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Reversible Electrochromism in the Thin Films of Single-Transition Metal Phthalocyanines

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The reversible electrochromism in the thin films of single-transition metal phthalocyanines is reported. Copper and nickel phthalocyanine films can be oxidized and rereduced reversibly, when the film is enough thin, the scan range is well controlled, and the appropriate anion is used as the electrolyte. Especially, the cyclic voltammogram of nickel phthalocyanine films in a sodium nitrate solution is almost Nernstian.

Phthalocyanine (Pc) has recently received much attention in connection with its electrochemical and photochemical properties. Since the electrochromism of rare-earth diphthalocyanines is of interest from the viewpoint of the application to display, many investigations have been performed on it.1, 2) However, only few attempts have so far been made for the electrochromism in the films of transition metal phthalocyanines. It is because their electrochromisms were reported irreversible.3) In the last decade, only few articles have been published on the electrochromic study of single-transition metal phthalocyanine films.4-6) Recently Silver et al. reported that reduction and reoxidation cycling can successfully occur but oxidation and rereduction cycling is irreversible in the case of iron phthalocyanine.6) In the present letter, we report for the first time that copper and nickel phthalocyanine films can be oxidized and rereduced reversibly. The thickness of the thin films, the scan range in the oxidation and rereduction cycling, and the kind of anions as the electrolyte are the important factors for the reversible electrochromism.

The phthalocyanines were purified by vacuum sublimation. The phthalocyanine thin film (30 - 160 nm) was prepared by vapor deposition onto an ITO glass (30 Ω/□) at 400 - 430 °C under ca. 1×10^{-5} Torr at the rate of 6 nm min^{-1}. The ITO glasses used for the deposition had been cleaned in advance by washing ultrasonically with dichloromethane and 2-propanol.

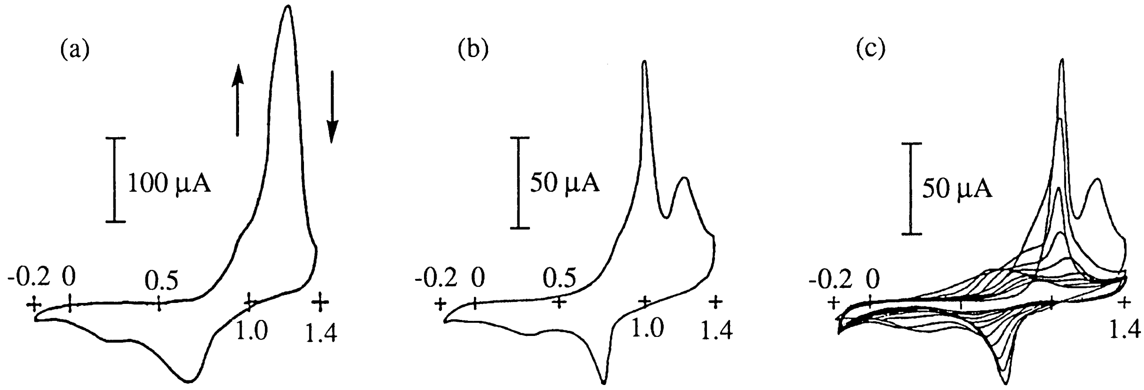

Fig. 1. Cyclic Voltammograms for copper phthalocyanine films in 0.1 mol dm^{-3} $NaClO_4$, scan speed = 20 mV s^{-1} : (a) The first scan for a 160 nm thick film, (b) The first scan for a 30 nm thin film, and (c) ten cycling for a 30 nm thin film. All x-axes are the potential (V vs Ag-AgCl).

Electrochemical measurements for the thin films were carried out at room temperature in a 0.1 mol dm^{-3} solution of various electrolytes. The working electrode was the ITO glass covered with the phthalocyanine thin film by the vapor deposition. A platinum wire and an Ag/AgCl saturated KCl electrode were used as a counter and a reference electrode, respectively. The cycle voltammograms were recorded by scanning the potential at the rate of 20 mV s^{-1}. In order to measure the transient spectral change during the electrochemical processes, a rapid scanning multichannel photodiode array spectrometer (Otsuka Electronics Co., MCPD-110A) was used with a Toho Technical Research model 200 potentiostat/galvanostat.7) The MCPD coupled with the Toho's model FG-02 function generator was triggered and operated by a NEC model 9801-VX personal computer.

