4278 *Chem. Mater.* **2005,** *17,* 4278−4281

Modifying Carbon Particles with Polypyrrole for Adsorption of Cobalt Ions as Electrocatatytic Site for Oxygen Reduction

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Received May 7, 2005
Revised Manuscript Received July 9, 2005

Here, we report that a carbon nanoparticle modified with a cobalt-adsorbed polypyrrole (PPy) film is a good electrocatalyst for the reduction of O_2. Extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray diffraction experiments reveal that the cobalt ion is coordinated by four nitrogens as the donor atoms and that the Co−N_4 structure is successfully maintained after heat treatment under an inert atmosphere up to ca. 700 °C without deposition of metallic cobalt. The cobalt PPy complex has only few precedent examples,[1] to the best of our knowledge.

Finding a nonnoble metal catalyst for fuel cell electrodes is an important subject of recent study.[2] Metal complexes with macrocyclic ligands such as porphyrins and phthalocyanines that contain four nitrogen donors (i.e., metal−N_4 chelates), adsorbed on carbon and heat-treated, are expected to be alternates to the conventional carbon-supported platinum catalyst.[3−9] The improvement of electrocatalytic activities of these precursors has been accomplished by heat treatment in the temperature range between 500 and 700 °C.[10,11] The source of nitrogen atoms does not necessarily have to be macrocyclic ligands. Yeager et al. found activity with a heat-treated mixture of transition metal salts, such as cobalt and iron, and nitrogenous polymers such as polyacrylonitrile adsorbed on charcoal.[12] Dodelet and co-workers have employed NH_3 and CH_3CN as the precursors of nitrogen atoms and found that, for iron-based catalysts, the nitrogen atoms on the carbon support must be of a pyridine type.[13−15] It was reported that heat treatment of carbon supports in an NH_3/H_2/argon atmosphere was effective in enriching their surfaces with nitrogen atoms and in providing the pyridine-type coordination site.[16] Activities of the resulting catalysts after adsorbing iron ions were comparable to those of conventional iron complexes with pyridine-type ligands adsorbed on carbon supports.[17−19] For cobalt-based catalysts, on the other hand, a pyrrole-type nitrogen atom is preferred,[20] and its development has awaited a convenient method to provide a tetrapyrrole-type coordination site on carbon such as those of porphyrins and phthalocyanines.

While PPy is a well-known electrically conducting polymer, the lack of solubility has prevented the use of PPy as a polymeric ligand. Indeed, PPy has only been applied as a conducting material to support catalysts such as metal oxides[21−24] and complexes[25] at the electrode surface. We anticipated that carbon-supported PPy layers, impregnated with a solution of a cobalt salt, should give active electrode materials. To accommodate cobalt ions at a coordination site within the PPy layer by a heterogeneous process, the PPy layer was produced at the surface of a high surface-area carbon nanoparticle by a fluid-bed electrolysis (vide infra). We chose carbon black (Ketjen black EC, $\phi_{av} = 30$ nm) with a Brunauer−Emmett−Teller surface area of 800 m^2/g because it is a common support used for platinum-based catalysts. Obtaining a PPy coating on carbon black involved the electropolymerization of pyrrole at the surface of carbon black, which was accomplished by suspending carbon black into an electrolyte solution of pyrrole and electrolyzing the suspension with a platinum wire as a working electrode with vigorous stirring.[26] Carbon black, upon continuous contact with the platinum electrode, served as the working electrode

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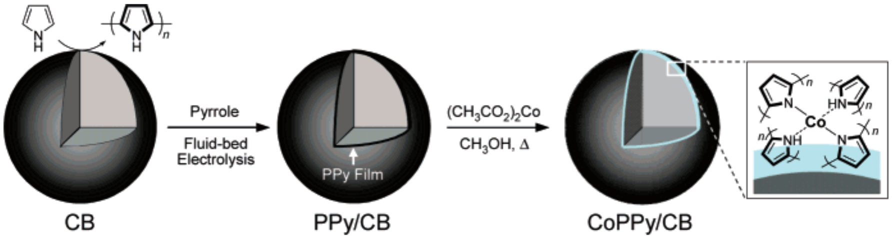

Figure 1. Schematic of the procedure for preparation of the CoPPy/CB catalyst and the proposed moiety of the catalytic site. Coordination of a single PPy chain as a multidentate ligand is also anticipated.

