Platinum-free Catalyst for Efficient Reduction of Oxygen at Air Cathode

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Electrocatalytic activity and selectivity for oxygen reduction to water on platinum-free catalysts prepared from transition metal hexacyanometallate precursors have been examined using a rotating ring-disk electrode technique. The results obtained indicated that a catalyst containing copper and iron promotes so-called four-electron reduction reaction of oxygen at a potential close to or higher than that of a Pt electrode, so that it could be a possible candidate substituting for Pt-based catalysts of air cathodes.

Electrochemical reduction of oxygen has been of great importance in various applications, such as air cathodes of fuel cells and metal/air batteries to generate electrical energy, and air cathodes of electrolytic processes to reduce power consumption. For oxygen reduction at low and moderate temperatures, Pt or Pt alloy catalysts have been most widely used, because Pt-based catalysts are the most efficient catalyst for oxygen reduction by transferring totally four electrons,[1] so-called four-electron reduction. However, inexpensive catalysts with employing abundant nonnoble elements are desired. Many efforts have been made to explore Pt-free catalysts, such as transition-metal oxides,[2] transition metal macrocycles,[3] and alternative catalysts,[4] for both high activity and selectivity for four-electron reduction of oxygen to yield water as product.

Recently, we have reported an easy and inexpensive method to prepare Pt-free catalysts from the nitrogen-containing inorganic precursors (transition metal hexacyanometallates, Prussian blue analogs, PBs) dispersed on a carbon support.[5] An advantage of using such inorganic precursors is that a series of compound consisting of various combinations of transition metal ions located at nitrogen-coordinated and carbon-coordinated sites can be easily prepared from popular transition-metal salts to examine the effect of combination of transition elements together with the effect of coordination field in the precursor upon the catalytic activity for oxygen reduction. By taking such an advantage, it was found that the combination of cobalt and iron leads to the prominent synergistic effect of cobalt and iron on the catalytic activity for oxygen reduction.[5] However, there still seemed to be a problem concerning generation of an intermediate, hydrogen peroxide, during oxygen reduction. Hydrogen peroxide is a strong oxidizing species, so that the peroxide generation during oxygen reduction is a crucial factor on deterioration of air cathode. Here, we report a novel Pt-free catalyst showing both high activity and selectivity for four-electron reduction of oxygen.

The catalysts were prepared as described previously.[5] The carbon black powder (Vulcan XC-72R, Cabot Corp.) was pretreated in 9 M (1 M = 1 mol dm^{-3}) HNO_3 at room temperature for ca. 12 h. The precursors were prepared by slowly adding 0.024 M aqueous $M'SO_4$ (M′ = Mn, Fe, Co, Ni, and Cu) solution into a vigorously stirred suspension of the pretreated carbon black in 0.02 M $K_3M''(CN)_6$ (M″ = Fe and Co) solution. The molar ratio of M′ to M″ in the mixed solution was 1.2. The loaded amount of the Prussian blue analogs was ca. 5×10^{-4} mol on 0.1 g of carbon support. The obtained precursor was heated up to 800 °C at a rate of ca. 200 deg/h under a nitrogen flow, followed by keeping at 800 °C for ca. 10 min. For brevity, the obtained sample was denoted as HT-M′[M″]PB/C.

Polarization measurements for oxygen reduction were carried out in a glass cell with a rotating ring-disk electrode. A platinum ring–glassy carbon (GC) disk electrode assembly (disk diameter 5 mm, ring inner diameter 5.5 mm, ring outer diameter 8 mm) was used as a working electrode. The collection efficiency of the ring-disk electrode was determined to be 0.48 by using $Fe(CN)_6{}^{4-}/Fe(CN)_6{}^{3-}$ redox couple. The GC disk electrode was coated with a catalyst layer by applying catalyst dispersion in a diluted Nafion® solution. The amount of catalyst loaded on GC disk was ca. 0.25 mg (ca. 0.1 mg as transition-metal weight). The thickness of Nafion film was estimated to be 0.12 μm by assuming a density of 2 g cm^{-3}. Oxygen reduction reaction was also examined using a Pt ring–bright Pt disk electrode for comparison. The electrolyte used was a 1 M potassium phosphate buffer solution (pH 7.6). An Ag/AgCl/satd. KCl was used as a reference electrode, while the electrode potential was represented against a hydrogen electrode (RHE). All electrochemical measurements were carried out at room temperature.

