Enhanced Catalytic Activity of Non-platinum Catalyst for Oxygen Reduction in Alkaline Solution

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Remarkable enhancement in catalytic activity of a non-platinum catalyst for oxygen reduction in alkaline solutions has been achieved by an oxidative pretreatment of a high-area carbon support before dispersion of catalyst precursor (cobalt hexacyanoferrate), followed by pyrolyzing the precursor under an inert atmosphere. The polarization potential for oxygen reduction at substantial current densities at room temperature under air was higher than a potential corresponding to a limit of relative predominance for O_2/HO_2^- couple.

Electrochemical reduction of oxygen has been of great importance in various electrochemical applications, such as air cathodes in fuel cells, metal/air batteries, and energy-saving brine electrolytic processes. Pt and Pt-based catalysts have been most widely used for oxygen reduction because of their high activity and stability. However, less expensive catalysts, if available, are preferred over noble metals. Many efforts have been made to investigate non-noble metal catalysts, such as transition metal oxides,[1] transition metal macrocycles,[2] and alternative catalysts.[3] Despite such extensive studies, the activation overpotential for oxygen reduction is typically -0.3 to -0.45 V at practical current densities even with highly dispersed platinum black catalysts.[4]

Recently we have reported an easy method to prepare non-platinum electrocatalysts for oxygen reduction.[5] The catalysts were prepared simply by pyrolyzing the nitrogen-containing inorganic precursors (transition metal hexacyanometallates, Prussian blue analogs) dispersed on carbon black under an inert atmosphere. The method uses only popular transition metal salts dissolved in aqueous solutions to disperse the precursor on carbon support. Among several combinations of 3d-transition metals, the combination of cobalt and iron incorporated at neighboring sites in the precursor gave the prominent synergetic effect on the catalytic activity for oxygen reduction.[5] To enhance the electrode performance for oxygen reduction in gas-diffusion electrode, high dispersion of catalyst on a high surface area of carbon support would be a key factor for preparing a highly active catalyst. Here we report a preliminary study on remarkable enhancement in the electrode performance for oxygen reduction in alkaline solutions by using a surface-modified high-area carbon when dispersing the precursor.

The carbon supports used for dispersing the catalyst precursor were a high-area carbon (M-40, Osaka Gas Co.: BET area = $4000\,m^2\,g^{-1}$) and acetylene black (Denka Co.: BET area = $70\,m^2\,g^{-1}$), respectively, denoted as M40 and AB hereafter. Prior to dispersing the catalyst precursor, the carbon powder was treated with nitric acid to increase hydrophilicity of carbon surface, by which the aqueous solution of transition metal salts for depositing the precursor would soak well into pores in carbon. The carbon powders were immersed in 9 M ($1\,M = 1\,mol\,dm^{-3}$) HNO_3 and stirred by magnetic stirrer at room temperature for 12 h. The pretreated carbon powder was collected by filtration, washed well with distilled water to eliminate the acid, and dried at 80 °C in an oven under air.

The catalysts were prepared by heat-treating the inorganic precursor dispersed on carbon support under a nitrogen atmosphere. The precursor were prepared by slowly adding 0.024 M $CoSO_4$ aqueous solution ($25\,cm^3$) to a vigorously stirred suspension of carbon (0.1 g) in 0.02 M $K_3Fe(CN)_6$ aqueous solution ($25\,cm^3$), and stirring the mixture at room temperature for 30 min. The loaded amount of the Prussian blue analogs (PB) was ca. 5×10^{-4} mol on 0.1 g of carbon. The resulting mixture was collected by filtration, washed well with distilled water, and dried at 80 °C in an oven under air. The dried sample was wrapped with a copper foil, heated up to 800 °C at a rate of about 200 deg/h in a horizontal quartz tube under a nitrogen atmosphere followed by keeping at 800 °C for ca. 10 min. For brevity, the obtained sample is denoted as HT(800)-CoFePB/AB and HT(800)-CoFePB/M40. The catalytic activity of the prepared samples was compared with a carbon-supported Pt-black catalyst: 50 wt % Pt/Ketjenblack (TEC10E50E, Tanaka Precious Metals Co.)

The activity for oxygen reduction was examined by polarization measurements with a floating electrode, as described previously.[5] The hydrophobic gas-diffusion electrode ($1\,cm^2$) was placed on the surface of electrolyte and used as a working electrode. Amounts of catalyst in the electrode mix were calculated to be ca. 18 mg (as transition metal weight)/cm^2 for the catalysts prepared in this work and ca. 16 mg(Pt)/cm^2 for the 50 wt % Pt/Ketjenblack, respectively. A reference electrode was an Ag/AgCl/satd. KCl electrode, which was separated from the working compartment by porous glass. The potential measured against this reference electrode was also represented on the reversible hydrogen electrode (RHE) scale in an electrolyte of the same composition as in the studied cell.[6] The counter electrode (Pt plate) was placed in a compartment separated by glass frits. The polarization measurements were carried out at room temperature under an ambient air atmosphere and the polarization data were not corrected for IR-drop.

