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ELECTROCHEMICAL PROPERTIES OF POLYTETRACYANOETHYLENE METAL CHELATE FILMS PREPARED ON METALS BY GAS PHASE REACTION

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Current-potential characteristics of iron, copper and nickel chelate films prepared by gas phase reaction of tetracyanoethylene with metals have been measured by cyclic voltammetry. The iron chelate film electrode showed a nearly reversible voltammogram for the reduction of iron(Ⅲ) ethylenediaminetetraacetate and exhibited electrocatalytic activity for the oxygen reduction.

There has been considerable interest in the electrocatalysis of organo-metallic complexes, such as metal phthalocyanines and porphyrins. Their catalytic effects on the electroreduction of oxygen,[1-4] hydrogen peroxide,[5] and carbon dioxide[6] have been reported. In previous studies, these complexes were deposited on electrode surfaces by solvent evaporation, adsorption from solution[7] or vacuum evaporation. Recently, new methods for the attachment of molecules including metal complexes[8] to the electrode surfaces by covalent bonding have been developed.

Berlin et al.[9] and Naraba et al.[10] have reported that the vapor of tetracyanoethylene(TCNE) reacts with various metals at high temperatures to give polytetracyanoethylene metal chelate(PTCNE-metal) film on the metal surfaces. The polymer films were found to behave as a typical organic semiconductor and to have molecular structures similar to that of phthalocyanine polymers. These results prompted us to apply the gas phase reaction of TCNE with metals to the modification of metal electrode surfaces by direct coating with the PTCNE-metal films.

In the present study, to elucidate new electrochemical properties resulting from the PTCNE-metal film preparation on iron, copper and nickel electrodes, the current-potential curves for the reduction of iron(Ⅲ) ethylenediaminetetraacetate(EDTA) and for the reduction of oxygen in neutral solutions were measured at the PTCNE-metal film electrodes.

The polymer film preparation and the fabrication of the polymer film electrodes were performed as follows. TCNE was purified by sublimation. The metals were of 99.999% purity. Metal rods of 5mm in diameter and 17mm in length were polished at one end with alumina paste and then annealed at 350°C for 12 hours in the atmosphere of hydrogen in order to remove surface oxides of the metals. The pretreated metal rods and a small amount of TCNE were sealed in a 20ml glass ampule evacuated at about 10^{-4}mmHg and then heated in a furnace; the reaction time and temperature and the amount of TCNE are shown in Table 1. The powder of TCNE was vaporized by heating and polymerized on the metal surface. The order of reactivity of metals with TCNE was: copper>iron>nickel. The black polymer films formed under the condition as listed in Table 1 were strongly attached to the metal surfaces. The metal rod coated with the polymer film was washed with acetone and then cemented with epoxy resin in a glass tube so that only the polymer surface of the polished end was in contact with the electrolyte. An electrical contact was made by soldering on the metal surface which was revealed by stripping the polymer film.

Current-potential curves were measured under potentiostatic condition. The counter electrode was a platinum net and the reference electrode was a saturated calomel electrode. The phosphate buffer solution of pH 7.0 or 0.1M $NaNO_3$ solution prepared from reagent grade chemicals and twice distilled water were used as an electrolyte. Nitrogen gas used for deaerating the electrolyte was purified by passing through a hot copper net.

Table 1. Conditions of PTCNE-metal film preparation

Metals	Amount of TCNE/ mg	Temperature/$^{\circ}$C	Time/min
Cu	5	250	24
Fe	10	350	240
Ni	10	350	210

The resistive component of electrode impedance at 1kHz in the deaerated phosphate buffer solution was measured by a lock-in amplifier. The resistances of the PTCNE-Cu and the PTCNE-Fe films in the potential range -0.3 to -0.6 V were estimated to be about $4 \cdot 10^3$ and $3 \cdot 10^2$ohm, respectively. The thickness of the PTCNE-Cu film, calculated from the resistace measured and the specific resistivity taken from ref.10, is about 10^{-5}cm or above.