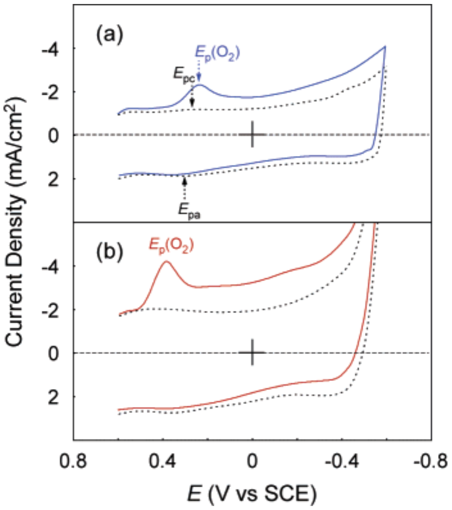

Figure 2. (a) Cyclic voltammogram for the reduction of O_2 at edge-plane pyrolytic graphite electrodes (0.28 cm^2) coated with a Nafion film containing the CoPPy/CB catalyst. The modified electrode was prepared by transferring 20 μL of a suspension of CoPPy/CB (2 mg) in 2-propanol containing 5 wt % Nafion (0.25 mL) and was air-dried. The supporting electrolyte, 1 M $HClO_4$, was saturated with O_2 (solid curve) or argon (dotted curve). Scan rate = 0.1 V s^{-1}. (b) Repeat of a using the CoPPy/CB catalyst after heat treatment at 700 °C under a vacuum.

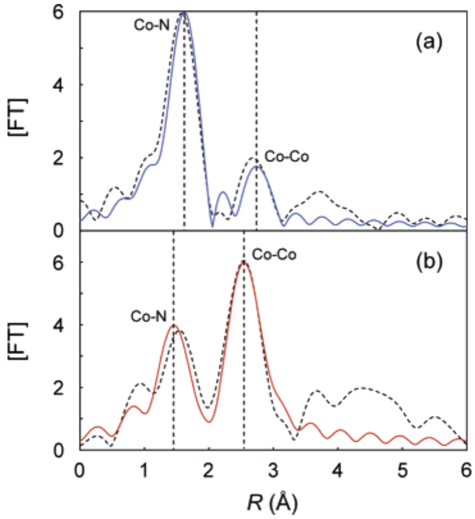

Figure 3. Fourier transformed k^3-weighted EXAFS functions at the Co K-edge for CoPPy/CB (dashed curves) and the simulated functions (solid curves) obtained by curve-fitting calculations using the FEFF8 code[29] before (a) and after (b) the heat treatment at 550 °C under a vacuum. The simulated curve in a corresponded to atomic distances of $R_{Co-N} = 2.07 \pm 0.01$ Å and $R_{Co-Co} = 3.10 \pm 0.02$ Å and coordination numbers of $N_{Co-N} = 4.0 \pm 0.6$ and $N_{Co-Co} = 0.7 \pm 0.2$. The simulated curve in b corresponded to $R_{Co-N} = 2.04 \pm 0.03$ Å, $R_{Co-Co} = 2.96 \pm 0.03$ Å, $N_{Co-N} = 4.0 \pm 0.9$, and $N_{Co-Co} = 2.4 \pm 0.5$.

during the electrolysis. The resulting PPy/CB particle was suspended into a solution of cobalt acetate in CH_3OH, which was then refluxed for a sufficiently long time to allow accommodation of cobalt ions at the suitable site.[27] In Figure 1, the preparative method for the CoPPy/CB catalyst is summarized.