Figure 1 shows the polarization curves for oxygen reduction on 0.25 M KOH solution. When HT(800)-CoFePB/AB was used as catalyst, the cathodic current was increased in the potential region lower than 0.8 V vs RHE. To check stability of the catalyst, the catalyst was soaked in 0.25 M KOH solution for a week, washed with distilled water, and the electrode was prepared using such treated sample. The result for polarization measurement using such treated sample is shown as curve (b) in Figure 1. No noticeable deterioration in the catalytic activity was recognized after soaking in the solution, suggesting catalyst stability for use

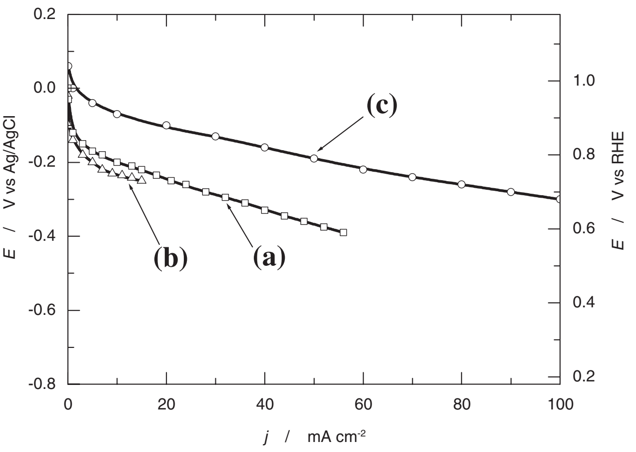

Figure 1. Polarization curves for oxygen reduction using a floating electrode on 0.25 M KOH under air at room temperature: (a) HT(800)-CoFePB/AB, (b) HT(800)-CoFePB/AB after soaking in 0.25 M KOH for a week, and (c) HT(800)-CoFePB/M40.

in alkaline solution.

The preparation procedure of the present catalyst involves colloidal dispersion of the inorganic precursor on carbon support suspended in aqueous solution. To attain higher dispersion of the precursor, the surface-modified high-area carbon was used in preparing the catalyst. The curve (c) in Figure 1 shows the polarization curve using such prepared catalyst. The polarization curve for HT(800)-CoFePB/M40 appears in ca. 0.2 V higher potential region than that with HT(800)-CoFePB/AB.

Figure 2 shows the polarization curve with HT(800)-CoFePB/M40 on 10 M NaOH solution at room temperature under an air atmosphere. The open circuit potential was ca. 1.1 V vs RHE. The oxygen reduction current was increased at ca. 1.0 V vs RHE by cathodically polarizing the electrode slightly from the open circuit potential. The polarization potential at 100 mA cm^{-2} is higher than 0.8 V vs RHE. Such high performance has not been reported so far for transition metal-based catalyst under these conditions. Polarization curve using a carbon-supported platinum black catalyst (50 wt % Pt/Ketjenblack) is also shown in Figure 2 in comparison. The performance of the present non-platinum catalyst for oxygen reduction is remarkable, although the preparation conditions and the structure of the gas-diffusion electrode are not optimized yet.

Particularly in alkaline solutions, the oxygen reduction proceeds virtually through the peroxide pathway on a number of electrode surfaces.[4] Assuming that the potential determining reaction is the 2-electron reduction of oxygen to peroxide, the equilibrium potential for O_2/HO_2^- couple is calculated by the Nernst equation. When the pressure of oxygen is 0.2 atm (in air) and the concentration (activity) of peroxide is 10^{-4} M in 10 M NaOH, for example, the potential is calculated to be 0.908 V vs RHE. As can be seen in Figure 2, the polarization potentials at current densities up to 40 mA cm^{-2} is higher than such a thermodynamic potential for O_2/HO_2^- couple. Although the reduction mechanism on the present catalyst is not clear at this stage and the oxygen reduction current is under a mixed control of gas diffusion and reaction kinetics, the peroxide activity would be depressed to a low value on the present catalyst electrode. Concerning reaction mechanism for oxygen reduction on the present catalyst, further study is needed together with optimization of the preparation conditions and electrode structure.

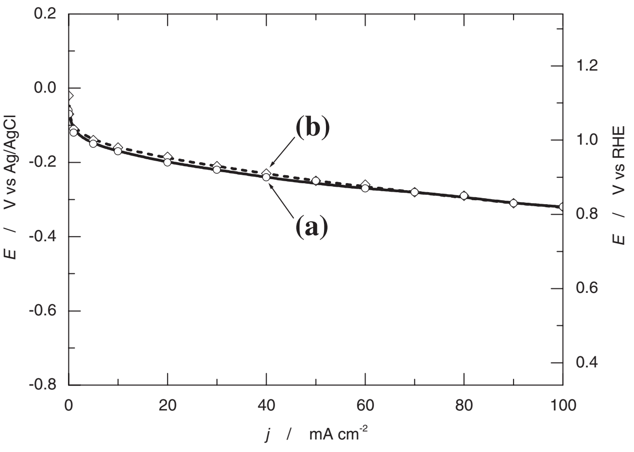

Figure 2. Polarization curves for oxygen reduction using a floating electrode on 10 M NaOH under air at room temperature: (a) HT(800)-CoFePB/M40 and (b) 50 wt % Pt/Ketjenblack.

In conclusion, the catalytic activity of the non-noble metal-based catalyst for oxygen reduction in alkaline solutions has been remarkably enhanced by using the surface-modified high-area carbon when dispersing the inorganic precursor, followed by pyrolyzing the precursor under an inert atmosphere. The enhancement in the activity of the cost-effective catalyst as described herein is expected to stimulate further research and development of air cathodes.

References and Notes

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