

Thermal Modulation Voltammetric Observation of Cyanide Ion in the Membrane Part of an Ion-Selective Electrode Based on a Polymer Modified with Cobalt Phthalocyanine in Acetonitrile

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A platinum disk coated with polyacrylamide modified with phthalocyanine complex (Pt-PAA-[M(pc)], M = Co, V) serves as an ion-selective electrode of CN⁻ and F⁻ in nonaqueous media.^{1,2} Because of its Nernstian response in the proper concentration range, the Pt-PAA-[M(pc)] electrode has been available for analytical and physicochemical studies of anions in nonaqueous solutions. On the other hand, it has been pointed out that the Pt-PAA-[Co(pc)] electrode is applicable to amperometric or voltammetric measurements, that is, the cyclic voltammograms exhibit oxidation peaks of the anions.³ We have remarked on the fact that one electrode can exhibit both potentiometric and amperometric responses, and have been thinking that a voltammetric investigation is important in order to specify chemical species responsible for the potentiometric response of the electrode. We thus tried to apply thermal modulation voltammetry (TMV) as well as cyclic voltammetry (CV) to the Pt-PAA-[Co(pc)] electrode and to examine chemical forms of the anions in the membrane part of the Pt-PAA-[Co(pc)] electrode.

TMV is a kind of alternative-current voltammetry.^{4,5} In voltammetry, the periodic thermal modulation produces an alternative current and the magnitude of the alternative current is recorded as a function of the electrode potential; that is, a TM voltammogram (ΔI - E curve) is obtained. (In this work, an intermittent laser beam was applied to generate periodic thermal modulation.) Because TMV is generally used to examine the entropy change of an electrode reaction,⁵⁻⁸ a naked electrode is usually used. However, this work was the first case applied to a film-coated electrode, such as the Pt-PAA-[Co(pc)] electrode. The main purpose of this work was not to determine the precise entropy change by the usual use of TMV, but to extend its applicability to a film-coated electrode.

Experimental

Working electrode (Pt-PAA-[Co(pc)])

Tetraaminophthalocyanine cobalt of Wako was conjugated with carboxyl-modified PAA (Aldrich Chemical Co., 19,093-4) by amide bonding in dimethylformamide.^{9,10} A small amount of the pigment was coated on a platinum disk, as previously described.¹ A silver-containing paste (Lexbond T-700, Toyo Ink Co., Ltd.) was used to connect the platinum disk to a

stainless-steel lead wire.

Apparatus

Voltammetric measurements were performed with a potentiostat for a microelectrode (Model HECS-972) and a potential sweep unit (Model HECS-980) of Huso Seisakusyo Co., Ltd. Although TMV was performed as previously described,⁵ it is briefly described here. A He-Ne laser (NEC Co., Ltd., Model GLG-5800) was operated with a power of 20 mW at 632.8 nm in order to modulate the temperature at the electrode surface and in its neighboring region. The laser beam was mechanically chopped at 35 Hz with an optical chopper (Crystal Spectra Co., Ltd. Model L157-4). An intermittent laser beam was focused onto the electrode surface through an objective lens of a microscope (Olympus Co., Ltd., BH2-UMA, $\times 10$). An alternative component of the current signal from the potentiostat was amplified with a lock-in amplifier (NF Co., Ltd., Model LI-570A) and the magnitude of the alternative component was recorded on an X-Y recorder (Graphtec Co., Ltd., Model WX1200) as a function of the electrode potential. The reference signal for the lock-in amplifier was supplied from the optical chopper, and the phase of the lock-in amplifier was adjusted so that the magnitude was maximized at the peak potential of a TM voltammogram. In general, the phase depends on the electrode potential. However, even when the phase was turned from the adjusted one, the TM voltammogram varied little in shape, though it decreased in magnitude and reversed in sign normally according to the phase turning. A flow-type electrolytic cell, which was machined from a PCTFE resin block, was used with an optical window. The reference electrode (Ag/0.01 M Ag⁺, 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile (AN), M = mol dm⁻³) was attached to the cell so that the electrode was in contact with the flowing sample solution through a chip of porous glass. A stainless-steel tube, being a part of the flow system on the outlet side, was used as a counter electrode. The sample solution was supplied to the cell at a flow rate of 0.05 cm³/min with an automatic buret (Metrohm Co., Ltd., Model 665 Dosimat) serving as a pump. CV was also carried out in the flow cell, although the sample solution was kept stationary. All of the voltammetric measurements were performed at a room temperature, 20–25°C.

