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ELECTROCATALYTIC REDUCTION OF OXYGEN ON COBALT-DOPED POLYPYRROLE FILMS

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A polypyrrole film electrochemically deposited on metal electrodes from an acetonitrile solution containing pyrrole, cobalt(II) acetate, and lithium perchlorate shows the electrocatalytic activity for oxygen reduction. It is found that this polymer film contains cobalt species in the polymer structure.

Polypyrrole is an interesting electroconductive polymer because of its easy preparation and stability.[1-3] Its use as a protecting film against corrosion of substrates[4-6] and solid state properties[1-3] have been studied, but attempts to give any catalytic activity to a polypyrrole film are quite limited.[7]

It was found in the present study that a polypyrrole film can be made electrocatalytic by introducing cobalt species into the polymer structure. We report here some characteristics of an activated polypyrrole (APP) as a catalyst for the cathodic reduction of oxygen. The term "activated polypyrrole" is used for the polypyrrole (PP) which contains cobalt species and has the catalytic activity for oxygen reduction.

The APP film was anodically deposited on an Au electrode with the surface area of 0.25 cm^2 in an acetonitrile solution containing 0.1 M[8] $LiClO_4$, 0.05 M pyrrole, and $5x10^{-3}$ M $Co(OAc)_2$ (Ac: CH_3CO) at a constant current density of 400 $\mu A\ cm^{-2}$. The deposition time was usually 30 s. Thickness of the film deposited under the above condition was about 100 Å, which was measured with a multiple beam interferometer (MIZOJIRI KOGAKU, MULTIPLE BEAM INTERFEROMETER type 2). Electrochemical measurement for oxygen reduction was carried out in an O_2-saturated 0.05 M H_2SO_4 using cyclic voltammetry and rotating ring-disk technique. A KCl-saturated calomel electrode (SCE) and a platinum net were used as the reference and the counter electrodes, respectively.

Figure 1 shows the cyclic voltammograms for O_2 reduction on three types of electrode: (a) bare Au electrode, (b) pure polypyrrole-coated Au electrode (PP/Au), and (c) activated polypyrrole-coated Au electrode (APP/Au). The cathodic peak potential (E_{pc}), which is a measure of the catalytic activity for O_2 reduction, was -0.20 V vs. SCE on both (a) and (b). On the APP-coated electrode (c), however, the E_{pc} was 0.20 V vs. SCE indicating a significant activity for O_2 reduction.

Voltammograms at the Pt ring and APP-coated disk electrode for O_2 reduction are given in Fig. 2. The potential at the Pt ring electrode was fixed at 1.1 V

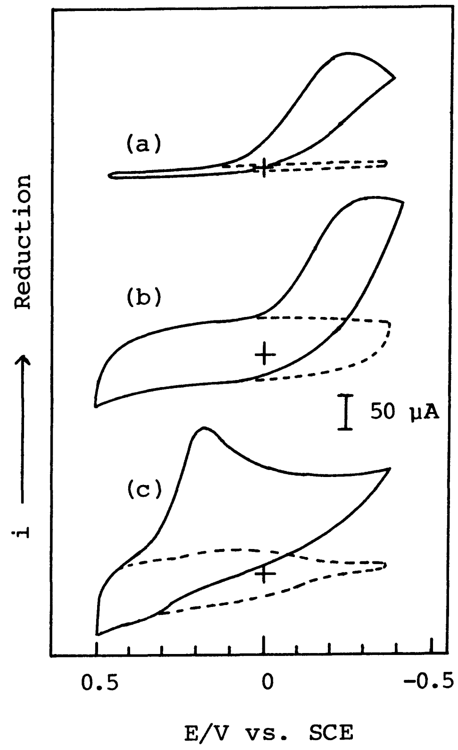

Fig. 1. Cyclic voltammograms in O_2(——)- and N_2(---)-saturated 0.05 M H_2SO_4 for (a) bare Au, (b) PP/Au, and (c) APP/Au electrodes. Scan rate, 100 mV s^{-1}.

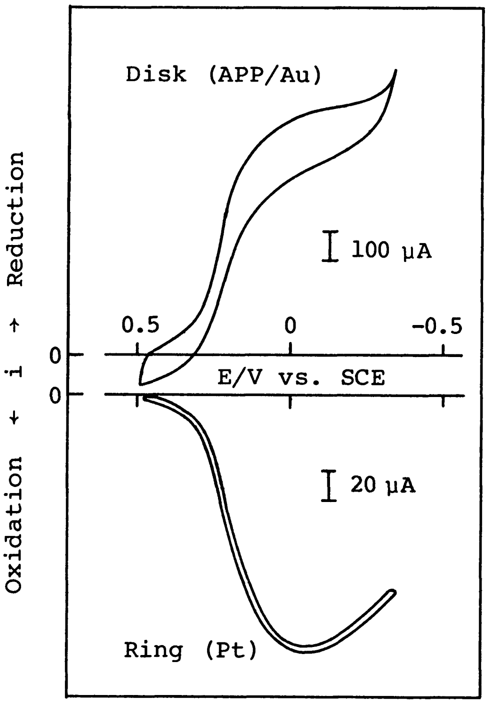

Fig. 2. Voltammograms at the rotating ring(Pt)-disk(APP/Au) electrode for O_2 reduction in O_2-saturated 0.05 M H_2SO_4. Scan rate at the disk, 100 mV s^{-1}; ring potential, 1.1 V vs. SCE; rotation rate, 1000 rpm.

vs. SCE, where the diffusion limiting current is observed for the oxidation of H_2O_2. It is obvious from Fig. 2 that H_2O_2 is formed at potentials where the O_2 reduction occurs on the APP-coated disk electrode. The current efficiency of H_2O_2 formation at the disk electrode was estimated to be about 60% by using the collection efficiency of 0.35, which was determined by the reduction of hexacyanoferrate(III) ion.9) This indicates that the main product in the O_2 reduction on the APP film electrode is H_2O_2, namely the O_2 reduction occurs through a two-electron pathway.

