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Reversible Electrochromism of Copper Phthalocyanine Thin Film

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The electrochromism of copper phthalocyanine thin films was examined in detail under various conditions. The application of a positive voltage to copper phthalocyanine thin film exhibited two oxidation peaks in the range from 0 to 1.4 V. Although the color of the film changed from sky blue to pale gray upon scanning the voltage in this region, irreversible electrochromism was observed, leading to a deterioration of the film. The two oxidation peaks were concluded to represent two types of appearances of one reaction with different overpotentials caused by the structure of the crystal grains of the film. Control of the scan range to admit only the first oxidation peak provided a reversible electrochromism between sky blue and bluish purple. Electrolyte anions are also of great importance to accomplish reversible electrochromism. Thus, the anions should be stable for the application of a positive voltage, and their Stokes radii should be neither too large nor too small in order to achieve reversible electrochromism. Rather small anions provide almost Nernstian cyclic voltammograms and the quick color change.

Metallophthalocyanine [M(pc)] has attracted a great deal of attention in connection with its electrochemical and photochemical properties, which originate from its molecular structure. A considerable number of applied and fundamental studies have been made concerning the properties.[1,2) Especially, from the viewpoint of easy formation of a homogeneous organic thin film by vacuum deposition, [M(pc)] is proposed for one type of new advanced materials. In fact, various challenges, such as electrochromic devices,[3—5) organic solar cells,[6,7) switching devices,[8,9) and field effect transistors,[10) are being pursued for this purpose.

Focusing attention on electrochromism, rare-earth bis(phthalocyaninate) has been widely studied from the viewpoint of applications to new-type displays.[3—5) Since it accomplishes multiple color changes by redox reactions with good reversibility, several groups have systematically investigated the color changes of these dual-ring pcs.[11—15)

On the other hand, few attempts have ever been made to examine the electrochromism of light transition-metal complexes of phthalocyanines in thin films.[16—21) This is because their electrochromisms were reported to be irreversible, showing poor color changes. Although thin films of these pcs are often used in attempts to construct new organic devices (as mentioned above), their basic electrochemical properties have never been investigated well. Thus, it is worth studying the mechanism to control the electrochromic properties of [M(pc)] films, which can provide information concerning the ion and/or electron-transfer properties of compact organic thin films on electrodes. This is one of the fundamental standpoints to develop novel advanced materials.

To our knowledge, Faulkner et al. first discussed the electrochromism of these pcs, among which [Zn(pc)] was most intensively studied.[16) Although they used the word "reversible", the current response of [Zn(pc)] decreased with successive oxidation and rereduction cycle, and no steady cyclic voltammogram (CV curve) was shown in their article. They also studied the electrochromism of [Mg(pc)] film, which showed steady CV curves in a potassium hydrogen phthalate (KHP) solution.[17) Recently, Silver et al. reported that although reversible reduction and re-oxidation cycling can successfully occur, the oxidation and rereduction cycling is irreversible in the case of [Fe(pc)].[20)

In independent research we have reported that when the experiments are carried out under the designed conditions (to be precise, when the film is sufficiently thin, the scan range is well controlled, and the appropriate anion is used as an electrolyte), [Cu(pc)] and [Ni(pc)] thin films can then be oxidized and rereduced reversibly.[22) We would like to emphasize that the CV curves of [Ni(pc)] films in a sodium nitrate aqueous solution are almost Nernstian, and never decay for more than 100 cycles.

In this paper, the electrochromism of [Cu(pc)] film is examined from the viewpoint of the effects of the scan range upon applying a positive voltage, and of the electrolyte used as the charge-compensating anion, since both effects have been considered to be very important for "reversible" electrochromism. The mechanics of the reversible as well as irreversible electrochromism are also discussed.

Experimental

Preparation of Phthalocyanine Thin Films. Copper phthalocyanine was purified by vacuum sublimation before preparing thin films. Phthalocyanine thin films (about 40 nm in thickness) were prepared by vapor-deposition using a Shinku-kiko VPC-260 vacuum-deposition apparatus. The depositions were performed at 340—430 °C under ca. 1×10^{-5} Torr (1 Torr = 133.322 Pa) at a rate of 0.1—10 nm min^{-1}. The films were deposited onto indium–tin oxide (ITO) glass (10 Ω/□) previously cleaned by washing ultrasonically with dichloromethane and 2-propanol. The film thickness was monitored during deposition by a quartz crystal microbalance (Anelva EVM-32B) located adjacent to the sample position within the bell jar.

Voltammetric and Spectroelectrochemical Measurement. Electrochemical measurements of the thin films were carried out at room temperature in 0.1 mol dm^{-3} aqueous solutions of various electrolytes. All of the electrolytes were of reagent grade and were used without further purification. Aqueous solutions were prepared using distilled water. The working electrode was ITO glass covered with phthalocyanine thin film by vapor deposition. Electrical contact was made with the ITO glass using a glass tube-covered copper wire and silver paste, and sealed with epoxy resin. After the epoxy resin was completely dried (after ca. one day), the working electrode was used. A platinum wire and an Ag/AgCl-saturated KCl electrode were used as a counter and a reference electrode, respectively. Electrochemical measurements were performed on a Toho Technical Research model PS-2000 potentiostat, a model 3320 coulometer/ampere hour meter, a model FG-02 function generator, and a Graphtec model WX2400 X-Y recorder, as previously reported.[23] In order to measure the transient spectral change during the electrochemical process, rapid scanning multichannel photodiode array spectrometers (Otsuka Electronics Co., MCPD-100A and IMUC-7000S) were used with an ITO working electrode, being triggered and operated by an NEC model 9801-VX personal computer. The transient absorption spectra were recorded at a 2.5-s interval with slow scanning (20 mV s^{-1}) of the ITO potential, and at a 0.5-s interval with stepping of the ITO potential. All of the potential values cited in this paper refer to Ag/AgCl.

