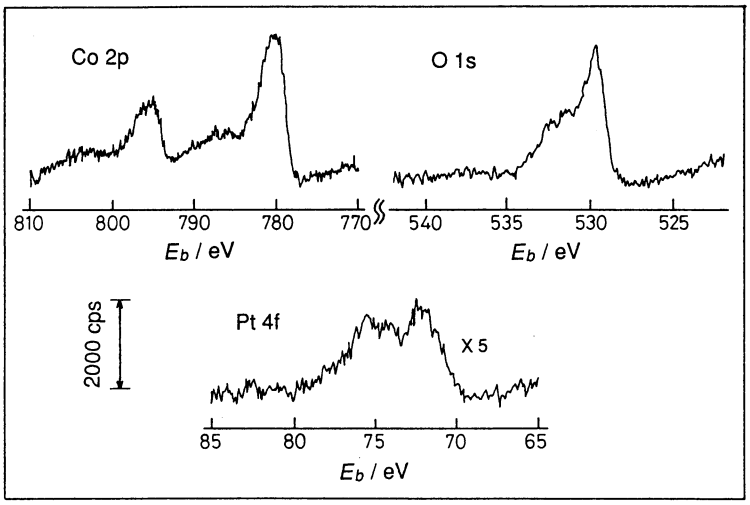

Fig.3. XPS spectra of Co2p, Pt4f and O1s of the glassy carbon-supported Pt + Co_3O_4 electrode (11 mol%-Pt).

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