Reagents

Tetraethylammonium cyanide (Et₄NCN) and AN as a solvent

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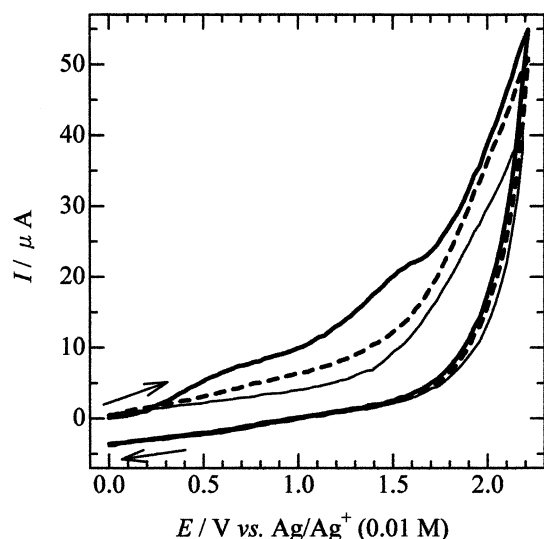


Fig. 4 Cyclic voltammograms at the Pt-PAA-[Co(pc)] electrode. The thin and thick lines illustrate the cyclic voltammograms for the blank and sample solutions, respectively. The thick solid and broken lines denote the cyclic voltammograms measured after 10-min standing and immediately after the first potential cycling, respectively. The sample AN solution contained 3.0 mM cyanide ions and 0.1 M TEAP as a supporting electrolyte. The scan rate was 100 mV/s.

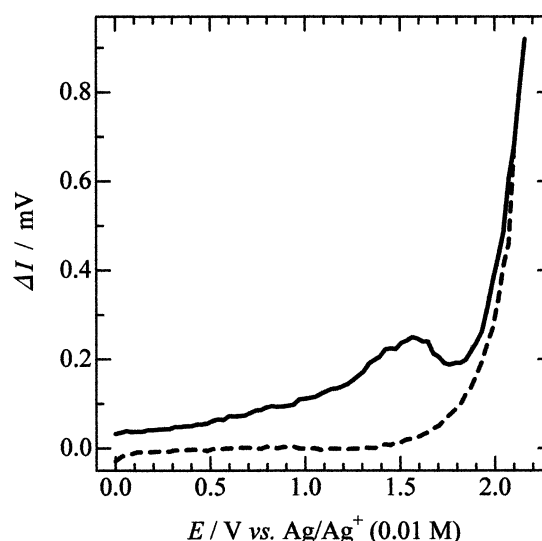


Fig. 5 Thermal modulation voltammograms at the Pt-PAA-[Co(pc)] electrode. The broken and solid lines illustrate the TM voltammograms for the blank and sample solutions, respectively. The TM voltammogram for the sample solution was measured after 10-min standing. The sample AN solution contained 5.0 mM cyanide ions and 0.1 M TEAP as a supporting electrolyte. The scan rate was 5 mV/s, the flow rate 0.05 ml/min, the chopping frequency 35 Hz and the phase 22°.

oxidation wave is due to the oxidation of the complex between CN^- and $[\text{Co}(\text{pc})]$, rather than that of CN^- , itself.

The TM voltammogram at the Pt-PAA-[Co(pc)] electrode exhibited no peak at 0.6 V, but a clear peak at 1.55 V, as can be seen in Fig. 5. In addition, the height of the peak at 1.55 V was proportional to the CN^- concentration in the range to 5.0 mM. From the good correspondence between the peak at 1.55 V in the TM voltammogram and the wave around 1.55 V in the cyclic voltammogram, the peak in the TM voltammogram is assigned to the oxidation of CN^- bonded chemically to $[\text{Co}(\text{pc})]$ conjugated with the polymer matrix.