Results and Discussion

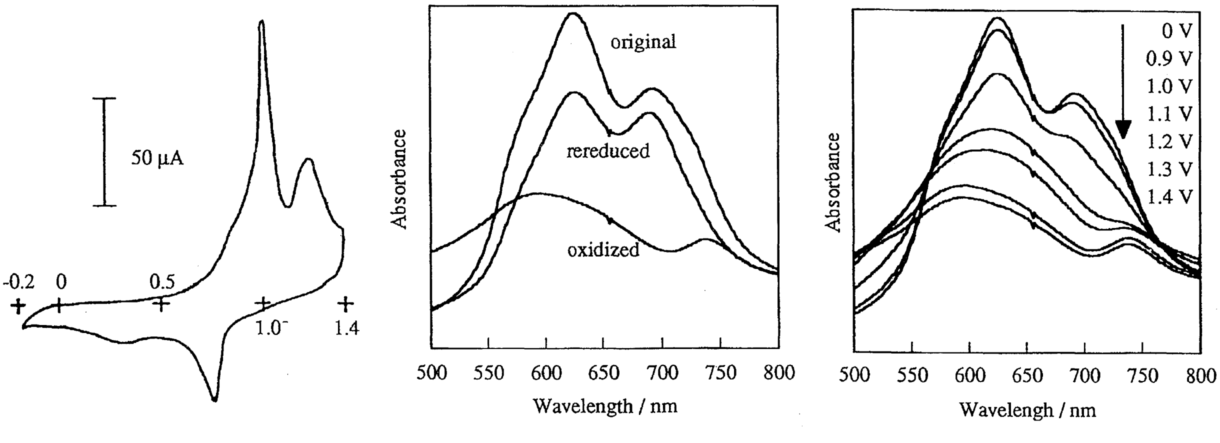
Oxidation of [Cu(pc)] Thin Film and Effect of the Scan Range. Figure 1 shows the oxidation and rereduction of a [Cu(pc)] thin film of 30 nm thickness in a 0.1 mol dm^{-3} $NaClO_4$ aqueous solution. In the cyclic voltammogram (CV curve), two oxidation peaks appear at 1.0 and 1.2 V, respectively, and two rereduction ones at 0.7 and 0.3 V, respectively. The visible absorption spectrum of the rereduced film does not match that of the original one, indicating that the cycled film has a different state from the original one. The color of the [Cu(pc)] film changes from sky blue (original) to pale gray (oxidized), and back to bluish green. From a subsequent scan, as shown in Fig. 2, both the CV curve and the visible absorption spectrum of the rereduced [Cu(pc)] film decay with repeated scanning of the oxidation and rereduction. These results show that this electrochromic process is irreversible.

In the spectral change during the first anodic scan until 1.1 V, two isosbestic points can be observed at 560 and 750 nm, as shown in Fig. 1(c). Above 1.1 V, however, no isosbestic point can be observed in the visible region. This result clearly indicates that two different phenomena occur at the voltage bordering 1.1 V in the oxidized process, and that the [Cu(pc)] film can be oxidized reversibly until 1.1 V.

The phenomenon observed over 1.1 V admits two interpretations: One of them is the formation of a chemical species different from both the original and oxidized [Cu(pc)] below 1.1 V; the other is a deterioration of the [Cu(pc)] film. The latter one seems to be reasonable because the absorbance of the rereduced film decreases with a repeated scan of the oxidation and rereduction, as if the quantity of [Cu(pc)] has decreased (Fig. 2(b)). In fact, the deterioration of the film can be recognized by the naked eye in the case of other [M(pc)].

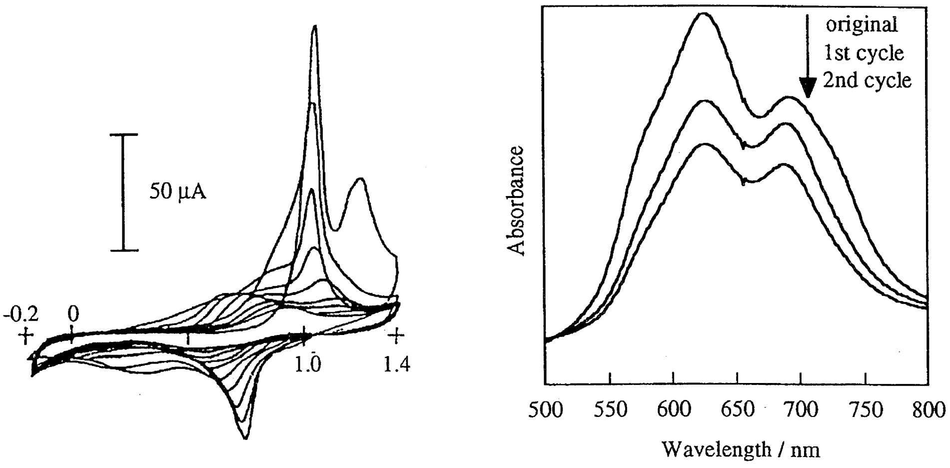
An electrochemical measurement was performed under the condition that the scanning range was made slightly narrower, from 0 to 1.1 V, which gave completely different results, as shown in Fig. 3. In this case, the CV curve does not decay with repeated scans, and the absorption spectra of the rereduced film almost match that of the original one, demonstrating that reversible electrochromism can be achieved.

All of these results can be observed independent of both the deposition rate (0.1—10 nm s^{-1}) in the film preparation and the atmosphere in the electrochemical measurement. The oxidation current and the spectral change are smaller in the present case compared to those in the case of a scan from



(a) (b) (c)

Fig. 1. Cyclic voltammogram (a), visible absorption spectra at the three states (b) and visible absorption spectral changes during the oxidation process (c) for the first oxidation and rereduction cycle of the [Cu(pc)] thin film in a 0.1 mol dm^{-3} $NaClO_4$ aqueous solution at the scanning rate of 20 mV s^{-1}.



