

## A High-active Oxygen Electroreduction Catalyst Insensitive to the Presence of Methanol

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A high-active oxygen reduction catalyst was prepared by heat-treatment of transition metal hexacyanometalate precursors containing cobalt and iron dispersed on carbon black under an inert atmosphere. The catalytic activity for oxygen reduction was insensitive to the presence of high concentration of methanol and was comparable to that of the platinum catalyst in the absence of methanol.

For oxygen reduction catalysts, Pt and Pt-based catalysts have been most widely investigated because of satisfactory activity and stability for practical applications to fuel cells. A drawback in using Pt-catalysts in an air cathode for a direct methanol fuel cell is catalytic oxidation of methanol diffused through an electrolyte from the anode side, resulting in a lower operating cell voltage due to a mixed potential of the air cathode.

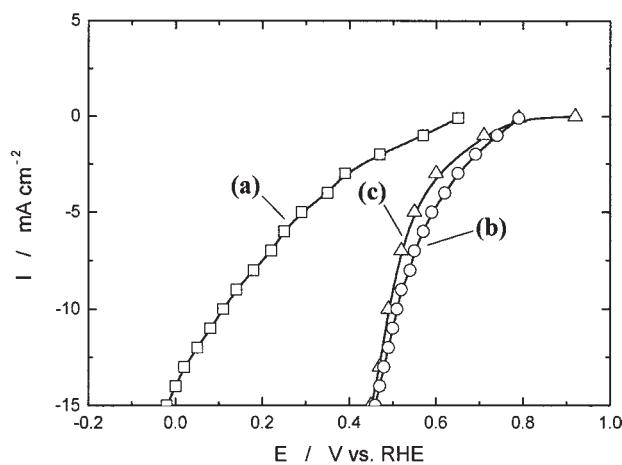
A possible approach to cope with these problems is to allow a presence of methanol at the air cathode with using relatively inexpensive catalysts active for oxygen reduction but inactive for methanol oxidation. Many efforts have been made to find materials which exhibit oxygen-selective reduction activity. Recently, several transition metal-based catalysts, such as the catalysts prepared from transition metal macrocycles<sup>1-4</sup> or transition metal salts and nitrogen-containing organics,<sup>5,6</sup> have been proposed as potential catalysts for oxygen reduction. Common factors of these materials preparations seem to be a combination of transition metal, nitrogen donor and carbon support, and heat-treatment under an inert atmosphere, although the origin of catalytic activity of these heat-treated materials is still under discussion. Since the various transition metals can be incorporated in the transition metal hexacyanometalates (Prussian blue-related compounds) in which each metal atom is surrounded by nitrogen or carbon atoms and CN groups bridge between the metal atoms, it can be intuitively expected that transition metal hexacyanometalates could be used as the starting material to prepare alternative catalysts for oxygen-selective reduction. Here we report the preparation of oxygen reduction catalyst from such starting materials and its electrocatalytic activity for oxygen reduction in the presence of methanol.

The catalysts were prepared by dispersing Prussian blue-related compounds (PB) on acetylene black (AB), and heat-treatment at several temperatures under a nitrogen atmosphere. An aqueous solution of transition metal salt ( $M'SO_4$ ;  $M' = Fe, Co$ ) was slowly added with stirring into a mixture of acetylene black in the solution of hexacyanometalate salt ( $K_3M''(CN)_6$ ;  $M'' = Fe, Co$ ). The loaded amount of the Prussian blue analogs was  $5 \times 10^{-4}$  mol on 0.1 g of acetylene black. The resulting mixture was filtrated with a filter paper, dried at 80 °C, and heat-treated at several temperatures in a horizontal quartz tube for ca. 30 min under flowing nitrogen gas. For brevity, the starting mixture using

$M^{2+}$  and  $M''(CN)_6^{3-}$  is denoted as  $M'M''PB/AB$  and the heat-treated sample as  $HT(\text{temp. in } ^\circ\text{C})-M'M''PB/AB$ , such as  $CoFePB/AB$  and  $HT(800)-CoFePB/AB$ . The Pt/C catalyst (20 wt% Pt/Vulcan XC-72R, EC-20-PTC, ElectroChem, Inc.) was used as a reference.