Appearance of the peak in the TM voltammogram

As described above, the cyclic voltammograms exhibited one wave around 0.6 V at the Pt-PAA electrode and two waves around 0.6 and 1.55 V at the Pt-PAA-[Co(pc)] electrode, whereas the TM voltammograms exhibited only a small hump around 0.6 V at the Pt-PAA electrode and a peak around 1.55 V at the Pt-PAA-[Co(pc)] electrode. The following reasons are proposed for such appearance of the peaks in the TM voltammograms. The first concerns a difference between heat generation at the Pt-PAA and Pt-PAA-[Co(pc)] electrodes. In conventional TMV, where a naked electrode is used, the heat generation due to an optical absorption by the electrode is only contributed to the thermal modulation. On the other hand, when a metal disk covered with a membrane is used as the electrode, the heat generation depends on an optical absorption of the membrane as well as the metal, unlike the conventional TMV. In fact, an AN solution containing $[\text{Co}(\text{pc})]$ exhibited a strong absorption at 632.8 nm, which is a wavelength of the He-Ne laser. Because of this optical absorption, the thermal modulation is expected to be enhanced at the Pt-PAA-[Co(pc)] electrode more than at the Pt-PAA electrode. That is, even the peak, which is not observed at the Pt-PAA electrode, may be observed by using the Pt-PAA-[Co(pc)] electrode. However, no peaks could be observed around 0.6 V in spite of using the Pt-

PAA-[Co(pc)] electrode, while the peak was observed at 1.55 V. This fact indicates that the optical absorption by the membrane little enhanced the thermal modulation. Secondly, the chemical forms of CN^- in the membrane should be discussed, because the peak height of the TM voltammogram depends on the entropy change of the electrode reaction. In general, a larger entropy change leads to a higher peak, particularly for a reversible electrode reaction.⁵ As discussed above, cyanide ions exist in two chemical forms, that is, cyanide ions merely retained in the polymer matrix (retained CN^-) and chemically bonded to $[\text{Co}(\text{pc})]$ (bonded CN^-). The retained CN^- and bonded CN^- are responsible for the waves around 0.6 and 1.55 V in the cyclic voltammogram at the Pt-PAA-[Co(pc)], respectively. Because the bonded CN^- is chemically restricted more strongly than the retained CN^- , it is reasonable that the oxidation of the bonded CN^- accompanies an entropy change larger than that of the retained CN^- , if the oxidation products from the two forms are identical. This idea supports the experimental fact that only one peak was observed at 1.55 V in the TM voltammogram, because the peak at 1.55 V is due to oxidation of the bonded CN^- . On the other hand, the electrode kinetics may influence the peak height of the TM voltammogram.⁵ As the reversibility of the electrode reaction decreases, the peak height tends to decrease. The two waves in the cyclic voltammogram suggest that the electrode reactions around 0.6 and 1.55 V are both irreversible. Thus, the effect of the electrode kinetics on the peak height of the TM voltammogram is unclear at present. However, the assumption that the oxidation of the bonded CN^- is more reversible than that of the retained CN^- , which is likely because of the complex formation between CN^- and $[\text{Co}(\text{pc})]$, is not contradictory with the experimental fact. At the present stage, the idea based on the entropy change is fairly promising to explain the TM voltammograms obtained at the Pt-PAA and Pt-PAA-[Co(pc)] electrodes.

By applying TMV to the film-coated electrodes and

considering the voltammograms based on the entropy change of the electrode reaction, we could confirm that cyanide ions exist in two chemical forms in the film. It has thus been proved that TMV is useful for characterizing chemical species in the film. Various types of TM voltammetric experiments, including changing the chopping frequency and monitoring the phase automatically, will be available for the selective characterization and determination of the species in a thin film. This will clarify the response mechanism of the ion-selective electrode. Further, TMV is applicable to examining electrochemical reactions in a biological membrane as well as an artificially coated film. Owing to such possibilities, this first application of TMV to film-coated electrodes is thought to be a promising result.

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