(a) (b)

Fig. 2. Cyclic voltammograms of the 1st to 10th oxidation and rereduction cycles of [Cu(pc)] thin film (a) and the visible absorption spectra of original and rereduced films (b) in a 0.1 mol dm^{-3} NaClO$_4$ aqueous solution at the scanning rate of 20 mV s^{-1}.

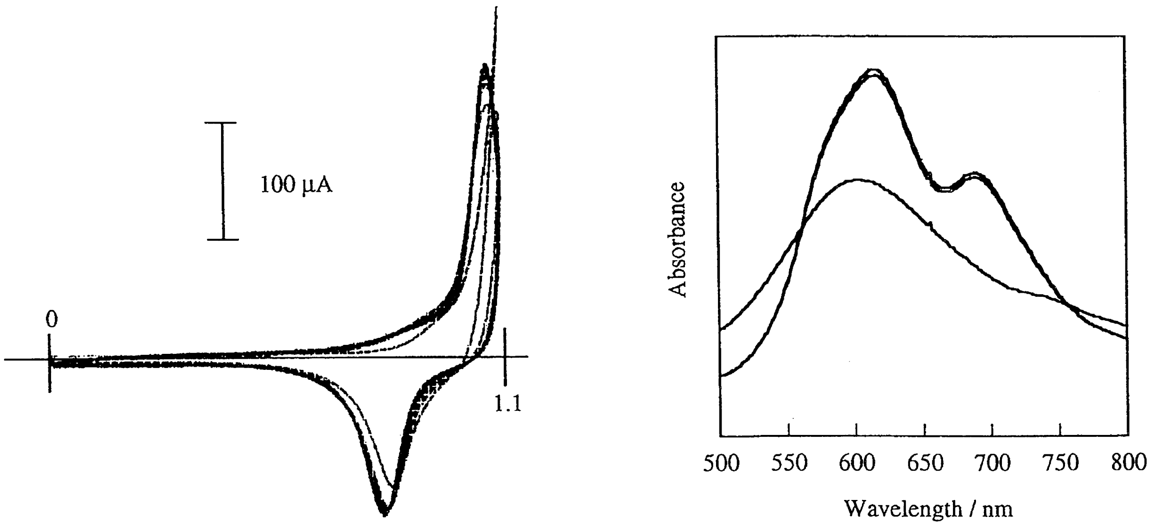


Fig. 3. Cyclic voltammograms (1st—10th) and the visible absorption spectra in oxidized and rereduced state at 10th cycling of [Cu(pc)] thin film in a 0.1 mol dm^{-3} NaClO$_4$ aqueous solution at the scanning rate of 20 mV s^{-1}.

0 to 1.4 V. Furthermore, the absorbance spectrum of the [Cu(pc)] film oxidized until 1.1 V (bluish purple color) is an intermediate in shape between the original one and that oxidized until 1.4 V. These results suggest that the same oxidized species were formed with the application of 1.1 V as those of 1.4 V, and that the amount of oxidized species formed at 1.1 V was less than that at 1.4 V.

This explanation is well supported by the CV curves of [Cu(pc)], scanning from 0 to 1.1 V, in which the rereduction peak at 0.3 V disappears. This result means that the rereduction peaks at 0.3 and 0.7 V correspond to the oxidation ones at 1.2 and 1.0 V, respectively, which completely differs from the CV curves with two redox reactions.

On the basis of these considerations, the two pairs of redox peaks in the CV curve with a wide scanning range do not mean two steps of redox reaction, but, rather, two types of appearances of one reaction with different overpotentials. In other words, one pair of 1.0/0.7 V peaks represents a process proceeded by a small overpotential; the other (1.2/0.3 V) also represents one requiring a large overpotential.

In order to confirm this explanation, n values for the oxidation of [Cu(pc)] films were determined using chronocoulometry by applying various positive voltages. The number of [Cu(pc)] molecules in a mole of the [Cu(pc)] film was estimated by dissolving the film in 1-chloronaphthalene and measuring the absorbance at λ_{max} on the basis of the reported extinction coefficient.[24)]

When [Cu(pc)] film was prepared on ITO glass by vapor deposition, six pieces of ITO glasses were placed at once in a sample holder inside a bell jar and [Cu(pc)] molecules were deposited onto them. One sample was used for electrochemical measurements, while another was for absorbance measurements. Before each measurement, the area of deposited [Cu(pc)] was carefully measured, and the number of moles of [Cu(pc)] for the electrochemical measurements was corrected. The resulting n values for the initial oxidation of [Cu(pc)] films by the potential step from 0 V to 1.1 and to 1.4 V were calculated to be 0.64 and 1.34, respectively. Thus, only some of the [Cu(pc)] molecules were oxidized by applying 1.1 V, and it was not until 1.4 V that all [Cu(pc)] molecules of the film underwent one-electron oxidation. This result supports the idea that the two pairs of redox peaks in the CV curve scanned from −0.2 V to 1.4 V mean two types of appearances of one reaction with different overpotentials, respectively.

It has been reported that the irreversibility is due to the phenomenon that some anions, which have entered the thin film to maintain a charge balance, remain inside the film after rereduction.[16] On the other hand, the structure of the vapor-deposited [M(pc)] thin film is revealed by the SEM and XRD measurements. The SEM photographs show that any kind of [M(pc)] film has rod-like crystallites, whose width is about 200 Å.[25] Furthermore, the XRD pattern of the [M(pc)] film on ITO glass exhibits a single sharp peak located at ca. $2\theta=7.0°$,[25] indicating that the [M(pc)] molecules are aligned in crystal grains with the molecular plane nearly perpendicular to the surface of the ITO substrate.[26,27]

Taking the above concept and the reversibility of electrochromism into consideration, the two oxidation peaks can be interpreted as follows in connection with anions as an electrolyte and the film structure. The oxidation peak at 1.0 V, where about half of the [Cu(pc)] molecules within the film are oxidized, is attributed to a reversible process in which anions adsorb onto the surface of crystal grains and enter the grains to some extent. In contrast, the peak at 1.2 V, where all of the remaining [Cu(pc)] molecules are oxidized, is attributed to an irreversible process in which anions completely enter the grains.