The electrochemical measurements for oxygen reduction were carried out with the floating electrode technique.<sup>7</sup> A hydrophobic gas-diffusion electrode was prepared by mixing the sample powder and the Teflon dispersion (T-30J, Du Pont-Mitsui Fluorochemicals Co., Ltd.), and kneading with a spatula. The Teflon content in the mix was 25–30 weight percent. The resulting paste was shaped in a thin sheet, sintered at 300 °C for 10 min, and finally pressed on a nickel screen at ca.  $10^3 \text{ kg cm}^{-2}$ . The loaded mix on the nickel screen was ca. 60 mg per 1  $\text{cm}^2$  of apparent electrode area. Amounts of catalyst in the mix were calculated to be ca. 19 mg(Co, Fe)  $\text{cm}^{-2}$  for the catalysts prepared in this work and ca. 8 mg(Pt)  $\text{cm}^{-2}$  for the Pt/C catalyst, respectively. The floating electrode was placed in a horizontal position on the surface of an electrolyte and used as a working electrode to obtain quantitative information on oxygen reduction activity of the different catalysts. An Ag/AgCl/satd. KCl electrode was used as a reference electrode. In this paper, all potentials were quoted with respect to a hydrogen electrode (RHE). A counter electrode was a Pt plate (1  $\text{cm}^2$ ). The electrolyte used in this study was a 1 M sodium phosphate buffer solution (pH 7.5). All electrochemical measurements using the floating electrode were carried out at room temperature under an air atmosphere.

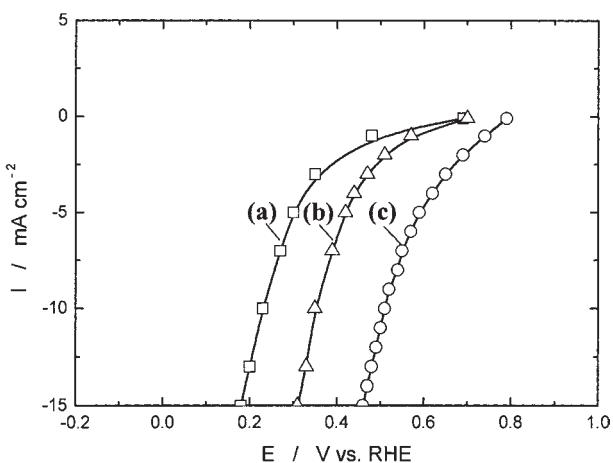
Figure 1 shows the polarization curves for oxygen reduction with  $CoFePB/AB$  and  $HT(800)-CoFePB/AB$ . The polarization



**Figure 1.** Polarization curves for oxygen reduction using a floating electrode with (a)  $CoFePB/AB$ , (b)  $HT(800)-CoFePB/AB$ , and (c) Pt/C under an air atmosphere.