Figure 1 shows the cyclic voltammograms measured at bare metals and the PTCNE-metal film electrodes in the deaerated buffer solution(pH 7.0). The anodic and cathodic current peaks corresponding to the surface oxidation and reduction of metal were vanished by the polymer film preparation. The PTCNE-Cu electrode showed a flat background response from -0.8 to 0.0V. The PTCNE-Fe and the PTCNE-Ni electrode had a flat region from -0.8 to 0.8V in the voltammogram. These facts indicate that the electrode surfaces are completely covered with the PTCNE-metal films which are stable electrochemically in these potential ranges.

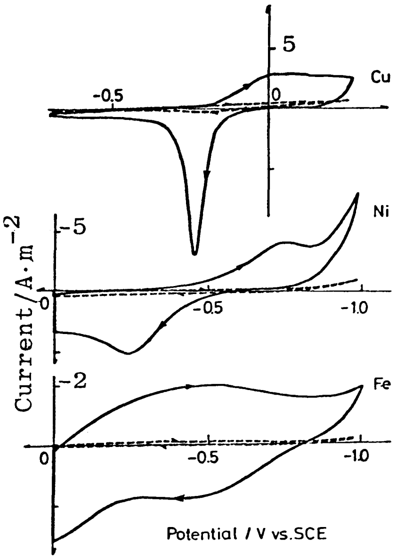

Fig.1 Cyclic voltammograms of metal electrodes and PTCNE-metal electrodes in deaerated phosphate buffer solution. ——, bare electrodes; ----, PTCNE-metal electrodes. Scan rate, 0.1V sec^{-1}

Figure 2 shows the cyclic voltammograms for the reduction of Fe(Ⅲ) EDTA obtained at a PTCNE-Fe and a PTENE-Cu electrode in deaerated 0.1M $NaNO_3$ solution. The curve measured at the PTCNE-Fe electrode showed a nearly reversible response for the redox reaction, but at the PTCNE-Cu electrode a irreversible response was observed. The high resistivity of PTCNE-Cu films appears to cause this irreversibility. The results shown inFigs.1 and 2 indicate that faradaic reactions really occur on the PTCNE-metal film surfaces.[11] It is unsuitable to observe a redox reaction on the metal electrodes in the potential range in which the PTCNE-metal film electrodes show a flat background response, because of the oxidation of the metal electrode surface(see Fig.1). Thus, one of the advantages of the PTCNE-metal film preparation on metal electrodes is the extension of working potential range.

The investigations of electrocatalytic activities for the reduction of oxygen on the PTCNE-metal films are very attractive, owing to the structural similarity to metal phthalocyanine polymers which are

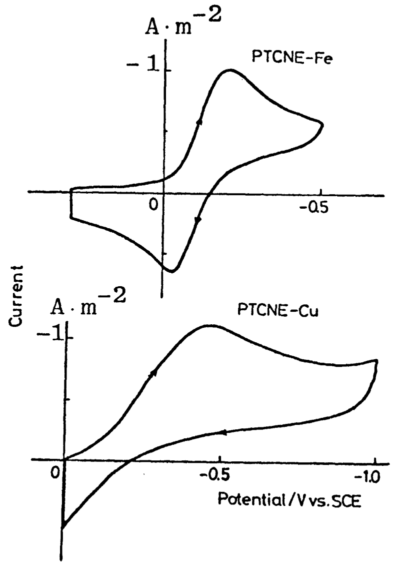

Fig.2 Cyclic voltammograms at PTCNE-Fe and PTCNE-Cu electrode in deaerated 0.1M $NaNO_3$ containing 1mM $Fe(NO_3)_3$ and 1mM EDTA. Scan rate, 0.1V sec^{-1}.