On the basis of these considerations, a crystal grain within the film seems to consist of two regions: One is the core region where [Cu(pc)] molecules align compactly with each other; the other is the surrounding region where the molecules align rather roughly. The reversible process means that the anions go in and out from this rough region of a crystal grain smoothly with repeated scans. On the other hand, the irreversible process means that the anions enter the core regions of a crystal grain with a rather big overpotential, and remain there even after rereduction, which results in a deterioration of the film.[16] This might be the cause of irreversible electrochromism.

This interpretation is well reflected by the relationship between the film thickness and the CV curve. The thicker is the [Cu(pc)] film, the more the crystal grain grows within the film, which is revealed by SEM photographs. Consequently, the ratio of the surface region of the crystal grains in a thick film is much smaller than that of a thin film. Thus, by applying the above interpretation to the CV curves of a thick [Cu(pc)] film, the oxidation peak at 1.0 V is found to be much weaker than that at 1.2 V, because the former peak is attributed to oxidation of the surface region. This is quite different from the case of a thin film. Indeed, in the CV curves of 160 nm thick [Cu(pc)] film, the oxidation peak at 1.0 V is much weaker than that at 1.2 V, which is completely different from the case of a 40 nm thin film.[22]

On the other hand, the deposition rate (0.1—10 nm s^{-1}) in film preparation dose not affect the structure of the [Cu(pc)] film, which has been confirmed by a SEM measurement. Thus, the present oxidation process is considered to be independent of the deposition rate.

Effect of an Anion as an Electrolyte on the Irreversible Electrochromism. Faulkner et al. reported that the size of the anions affected their ability to enter the films, which determines the rate and degree of oxidation.[16,17] However, they did not discuss whether the anions can determine the reversibility of electrochromism as well, i.e., the stability of the cyclic voltammograms (CV curves) and spectral changes, because, in their case, both [Mg(pc)] and [Zn(pc)] do not show reversible CV curves.

In order to keep the charge balance with oxidation of a [Cu(pc)] thin film, the anions of electrolytes in the solution must enter the film, and then go out from the film with rereduction. From this standpoint, in order to achieve the reversible electrochromic property, the anions in the electrolyte should be chosen as those which can stably compensate the charge of the oxidized pc cations, and smoothly move in and out from the thin film with oxidation and rereduction in the repeated cycles. As the first requirement, the electrolyte anion should be stable during the application of a positive voltage. Therefore, the scan range was determined by a blank measurement for each electrolyte, i.e., an electrochemical measurement was performed on a piece of naked ITO glass as a working electrode instead of [Cu(pc)]-deposited ITO glass for each electrolyte solution to observe the background current. Secondly, the Stokes radii of anions have been regarded as being the most appropriate criterion, because the Stokes radius of an anion in an aqueous solution represents the size, including the hydrating water molecules, and is calculated on the basis of the molar conductance and diffusion coefficiency of the anion.[28] Thus, the larger is the Stokes radius of an anion, the more difficult is it for the anion to move into the solution.

Table 1 indicates the reversibility in electrochromism of the [Cu(pc)] film in the presence of electrolyte anions with various Stokes radii.[29] In the case of NO_3^-, BF_4^-, ClO_4^-, and PF_6^- as the electrolyte anion, the [Cu(pc)] film shows reversible electrochromism between sky blue (original and rereduced) and bluish purple (oxidized), when the positive voltage is applied to scan until the first oxidation peak current. The repeated CV curves using these anions are shown in Fig. 4. These CV curves are very stable for repeated oxidation and rereduction cycles. In the case of other anions, however, reversible electrochromism cannot be accomplished. Table 1 indicates that the [Cu(pc)] film shows irreversible electrochromism in the case of enough large anions. However, it is not clear whether the following is true or not: The smaller is the Stokes radius of an anion, the more reversible is the electrochromism.

Now, the behavior of irreversible electrochromism is discussed in detail. In a spectroelectrochemical measurement, the scan range was determined by a blank measurement, as mentioned above. The irreversible CV curves can be classi-