Figure 1 shows cyclic voltammograms (CVs) of copper phthalocyanine (CuPc) films. In the case of a 160 nm thick film, there exist a strong broad peak at ca. 1.2 V and a weak shoulder peak at ca. 1.0 V during the oxidation at the first cycling from -0.2 V to 1.4 V in a 0.1 mol dm^{-3} $NaClO_4$ solution. In the case of 30 nm thin film, on the other hand, the peak at 1.0 V becomes strong, resulting in the separation of two oxidation peaks (Fig. 1b). In this cycling, the color of the film changes from blue to bluish purple at 1.0 V, and then to pale gray at 1.2 V. If the CVs are continued to measure in the same range from -0.2 V to +1.4 V, the response gradually decay with the repeated scan as shown in Fig. 1c.

However, if the scanning range is made a little narrow as from 0.0 V to 1.1 V, then the decay is not observed. The reversible oxidation and rereduction successfully proceeds as shown in Fig. 2a. In this reversible scan, both the oxidation and the rereduction peaks are not separated into two like the CV curves in Fig. 1. This means that the two couples of redox peaks in Fig. 1c are not due to two steps of redox reaction, but to two types of appearance of one reaction with different overpotential. It has been reported that the cause of irreversibility is that some anions, which have entered into the thin film to maintain the charge balance, remain inside the film after the rereduction.3)

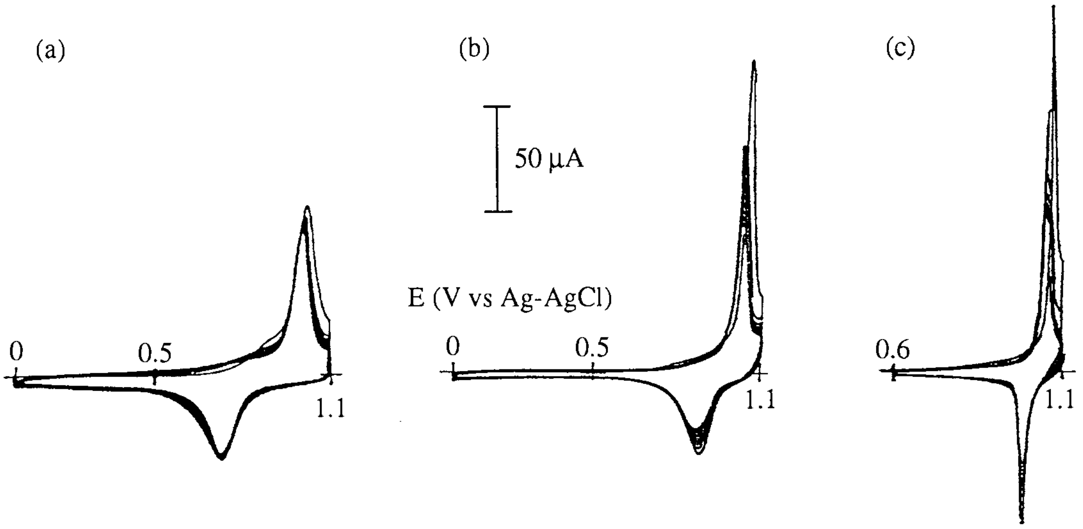

Fig. 2. Cyclic voltammograms (1st - 10th) of CuPc films in 40 nm thickness in various 0.1 mol dm^{-3} electrolyte solutions. Scanning rate ; 20 mV s^{-1}, the electrolyte ; NaClO$_4$ (a), NaBF$_4$ (b), and NaNO$_3$ (c).

According to this explanation, the present oxidation peak at 1.0 V stands for the reversible adsorption process of the anions on to the surface of crystal grains of thin film, and the peak at 1.2 V is the irreversible entering process of them.

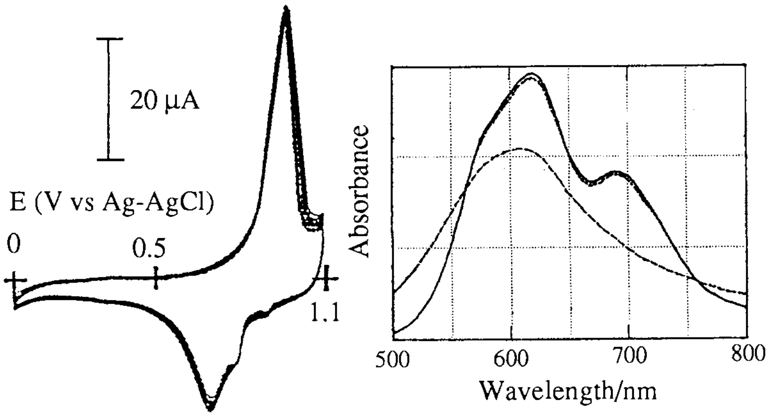

Fig. 3. Cyclic voltammogram (20 cyclings) and visible absorption spectrum changes (at 20th cycling) of CuPc films in 40 nm thickness in a 0.1 mol dm^{-3} NaPF$_6$, scanning rate is 20 mV s^{-1}.