The pristine CoPPy/CB catalyst showed moderate electrocatalytic activity for the reduction of O_2. To prepare a CoPPy/CB-modified disk electrode for evaluation of the catalytic activity, an alcoholic suspension of CoPPy/CB containing Nafion was used as a mother liquor for dip-coating. The solid and dotted curves in Figure 2a represent cyclic voltammograms in the presence and absence of O_2, respectively, obtained with the electrode modified with CoPPy/CB. The catalytic current for the reduction of O_2 appeared near $E_p(O_2) = 0.23$ V versus SCE, while the Co(III/II) couple appeared at a more positive potential in the absence of O_2 [$(E_{pa} + E_{pc})/2 \approx 0.3$ V]. The Co(III/II) potential was, however, much more negative than the $Co^{3+/2+}$ potential in aqueous solutions ($E^f = 1.68$ V vs SCE),[28] which suggested that the cobalt ion was coordinated by donor atoms in PPy, rather than merely adsorbed on the PPy/CB surface.

Added support for the coordination of PPy to the cobalt ion was furnished by EXAFS spectroscopy. The Fourier transformed EXAFS function (Figure 3a) yielded an atomic distance of $R_{Co-N} = 2.07$ Å, which was comparable to the typical coordinate bond lengths in cobalt complexes such as cobalt porphyrins and phthalocyanines.[2] The EXAFS function gave a first-shell cobalt−nitrogen coordination number of 4, which was suggestive of the $Co-N_4$ structure.

A significant feature of the CoPPy/CB catalyst is a positive shift in the O_2 reduction potential accomplished by heat treatment at elevated temperatures. After heat treatment of

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(26) Ketjen black EC from Akzo Nobel Co. was washed with benzene/hexane 1:1 (v/v) using a Soxlet extraction system for 6 h, dried under a vacuum at 120 °C for 3 h, and thoroughly ground with an agate mortar and pestle prior to use. The resulting particle (3 g) was suspended in 250 mL of methanol/water 4:1 (v/v) containing pyrrole (5.6 mL, 0.32 mol/L) and sodium *p*-toluenesulfonate (19.4 g, 0.1 mol/L). The suspension was placed in a two-compartment electrochemical cell equipped with a coiled platinum wire ($\phi = 1$ mm, $l = 30$ cm) and a stainless steel plate ($A = 35$ cm^2) as working and auxiliary electrodes, respectively, and kept at 5 °C under argon. A commercially available Ag/AgCl was used as a reference electrode, which was placed in the main cell compartment. The suspension was electrolyzed at 1.0 V vs Ag/AgCl for 45 min with vigorous stirring. The resulting particle was collected by filtration, washed with CH_3OH and water, dried under a vacuum at 120 °C for 3 h, and ground again to give a PPy/CB particle.

(27) The PPy/CB particle (1.5 g) was suspended in a solution of cobalt acetate tetrahydrate (2.8 g) in CH_3OH (80 mL) containing triethylamine (1 mL). The suspension was refluxed for 2 h under argon. After cooling to room temperature, the product was collected by filtration, washed thoroughly with CH_3OH and water, and dried under a vacuum at 120 °C for 3 h to give the CoPPy/CB catalyst.

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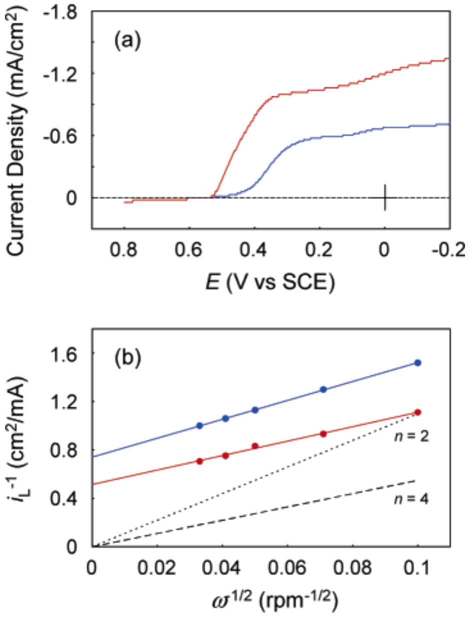