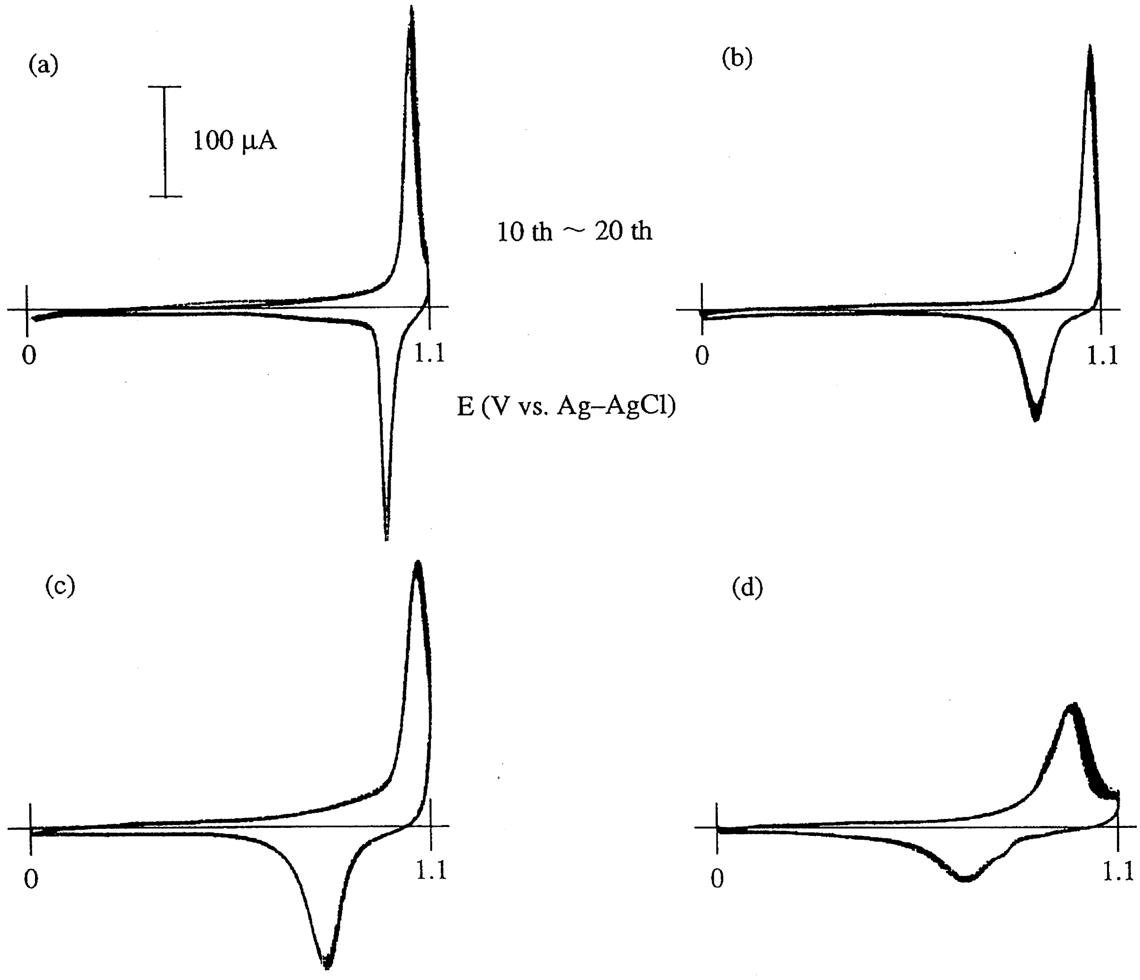


Fig. 4. Reversible cyclic voltammograms (11th—20th cycling) of [Cu(pc)] thin film in a 0.1 mol dm^{-3} aqueous solution of various electrolytes at the scanning rate of 20 mV s^{-1}; (a) $NaNO_3$, (b) $NaBF_4$, (c) $NaClO_4$, and (d) $NaPF_6$.

Table 1. Reversibility of Electrochromism of [Cu(pc)] Films in the Presence of Various Electrolyte Anions, and the Stokes Radii of the Anions (r_S)

Anion	Reversibility	r_S/Å[a]
Br^-	No	1.18
I^-	No	1.20
Cl^-	No	1.21
NO_2^-	No	1.28
NO_3^-	Yes	1.29
BF_4^-	Yes	—
ClO_4^-	Yes	1.37
SCN^-	No	1.38
PF_6^-	Yes	1.62
BrO_3^-	No	1.65
F^-	No	1.66
CH_3COO^-	No	2.25
IO_3^-	No	2.27

a) From Ref. 29.

fied into four types, whose CV curves are shown in Fig. 5.

(a) Electrochromism, itself, cannot be observed. The oxidation current begins to be detected at a certain voltage, and increases linearly with continuing application of a more positive voltage, and no rereduction current is observed. In a subsequent scan, the same behavior as in the case of the first scan is observed, except that the current slightly decreases according to repeated scans. The visible absorption spectrum never changes during this electrochemical measurement. NO_2^- and SCN^- belong to this type of group.

(b) Electrochromism itself cannot be observed as well although an oxidation peak is initially observed. At the first scan, a large oxidation peak current is observed, and the absorbance of the visible absorption spectrum decreases very much according to the oxidation current, although while keeping its shape. In the subsequent scans, the current responses behave like in the case of type (a), and the absorbance decreases with the oxidation current, while still keeping its shape. F^-, CH_3COO^-, IO_3^-, and BrO_3^- belong to this second type.

(c) Electrochromism between sky blue (original and rereduced) and purple (oxidized) is observed but irreversible. The color, observed at reduced and oxidized states, fades with repeated scans. The behavior of the oxidation current is the same as in the case of type (a), but a rereduction peak current is observed. The CV curves decay with repeated scans. The visible absorption spectrum changes in shape with oxi-