The reversible properties were also observed in the change of the electronic absorption spectra, which were taken at the same time with the CV curves during the redox cycling. Thus, the reversible electrochromism between sky blue and bluish purple was attained for the system of the reversible cyclic voltammogram. The example is shown Fig. 3, where the similar absorpotion spectrum to the original one (solid curve) was observed after a cycling.

Since usually moving between the electrolyte solution and the film, the ionic species, used as the electrolyte, can affect on the shape and the reversibility of the CV curves in the redox cycling. When the anion was altered in the present case, much different CV curves were obtained in fact, although the same reversible color change was observed. Examples are shown in Fig. 2. When the anion of the electrolyte is altered from ClO$_4^-$ to BF$_4^-$, and then NO$_3^-$, the potential difference between the oxidation peak and the rereduction peak decreases from 0.34 V to

0.15 V, and then 0.09 V, becoming more Nernstian in this order.

Next, the Pc films with various central metals were offered for the electrochromic measurements. The film thickness and the scan range were kept at 40 nm and in appropriate values, respectively. The results of electrochromism of MPc thin films are summarized in Table 1. The order of oxidation potential of MPc thin films is very similar to that measured in solutions.[8)] In $NaClO_4$, $NaBF_4$, $NaNO_3$, and $NaPF_6$ solutions, the CuPc and NiPc films have good reversibility. In the case of CoPc and ZnPc films, however, the reversibility is not so good as CuPc and NiPc. The FePc and Ag_2Pc films are entirely irreversible under the same conditions. Figure. 4 shows the reversible CV and electronic spectrum changes of NiPc films in a 0.1 mol dm^{-3} $NaNO_3$ solution. The electrochromism can occur quite reversibly. It is worthwhile to mention that the potential difference between the oxidation peak and the reduction peak is quite narrows, only 90 mV, which is almost Nernstian.

Table 1. Reversibility in Oxidation of Thin Films of Transition-Metal Phthalocyanines[a)]

Anion	NiPc	CuPc	ZnPc	CoPc	FePc
PF_6^-	⧺	⧺	±	±	±
ClO_4^-	+	+	±	—	—
BF_4^-	+	+	—	—	—
NO_3^-	⧺	⧺	—	—	—
Cl^-	—	—	—	±	—

a) ⧺ : reversible completely, + : reversible, ± : quasi-reversible, and — : irreversible
All phthalocyanines were irreversible in Br^-, BrO_3^-, IO_3^- and CH_3COO^- solutions.

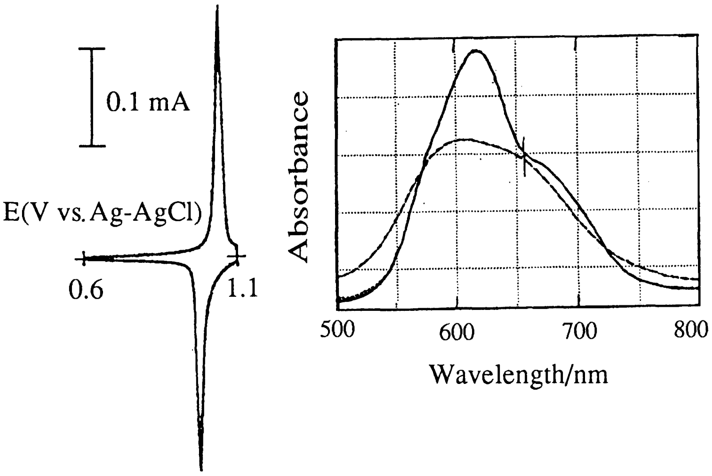

Fig. 4. Cyclic voltammogram (100 cyclings) and visible absorption spectrum changes (at the 100th cycling) of NiPc film with 40 nm in thickness in a 0.1 mol dm^{-3} $NaNO_3$ solution. Scanning rate ; 20 mV s^{-1}.

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