Figure 4. Current-potential responses for the reduction of O_2 at electrodes in Figure 2 operated as rotating disk electrodes (electrode rotation rate was $\omega = 100$ rpm) under O_2 (a), and Koutecky−Levich plots of [plateau current (i_L)]$^{-1}$ vs $\omega^{-1/2}$ (b). The blue and red curves (and lines) were obtained with the electrodes used in Figure 2a and b, respectively. The broken lines in b were calculated for the diffusion-convection-controlled reduction of O_2 by two ($n = 2$) or four ($n = 4$) electrons. Parameters used for the calculation were as follows: diffusion coefficient of $O_2 = 2.0 \times 10^{-5}$ cm^2 s^{-1}, kinematic viscosity of the electrolyte solution $= 0.01$ cm^2 s^{-1}, concentration of $O_2 = 1.5 \times 10^{-3}$ M.

the catalyst at 700 °C under a vacuum, the catalytic current for the reduction of O_2 appeared near $E_p(O_2) = 0.38$ V versus SCE (Figure 2b). Figure 4a shows current−potential curves for the reduction of O_2 at a slowly rotated disk electrode modified with the CoPPy/CB catalyst before and after the heat treatment. Heat treatment of the catalyst not only shifted the half-wave potential to a significantly positive side but also nearly doubled the plateau current, while the reduction of O_2 occurred in a single step for both pristine and heat-treated catalysts. No current response was obtained at the rotated electrode under argon, which confirmed that these currents were due to the reduction of O_2. Koutecky−Levich plots (Figure 4b) revealed that the heat-treated catalyst reduced O_2 mainly with four electrons ($n_{app} = 3.7$), while a two-electron reduction was predominant for the pristine catalyst ($n_{app} = 2.8$). One could speculate that such a difference in the reactivity comes from the presence of two parallel reactions,[30] one involving the bridging of O_2 to two proximate cobalt centers and giving rise to the four-electron reduction of O_2 according to $O_2 + 4e^- + 4H^+ = 2H_2O$ and the other involving a single cobalt center and yielding the two-electron reduction of O_2 according to $O_2 + 2e^- + 2H^+ = H_2O_2$. The most typical platform to promote the four-electron reduction of O_2 is covalently linked cofacial metalloporphyrins, allowing for both ends of the O_2 molecules to interact with the cobalt centers in the transition state.[31−34]

The improvement in the activity of CoPPy/CB upon heat treatment prompted us to study the structure of the catalytic site. X-ray photoelectron spectroscopy (XPS) analyses were conducted to obtain insight into the surface atomic composition of CoPPy/CB after the heat treatment (Figure 5). The N 1s peak in Figure 5b can be decomposed into several components. The major peaks are those of imine (−N═) and amine (−NH−) nitrogens that are centered near binding energies of 394 and 399 eV, respectively. These spectral features have been found for PPy films[35] and suggest the presence of pyrrole-type nitrogens in CoPPy/CB. It is these nitrogen atoms that coordinate to the cobalt ion. On the other hand, a single unimodal peak for Co 2p$^{3/2}$ in Figure 5a suggests that the chemical state of cobalt is relatively uniform. The chemical shift (781.7 eV) was higher than that for metallic Co 2p$^{3/2}$ (779.0 eV) as a result of the increased electronegativity of nitrogen (3.04) compared to that of cobalt (1.88), consistent with the presence of the cobalt−nitrogen bond even after the heat treatment. The EXAFS function in Figure 3b revealed that, during the heat treatment, the cobalt−nitrogen coordination number was unchanged while the cobalt−cobalt and cobalt−nitrogen distances were shortened. The resulting cobalt−cobalt distance was roughly in the range of those for the covalently bound cofacial porphyrins.[31−34] Together with the XPS results, the existence of a Co−N$_4$ structure, more closely packed at the surface of the carbon support after the heat treatment, is inferred. The improved catalytic activity would be ascribed to the shortening of the cobalt−cobalt distance, allowing for O_2 molecules to bridge the two proximate cobalt centers.