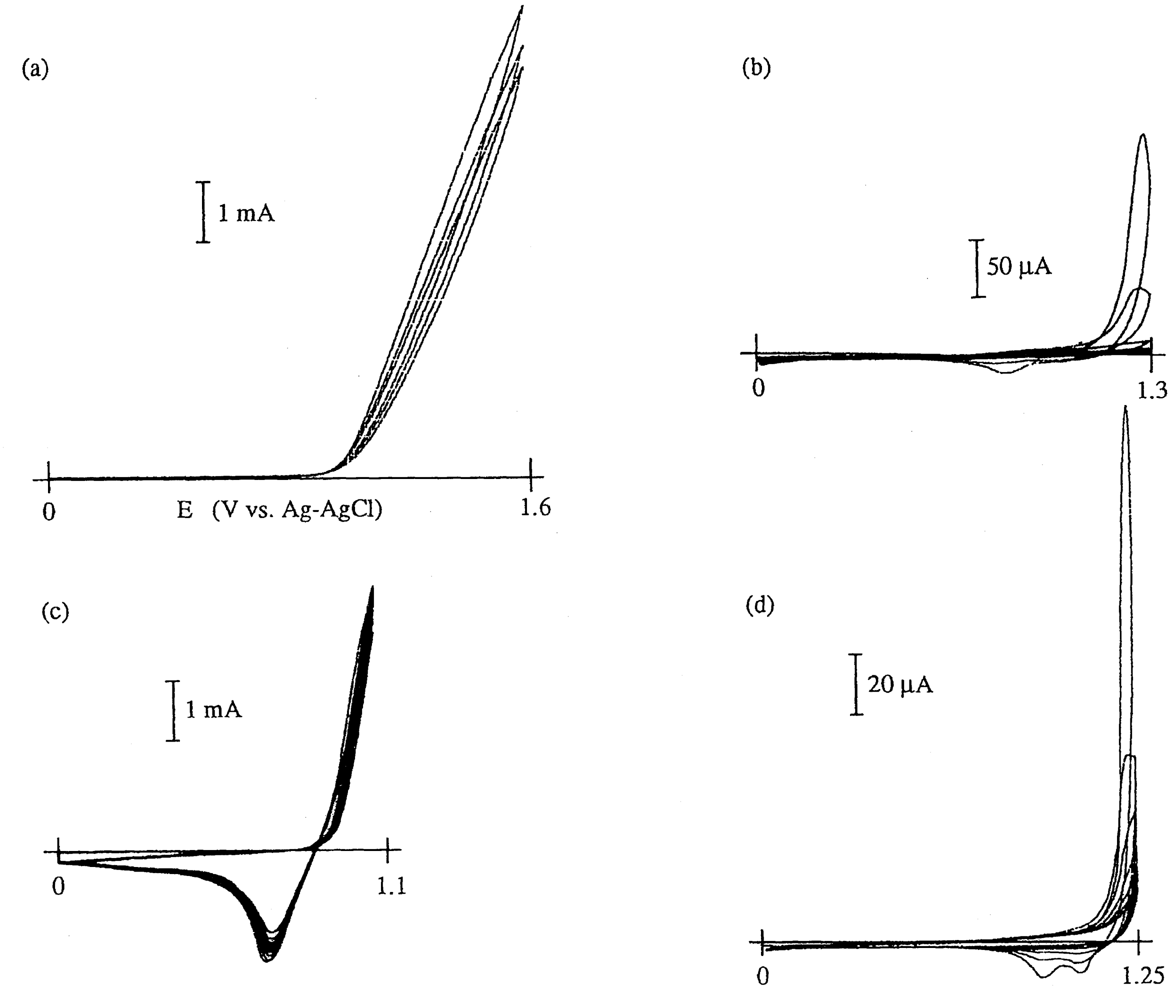


Fig. 5. Irreversible cyclic voltammograms (1st—10th) of [Cu(pc)] thin film in a 0.1 mol dm^{-3} aqueous solution of various electrolytes at the scanning rate of 20 mV s^{-1}; (a) NaSCN, (b) $NaBrO_3$, (c) NaBr, and (d) NaCl.

dation, and returns to the original one with rereduction, only slightly decaying with repeated scans. Br^- and I^- belong to this type of group.

(d) Electrochromism between sky blue (original and rereduced) and bluish purple (oxidized) is observed, but reversibility is not enough. Only in this type, the scan range is altered because two oxidation peaks are observed at the first electrochemical measurement. The CV curves decay in height with repeated cycles. Even though the scan range is altered, the [Cu(pc)] film shows irreversible electrochromism again. At the first anodic scan, there is observed one oxidation peak current which is accompanied by a change in the shape of the visible absorption spectrum. Then, two rereduction peaks are exhibited at the first cathodic scan, whereas no rereduction peak can be observed when applying a positive voltage to 1.4 V. Although the absorption spectrum gradually turns back to the original one with the cathodic scan, the absorbance is weaker than the original amount. In subsequent anodic scans, both the oxidation and rereduction currents decay to result in the disappearance of both peaks. Although electrochromism between sky blue and bluish purple is observed, the color of the [Cu(pc)] film fades with repeated cycles. Cl^- belongs to this type.

In the case of type (a), the Stokes radii of anions are almost the same as those of the anions which give reversible electrochromism. However, electrochromism is not observed, i.e., the visible absorption spectrum of the [Cu(pc)] thin film does not change its shape with this type of electrolyte anions. This means that the CV curves observed during electrochemical measurements originate not from the oxidation of the [Cu(pc)] film, but from that of the electrolyte anion and/or OH^- in an aqueous solution. In other words, these CV curves are independent of the [Cu(pc)] film. In fact, the behavior of the CV curves of the [Cu(pc)]-deposited electrode is almost the same as that of naked ITO glass, except that the positive voltage, at which the oxidation current is raised, is lower than that of the naked ITO glass electrode. In the CV curves, the current gradually increases with increasing the positive voltage in the anodic scan, and no current response can be detected in the subsequent cathodic scan. The presence of an extraordinary strong oxidation current and the absence of electrochromism indicate that electrolyte anions in an aqueous solution are oxidized, which could be promoted by [Cu(pc)] thin film on the electrode.

Type-(b) anions behave almost the same as type (a). However, there are remarkable differences in their behavior during the first scan and in the amount of oxidation current. In this type of electrolyte, the [Cu(pc)]-deposited electrode exhibits one large oxidation peak current at the first anodic scan, which cannot be observed in the case of a naked ITO glass electrode. The absorbance due to [Cu(pc)] decays dramatically according to the decrease in the oxidation peak current, while keeping its shape. Taking this behavior and the strength of the oxidation current into account, the OH^- anion in an electrolyte solution seems to be oxidized. The oxidized OH^- anion can be attributed to the H_2O molecules coordinating to the electrolyte anion. The Stokes radii of this type of anions are large enough compared with their crystal radii. According to a Frank–Wen hydration model, this type of anion is accompanied by H_2O molecules, which are called a "structure-maker", and strongly link with the central anion.[28] Consequently, the entrance of these large species into the film may destroy the [Cu(pc)] film, leading to a decrease in the absorbance of the [Cu(pc)] film according to the oxidation current. In this case, the [Cu(pc)] film seems to promote the oxidation of OH^- as well, which is suggested by a comparison with a blank measurement.