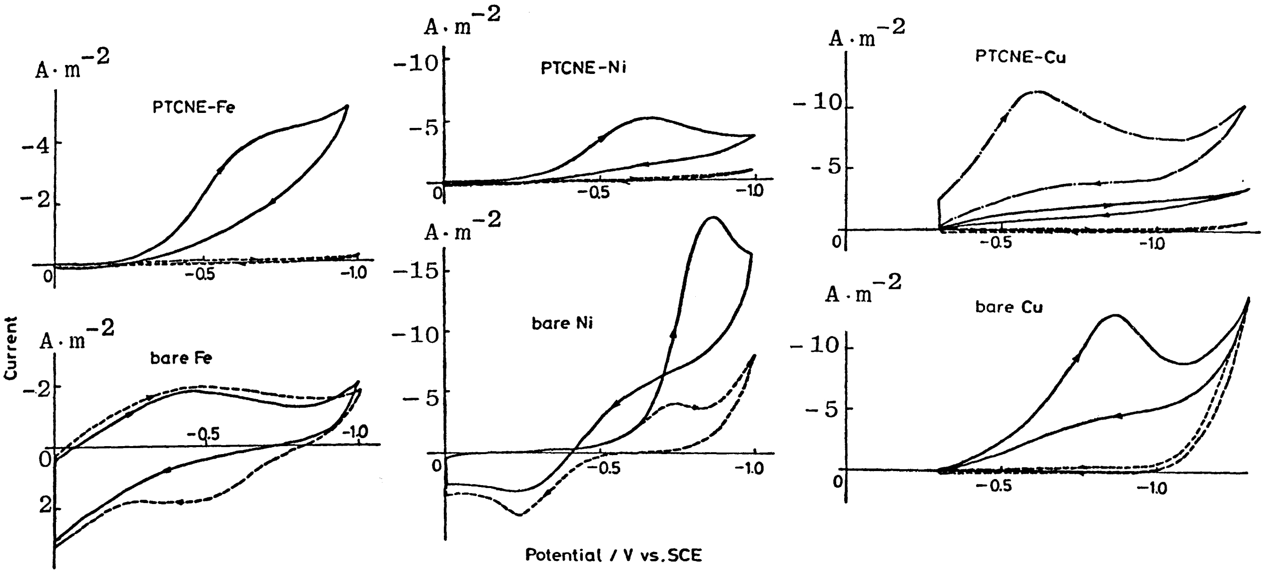

Fig.3 Cyclic voltammograms at PTCNE-metal electrodes and bare metal electrodes in oxygen saturated phosphate buffer solution(pH 7.0). ———, oxygen saturated; ----, nitrogen saturated; —•—, oxygen saturated, after the potential was held at -1.3V for 20min. Scan rate, 0.1V sec^{-1}.

known to be a very effective catalyst for the oxygen reduction.[1,12] Figure 3 shows the cyclic voltammograms for the oxygen reduction measured at the PTCNE-metal electrodes and the bare metal electrodes in the oxygen saturated phosphate buffer solution(pH 7.0). The polymer film preparation on the iron electrode considerably enhanced the catalytic activity for the oxygen reduction. The nickel electrode was also activated in a small current region, but the copper electrode was deactivated by the polymer film preparation. It was found that the PTCNE-Cu electrode was activated by the cathodic polarization of the electrode. After the potential was held in the potential region of hydrogen evolution for some time, an apparent current peak corresponding to the oxidation of metal copper appeared in the cyclic voltammogram and a current peak for the oxygen reduction was observed at the potential -0.2V more positive than the bare copper electrode (see Fig.3, ——•line). The actual reduction of oxygen on the activated PTCNE-Cu electrode at -0.7V for 12 hours did not deterioate its catalytic activity. The catalytic activity of metal phthalocyanines for the oxygen reduction have been found to depend on the nature of central metal ions.[13] In the case of the PTCNE-metal film, it is difficult to define the effect of central metal ions on the catalytic activity, because of a difference in the iR drop of polymer film and in the degree of polymerization, which may have an influence on the catalytic activity.[12]

Although the high resistivity of the PTCNE-metal film is the main disadvantage for electrochemical uses, the direct preparation of the polymer film on various base metal electrodes may provide a wider potential range, higher catalytic activities for various electrode reactions and the properties of organic semiconductors.

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