Figure 1 shows rotating ring-disk electrode voltammograms for oxygen reduction on the catalyst-coated GC disk electrode in

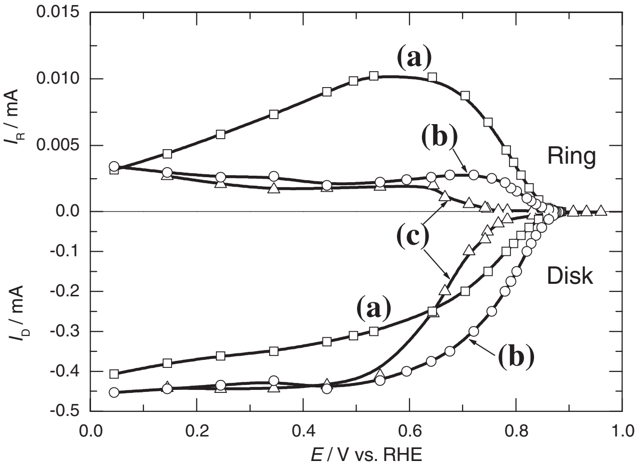

Figure 1. Rotating ring-disk electrode voltammograms for oxygen reduction on (a) HT-Co[Fe]PB/C, (b) HT-Cu[Fe]PB/C, and (c) bright Pt in 1 M potassium phosphate buffer solution (pH 7.6) saturated with oxygen. The collection efficiency of the ring-disk electrode is 0.48. The rotation rate of the electrode was 1500 rpm. The ring electrode potential was set at 1.35 V vs. RHE.

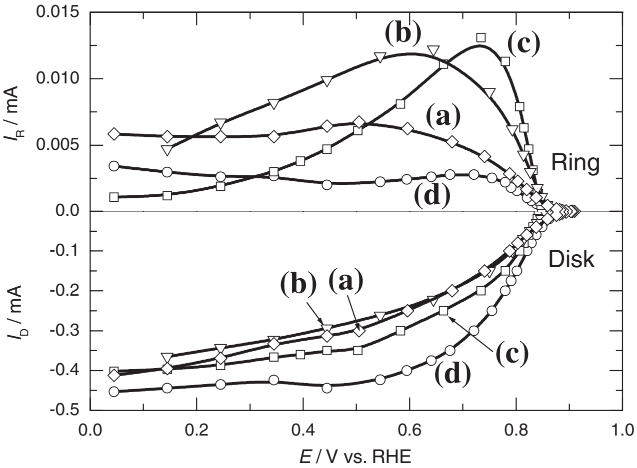

Figure 2. Rotating ring-disk electrode voltammograms for oxygen reduction on (a) HT-Fe[Fe]PB/C, (b) HT-Co[Co]PB/C, (c) HT-Cu[Co]PB/C, and (d) HT-Cu[Fe]PB/C. Other conditions were the same as in Figure 1.