In the case of type (c), the Stokes radii of the anions in this group are sufficiently small, and electrochromism is observed. However, it is an irreversible electrochromism. A too high oxidation current suggests that electrolyte anions are oxidized in the anodic scan. This is also suggested by the fact that the bottom of the transparent aqueous solutions turns yellow after spectroelectrochemical measurements, meaning that the following reactions occur:

$$3X^- \rightarrow X_3^- + 2e^-$$

$$X_3^- \rightleftarrows X_2 + X^-.$$

These reactions can be recognized with the naked eye. When a positive voltage is applied stepwise to the working electrode, the color of the [Cu(pc)]-deposited film turns from sky blue to purple, using a cylindrical sample tube as an electrochemical cell instead of a cube cell for spectroelectrochemical measurements. When the voltage is stepped back to 0 V, bluish-purple species separate from the [Cu(pc)] thin film and disperse into the solution; finally, the bottom of the solution turns yellow. Electrolyte anions, which are easily-oxidized halides in the present case, are oxidized with the application of a positive voltage to a working electrode.

In the case of type (d), the [Cu(pc)] film exhibits irreversible electrochromism, in which the electrolyte anion, Cl^-, is also sufficiently small. In this case, however, the anion seems not to be oxidized, unlike in the case of type (c). The CV curve of the [Cu(pc)] in a Cl^- electrolyte is quite different from those in the case of I^- and Br^-. In fact, the solution remains transparent after spectroelectrochemical measurements. The oxidation of neither Cl^- nor OH^- does occur because both anions cannot be easily oxidized. A change in the color of the [Cu(pc)] film has been observed. Thus, the Cl^- anion probably compensates for a charge in the [Cu(pc)] cation.

In the Cl^- solution, however, the [Cu(pc)] film shows irreversible electrochromism, although the Stokes radius of the Cl^- is smaller than those of the anions in which the reversible electrochromism is observed. The n value for the oxidized [Cu(pc)] film in an NaCl solution by the potential step to 1.2 V is 2.1, indicating that the [Cu(pc)] film undergoes two-electron oxidation. Indeed, two rereduction peaks can be observed at the first scan in the CV curve. This seems to show that Cl^- is so small that the anion can enter the crystal grains completely by the first overpotential unlike in the case of ClO_4^-, as mentioned in the previous section. The rereduction current is much smaller than both the oxidation current and the corresponding rereduction current in the case of anions with reversible electrochromism. This fact suggests that the anions still remain within the [Cu(pc)] film after rereduction, even though the scan range is carefully altered. Since the Cl^- anion is more easily oxidized than other anions during reversible electrochromism, the Cl^- anion has a strong linkage with the oxidized pc cation, and remains within the film even after rereduction. This remaining of Cl^- anions leads to the formation of electrically isolated domains, which is the cause of irreversible electrochromism. Thus, both the absorbance and the CV curve decay with repeated scans.

These considerations can conclude that the reversible electrochromism of [Cu(pc)] film can be accomplished when electrolyte anions are stable for the application of a positive voltage and at the same time the Stokes radii of the anions are not too large, i.e., the anions must not be strongly coordinated by water molecules. Moreover, too small anions are not suitable for reversible electrochromism because they easily remain in the film, even after rereduction by a strong linkage with the oxidized pc cations.

Effect of an Anion as an Electrolyte on Reversible Electrochromism. Let us now consider the effect of anions from the viewpoint of the *reversible* electrochromic property. Reversible CV curves using various electrolyte anions are shown in Fig. 4. As Fig. 4 demonstrates, the potential difference between the oxidation peak and the rereduction peak (ΔE) is 90, 160, 270, and 300 mV, depending on the anion: NO_3^-, BF_4^-, ClO_4^-, and PF_6^-, respectively. This order is in good agreement with that of Stokes radii of the anions ($NO_3^- < BF_4^- < ClO_4^- < PF_6^-$), suggesting that the Stokes radii of electrolyte anions affect the reversible electrochromism, and that the smaller the anion, the more smoothly it goes in and out of the [Cu(pc)] thin film with oxidation and rereduction, respectively, giving, at last, almost the Nernstian CV curves.

This concept is supported by experiments concerning the rate of color change in the electrolytes of these anions. The change in the transient absorbance at 625 nm (λ_{max} of [Cu(pc)]) was measured, where the potential was applied stepwise from 0 to 1.1 V vs. Ag–AgCl at first and then 15 s later in the reverse way from 1.1 to 0 V. The results are shown in Fig. 6, which are in good agreement with the order of the Stokes radii. The smaller is the Stokes radius, the faster does the absorbance decreases with the oxidation, and then

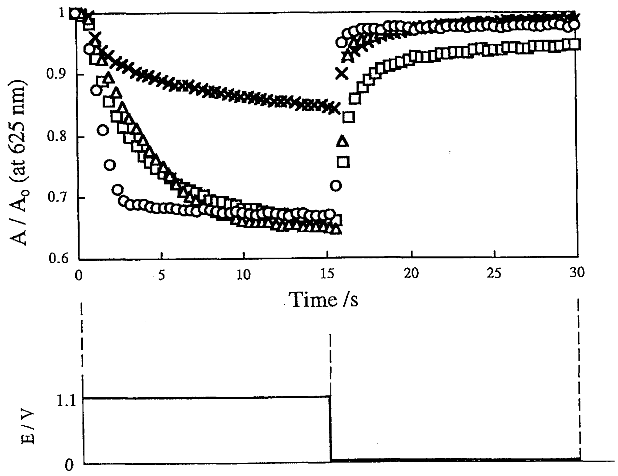


Fig. 6. Absorbance changes at 625 nm ($\lambda_{\max}$) of [Cu(pc)] thin film, when the potential is altered stepwise from 0 to 1.1 V and then from 1.1 to 0 V in an aqueous solution of various electrolytes; (○) NO_3^-, (△) BF_4^-, (□) ClO_4^-, and (×) PF_6^-.

increases with rereduction.