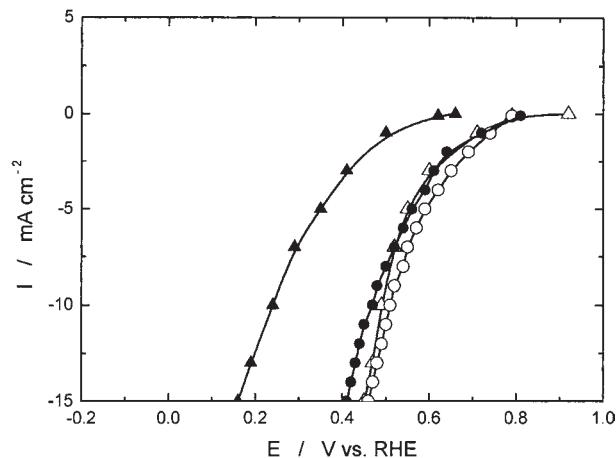
data were recorded during the potential scanning at a rate of  $2 \text{ mV s}^{-1}$ . The current density is given based on the apparent electrode area. As can be seen in Figure 1, CoFePB/AB exhibited an oxygen reduction activity, although the catalytic activity was not high. The catalytic activity of CoFePB/AB may be owing to a nature of PB analogs with channels for oxygen diffusion in the solid matrix.<sup>8</sup> The catalytic activity for oxygen reduction was drastically enhanced by the heat-treatment, as is shown for HT(800)-CoFePB/AB (curve (b) in Figure 1). No change in catalytic activity of the heat-treated sample was recognized during a preliminary stability check for a half day. Such an enhancement in the catalytic activity was observed for the samples heat-treated at temperatures higher than ca.  $500^\circ\text{C}$ . X-ray diffraction measurements of the prepared samples indicated that the skeleton structure of the Prussian blue-related compounds having a cubic lattice was not maintained after the heat-treatment at temperatures higher than ca.  $500^\circ\text{C}$ . The origin of catalytic activity for oxygen reduction seems to be different from that of the pristine (unheated) sample. The polarization curve with Pt/C catalyst is also shown in Figure 1 for comparison. The catalytic activity of HT(800)-CoFePB/AB for the oxygen reduction is comparable to that of the Pt/C catalyst, although the preparation conditions for the catalyst were not optimized.

An effect of transition metal in HT-M'M''PB/AB on oxygen reduction activity was investigated by using different transition metal ions in the precursor. Some of the results are shown in Figure 2. For the case of HT(800)-FeFePB/AB, the oxygen reduction current was increased in the potentials below 0.4 V. When HT(800)-CoCoPB/AB was used, the polarization curve was shifted to a more positive direction. When HT(800)-CoFePB/AB was used, the catalytic activity for oxygen reduction increased significantly, indicating a synergistic effect of a combination of cobalt and iron contained in the precursor on the catalytic activity for oxygen reduction.



**Figure 2.** Polarization curves for oxygen reduction using a floating electrode with (a) HT(800)-FeFePB/AB, (b) HT(800)-CoCoPB/AB, and (c) HT(800)-CoFePB/AB under an air atmosphere.

Figure 3 shows the polarization curves for oxygen reduction with HT(800)-CoFePB/AB and Pt/C in the absence and presence of 2.5 M methanol in the electrolyte. When the Pt/C electrode was in contact with the solution containing methanol, the open-circuit



**Figure 3.** Polarization curves for oxygen reduction using a floating electrode with HT(800)-CoFePB/AB (○, ●) and Pt/C (△, ▲) in the absence (○, △) and presence (●, ▲) of 2.5 M methanol in the electrolyte under an air atmosphere.

potential was negatively shifted by ca. 0.3 V. The polarization curve of the Pt/C electrode in the presence of methanol was also less steep, indicating the oxygen reduction activity of Pt/C being impaired by methanol.

When HT(800)-CoFePB/AB catalyst is used, the catalytic activity for oxygen reduction is not influenced by the presence of methanol. As shown in Figure 3, the open-circuit potentials and the shape of polarization curves for oxygen reduction are almost insensitive to the presence of methanol in the electrolyte. These results indicate that the prepared catalyst is a methanol-tolerant oxygen-selective reduction catalyst. The catalytic activity for oxygen reduction in the presence of concentrated methanol is comparable to that of the Pt/C catalyst in the absence of methanol.

In conclusion, a remarkably active catalyst for oxygen reduction was prepared from the inorganic precursors dispersed on carbon black in a single step simply by heat-treating the mixture under an inert atmosphere. Although the preparation conditions were not optimized, its catalytic activity even in the presence of methanol was comparable to that of the platinum catalyst in the absence of methanol, which allows methanol crossover to an air cathode of a direct methanol fuel cell. A detailed investigation is now under progress in our laboratory.

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