Stability of an APP film for O_2 reduction was tested by a constant current electrolysis. On the passage of a reduction current (current density, −40 μA cm^{-2}), the electrode potential decreased gradually (Fig. 3); but the activity of the APP film for O_2 reduction was still maintained after 24 h. Also the electrocatalytic activity of the APP/Au in 0.05 M H_2SO_4 for O_2 reduction remained unchanged after 10 cyclic potential sweeps over 0.5 — −0.8 V vs. SCE in aqueous 0.1 M $LiClO_4$, in which the electrochemical doping and undoping of perchlorate anion were observed for the PP/Au in this potential region.10) These results suggest that the active sites for O_2 reduction, probably cobalt species, are tightly held in the polymer structure.

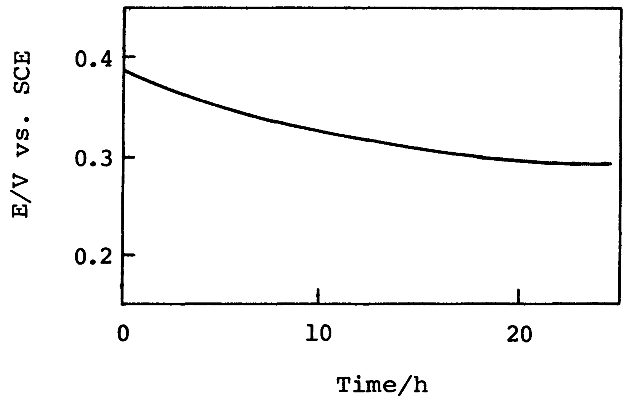

Fig. 3. Stability test of a stationary APP/Au electrode for O_2 reduction in O_2-saturated 0.05 M H_2SO_4 under a constant current density of -40 μA cm^{-2}.

The atomic composition of PP and APP was determined by elemental analysis, and the results are summarized in Table 1. The result for PP was in good agreement with that reported by other investigators.[1,3,11)] Though a minute amount of cobalt was found in APP, the atomic ratios of the other elements were almost the same in both polymers. Further, no significant difference between PP and APP was observed in the resistivity and in the infrared spectrum. It is presumed from these results that the structure of APP is quite similar to that of PP. Thus, the polymerized pyrrole rings seem to form the main structure of APP, and cobalt species being the active sites for O_2 reduction is considered to be dispersed in this polymer.

Table 1. Relative atomic ratio (N=1) for polypyrrole and activated polypyrrole

Polymer	H	C	N	Cl	Co
Polypyrrole	2.84	4.04	1.00	0.19	----
Activated polypyrrole	2.97	4.00	1.00	0.25	0.019

It is not clear whether cobalt species in APP exist as cobalt(II) acetate or other cobalt complexes. The catalytic activity of APP is, however, not due to incidental contamination of cobalt species into PP, because the activity appears only when the polymer was deposited from the acetonitrile solution containing pyrrole, cobalt(II) acetate, and perchlorate ion. Polypyrrole itself is well known to have a cationic character. Then, it seems likely that cobalt species is at first introduced into the polypyrrole film in the form of anionic complex such as $Co(OAc)_3^-$ or $Co(OAc)_4^{2-}$.[12)]

Systems other than $Co(OAc)_2$-$LiClO_4$-Au were also examined. Particularly, effects of electrode materials and ligands in cobalt complex on the catalytic activity for O_2 reduction were studied, and the results are summarized in Table 2. It is observed that the APP films deposited on various electrode materials show almost the same catalytic activity, and the cobalt(II) benzoate and cobalt(II) acetylacetonate systems also have the electrocatalytic activity for O_2 reduction. The former result indicates that the electrocatalytic activity of APP for O_2 reduction is certainly ascribed to cobalt species doped into the polypyrrole film. On the other hand, the latter result suggests that cobalt species in the above two systems is introduced into the polypyrrole film after the formation of anionic complex similar to that in Co(II) acetate.[12)]

Table 2. Catalytic activity for O_2 reduction of polypyrrole film prepared in various systems

Cobalt salt	Electrode material	Catalytic activity [b)]	E_{pc} V vs. SCE
Co(II) acetate	Au	yes	0.20
Co(II) acetate	Ni	yes	0.20
Co(II) acetate	Carbon	yes	0.18
Co(II) acetate	Pt	no	0.20
Co(II) benzoate	Au	yes	0.15
Co(II) acac [a)]	Au	yes	0.09
Co(III)acac [a)]	Au	no	-
Co(II) perchlorate	Au	no	-
Co(II) chloride	Au	no	-
Co(II) bromide	Au	no	-
Co(II) nitrate	Au	no	-
Co(II) oxalate	Au	no	-

a) acac: acetylacetonate. b) "no" means that the E_{pc} value is more negative than that on the bare electrode.
Deposition solution: acetonitrile containing 5×10^{-3} M cobalt salt, 0.05 M pyrrole, and 0.1 M $LiClO_4$.

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