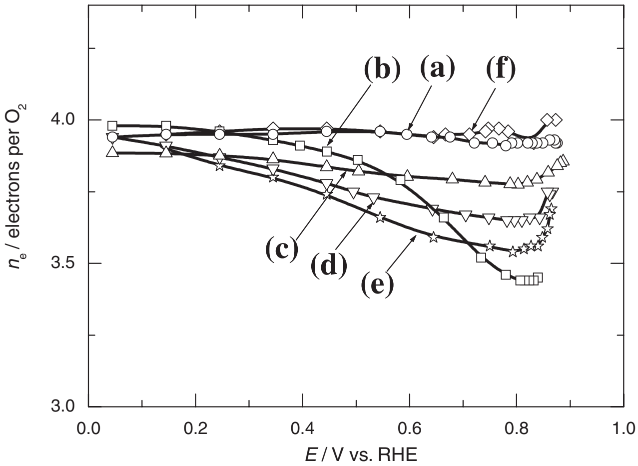

Figure 3. Average number (n_e) of electrons transferred per O_2 during oxygen reduction on the disk: (a) HT-Cu[Fe]PB/C, (b) HT-Cu[Co]PB/C, (c) HT-Fe[Fe]PB/C, (d) HT-Co[Fe]PB/C, (e) HT-Co[Co]PB/C, and (f) bright Pt.

a neutral buffer solution saturated with oxygen. The rest potential of the catalyst-coated GC disk electrode was somewhere between 0.85 and 0.9 V vs. RHE. Oxygen reduction current on HT-Co[Fe]PB/C, for which the synergistic effect of cobalt and iron upon oxygen reduction activity was observed,[5] increases at potentials below 0.85 V and draws a limiting current plateau in a potential region lower than 0.5 V. The onset potential of oxygen reduction reaction on HT-Co[Fe]PB/C was almost the same as that obtained by floating electrode measurements. The ring current for peroxide oxidation increases with decreasing disk potential with drawing a maximum at ca. 0.6 V. While the disk currents for HT-Co[Fe]PB/C was slightly smaller than that for Pt, the ring current for HT-Co[Fe]PB/C was quite larger than that for Pt, indicating that peroxide generation on HT-Co[Fe]PB/C is rather large at usual oxygen reduction potentials. To explore a Pt-free catalyst promoting four-electron reduction of oxygen, a series of Pt-free catalysts were prepared and examined. Thereby, it was found that HT-Cu[Fe]PB/C shows a prominent oxygen reduction activity with hardly any generation of peroxide during oxygen reduction. As can be seen in Figure 1, oxygen reduction reaction on HT-Cu[Fe]PB/C sets in higher potential region than others, while the ring current is comparably small as that for a bright Pt electrode.

Figure 2 shows an effect of combination of transition elements in the catalyst upon the peroxide generation and catalytic activity for oxygen reduction. Although active site structure and reaction mechanism for oxygen reduction reaction on the present Pt-free catalysts are not clear yet, peroxide generation is highly dependent on the combination of the transition elements incorporated in the catalysts. The ring current for HT-Fe[Fe]PB/C is smaller than that for HT-Co[Co]PB/C, while the polarization curves for oxygen reduction on both catalysts look alike. Substitution of copper for a half cobalt in HT-Co[Co]PB/C, i.e., HT-Cu[Co]PB/C, leads to slightly improved catalytic activity with lower generation of peroxide in a potential region lower than 0.7 V. When copper and iron are incorporated together in the catalyst, i.e., HT-Cu[Fe]PB/C, peroxide generation is quite depressed and oxygen reduction activity is remarkably enhanced, as can be seen in Figure 2. To examine a contribution of so-called two-electron reduction generating hydrogen peroxide, the average number (n_e) of electrons transferred during oxygen reduction was calculated from the ring and disk current data in Figures 1 and 2 with taking the collection efficiency (0.48) into account.[6] The results are shown in Figure 3. The n_e value for HT-Cu[Fe]PB/C was calculated to be ca. 3.95 in the whole potential region, whose value was almost the same as that for the Pt electrode under these conditions.

As were briefly described above, a highly active Pt-free catalyst showing the enhanced activity and selectivity for four-electron reduction of oxygen is prepared from popular transition metal salts. Such a cost-effective catalyst could be a possible candidate substituting for Pt-based catalysts of air cathodes. Detailed investigation together with optimization of preparation conditions is under way in our laboratory.

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