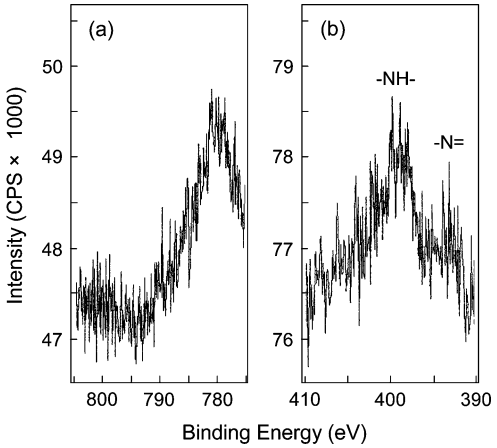

Figure 5. XPS narrow-scan spectra for Co 2p$^{3/2}$ (a) and N1s (b) for the CoPPy/CB catalyst after heat treatment at 600 °C under a vacuum, showing the presence of cobalt and nitrogen atoms at the surface. The surface cobalt and nitrogen concentrations of the heat-treated catalyst were 0.09 and 0.44 in atom percents, respectively. The peak intensities were relatively small because of the small amounts of these atoms in the catalyst.

A maximum in the electrocatalytic activity was obtained for the CoPPy/CB catalyst near 700 °C with a subsequent decrease. X-ray diffraction experiments (Figure 6) revealed that, at temperatures near 1000 °C, metallic cobalt aggregates

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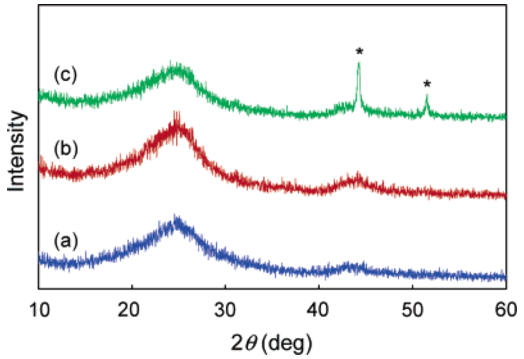

Figure 6. X-ray diffractograms of CoPPy/CB before (a) and after the heat treatments at 600 °C (b) and 1000 °C (c) under a vacuum. Diffraction peaks from metallic cobalt are shown as asterisks.

were formed and, consequently, the catalytic activity decreased. XPS measurements showed that nitrogen atoms were no longer detected after heat treatment near 1000 °C. The aggregation of metallic cobalt was, however, not significant up to 900 °C.

In conclusion, the surface modification of a carbon particle with PPy provided a simple system allowing the immobilization of cobalt ions at the surface by coordination processes and displaying electrocatalytic activity for the four-electron reduction of O_2. Spectroscopic and electrochemical experiments revealed no heterogeneity in the CoPPy/CB catalyst. The catalyst showed high stability against degradation after use for several hours. Tuning the atomic distance and analyzing the detailed structure of the heat-treated catalyst, in addition to the precise determination of the working life, are the topics of our continuing research.

Acknowledgment. This work was partially support by a Grants-in-Aid for Scientific Research (16550128 and 17550138) from MEXT, Japan.

Supporting Information Available: Current−potential responses for the reduction of O_2 at the electrode modified with the CoPPy/CB catalyst for all rotation rates used to prepare Figure 4b. This material is available free of charge via the Internet at http://acs.pubs.org.

CM050958Z