From these results it is clear that relatively small anions smoothly go in and out of [Cu(pc)] thin film, which leads to quick oxidation and rereduction of the film, respectively. A rapid color change is stably achieved using NO_3^- as an electrolyte anion.

It is noteworthy that the oxidation peak in the first cycle exhibits a overpotential compared with the subsequent cycles in the case of NO_3^-, BF_4^-, and ClO_4^-, whereas no remarkable oxidation peak is present in the first cycle in the case of PF_6^-. Moreover, only in the case of PF_6^- do both the oxidation and rereduction peaks gradually increase, reaching a steady state after about 10 cycles. This fact suggests that the PF_6^- anion allows only a limited oxidation before finishing the scans of several cycles, which is quite different from the case of other anions.

In order to examine the difference in the way of oxidation, the *n* values for the oxidation of [Cu(pc)] in various electrolyte solutions were determined by using chronocoulometry (as mentioned above). The results are collected in Table 2. In the case of NO_3^-, BF_4^-, and ClO_4^-, the amount of anodic charge (Q_j mC cm^{-2}) is largest at the first stepped application of a positive voltage, and then decreases steadily with repeated applications. In contrast, in the case of PF_6^-, the amount of anodic charge (Q_j), is 0.38 in the first scan, demonstrating limited oxidation, and then increases up to 0.85 by several applications, after which it keeps the value.

In the case of NO_3^-, BF_4^-, and ClO_4^-, the *n* values are about 0.6, independent of the kind of anions, indicating that these anions are small enough to go in and out of the rough region of the crystal grains of the film (as explained in the previous section). On the other hand, the PF_6^- anion is not sufficiently small to enter the rough region of the crystal grains, but can enter the film by moving grain by grain, since this film consists of many microcrystallines.[16] Thus, the limited oxidation of [Cu(pc)] film in a PF_6^- solution suggests the surface oxidation of the crystal grains of the [Cu(pc)] film. Repeated scans can make PF_6^- anions to gradually enter the crystal grains, like the other three anions.

At the first anodic scan of the CV curves of [Cu(pc)] film, an overpotential is observed in almost all cases (Fig. 2). This overpotential could be attributed to the hydrophobicity of the thin film, because the fresh [Cu(pc)] film, to be precise, fresh crystal grains of the [Cu(pc)] film could not yet have affinity for the hydrated electrolyte anions. Thus, once electrolyte anions enter the [Cu(pc)] film due to an overpotential to compensate for the charge, the film has an affinity for the hydrated electrolyte anions, making the anions enter the film without an overpotential in the subsequent scans.

In order to compensate for the charge, anions are considered to go in and out of the thin film with oxidation and rereduction, respectively, in the present experiments. However, there is another possibility that the positively charged species go out of the film with oxidation. One possible way is that when the [Cu(pc)]-deposited working electrode is immersed into the aqueous solution, some species, for example ions and water molecules, go into the film and positively charged species among them go out with oxidation. Another possible way is that no species can enter the compact thin film as soon as an electrode is immersed, but that positively charged species, originating from pc molecules, go out with the oxidation. This possibility is unreasonable because in this case the electrochromic process of [Cu(pc)] film must be independent of the electrolytes. Taking the idea into consideration that the electrochromic property depends extremely on the kind of anion among several kinds of experimental conditions, it seems reasonable that the oxidation and rereduction processes are greatly governed by the electrolyte anions.

In order to directly examine the influence of the cationic species, the CV curves and transient absorbance changes were measured, altering the electrolyte from $NaClO_4$ to $KClO_4$, and then to $LiClO_4$. However, no change was observed. This result again supports the idea that the electrochromic process is independent of the cationic species.

Table 2. *n* Values for the Initial Oxidation of [Cu(pc)] Films in the Various Electrolyte[a] Solutions, and the Stokes Radii of the Anions (r_S)

Anion	*n*	r_S/Å
NO_3^-	0.63	1.29
BF_4^-	0.54	—
ClO_4^-	0.64	1.37
PF_6^-	0.20	1.62

a) Potassium salts of anions were used for the experiments.

Conclusions

A copper phthalocyanine ([Cu(pc)]) thin film, prepared by vapor deposition, exhibits two oxidation peaks in an aqueous electrolyte solution with the application of positive voltages from 0 to 1.4 V, and the color of the film changes from sky blue to pale gray. However, this electrochromic process is irreversible, and the film gradually deteriorates with repeated oxidation and rereduction scans. The two oxidation peaks represent two types of appearances of one reaction with a different overpotential caused by the structure of the crystal grain of the [Cu(pc)] film. The oxidation required for a higher overpotential means that electrolyte anions enter the core region of the crystal grain, resulting in irreversible electrochromism. On the other hand, the oxidation for a lower overpotential is attributed to the reversible process of the anions at the surface rough region of the crystal grains. Thus, when the scan range is controlled so as to admit the first oxidation peak, the reversible electrochromism between sky blue and bluish purple can be achieved.

An electrolyte anion is also an important factor for reversible electrochromism. In order to accomplish reversible electrochromism of [Cu(pc)] film, the anion should be stable for the application of a positive voltage, and its Stokes radii should not be too large, i.e., the anions should be strongly coordinated by water molecules. Moreover, an anion that is too small is not suitable for reversible electrochromism, because a small anion easily remains in the film, even after rereduction.

Thus, smaller anions can go in and out of a thin film smoothly with oxidation and rereduction, respectively. Thus, the [Cu(pc)] film is quickly oxidized and rereduced; in other words, the CV curve becomes almost Nernstian and a quick color change can be accomplished. In contrast, bigger anions, for example PF_6^-, allow only the oxidation of the surface of the crystal grains of the film until several cycles, and gradually go in and out of the crystal grains with subsequent scans; at last, the CV curves reach a steady state.

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