Bull. Chem. Soc. Jpn., ***69***, *2111—2122 (1996)*

Electrochromism of Single Transition-Metal Phthalocyanine Thin Films: Effect of Central Metal and Composite Structure

Naoki Toshima*,# **and Tsuyoshi Tominaga**

Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received January 23, 1996)

Electrochromism of various transition-metal phthalocyanine thin films is studied in a sodium nitrate solution. Copper and nickel phthalocyanine show reversible electrochromism, while, zinc, cobalt, and iron phthalocyanine show the irreversible type. The transition-metal phthalocyanine film, which gives irreversible electrochromism, exhibits a new absorption peak in the NIR region under oxidation. This result indicates that some chemical changes of molecular structure occur with oxidation, and consequently the cyclic voltammograms and the absorbance are diminished with repeated scans, even under the well-designed experimental conditions. As for composite phthalocyanine, the high dispersibility of the phthalocyanine molecules in the codeposited thin film can improve the reversibility in electrochromism. In this case, chemical changes of the molecular structure of metal phthalocyanine with irreversible electrochromism can be prevented to some extents by the codeposition with another phthalocyanine with reversible electrochromism. Sequentially deposited double-layered thin films, in contrast, give completely different results. The electrochromism depends on the order of the oxidation potentials of simple phthalocyanine thin film, and the designed hole transfer compatible with the concept of "sequential potential field" can be accomplished in the double-layered thin film.

Metallophthalocyanine ([M(pc)]) exhibits a variety of interesting phenomena concerning electronic and photoelectronic properties due to the planar macrocyclic π-conjugated structure and to coordination to many kinds of metal.[1,2] In addition, [M(pc)] is stable enough against heat treatment to form a thin film with a uniform structure by vacuum deposition. Thus, [M(pc)] is expected to be one of key materials for new advanced technologies, and indeed, considerable numbers of articles have been published to further this purpose.[1—5]

Especially, transition metal phthalocyanine ([tM(pc)]) possesses a great potential as a material for this purpose, because the energy level of d orbitals of some [tM(pc)] can be located between HOMO and LUMO levels of the pc ligand and the redox potentials of [tM(pc)] can be altered in a wide range according to the central transition-metal.[6,7] In fact, it is known that only [Fe(pc)] and [Co(pc)] among first-row [tM(pc)] show an electrocatalytic activity in the reduction of molecular oxygen.[8,9] Recently we have reported that [Ni(pc)] and [Cu(pc)] thin films can be oxidized and rereduced reversibly, but [Zn(pc)], [Co(pc)] and [Fe(pc)] films cannot show the reversible electrochromism even under well-designed experimental conditions.[10]

We have reported the electrochromism of [Cu(pc)] thin films in detail from the viewpoint of the factors affecting the reversibility.[11] The [Cu(pc)] thin film was reported to show an irreversible electrochromism.[12] In the previous paper, however, the oxidation and rereduction process of [Cu(pc)] thin film has been found to be governed by the scan range in the application of positive voltage and by the kind of charge-compensating anions used as electrolytes.[11] Thus, when the scan range is controlled to admit the first oxidation peak and the appropriate anion is used as electrolyte, the electrochromism between sky blue and bluish purple is reversible.

In this paper, the electrochromism of [tM(pc)] thin films with various central metals is investigated in detail. It is important as a fundamental property to study the redox process of [tM(pc)] thin films, because this process reflects the differences in electron and/or ion transfer properties among various [tM(pc)]s. This provides some fundamental information needed to design organic solid-state devices.[12—21]

Furthermore, we compare electrochromic properties of the simple [tM(pc)] thin films with those of the composite ones, i.e., both simultaneously and sequentially deposited thin films consisting of two kinds of [tM(pc)].[22] Transition-metal complexes, such as [tM(pc)], are favorite materials for multi-electron transfer.[23] Designed alignment of the metal complex molecules can produce the "sequential potential field," which may allow only the forward electron transfer in the devices.[23,24] Taking this into consideration, we expect the composite [tM(pc)] thin films to have an unique electron-transferring property unlike the corresponding simple [tM(pc)] film, this is actually achieved in the present experiments.

Experimental

Preparation of Phthalocyanine Thin Films. Transition-metal

#Present address: Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, Daigaku-dori, Onoda, Yamaguchi 756, Japan.

phthalocyanines ([tM(pc)]) were purified by vacuum sublimation before preparation of thin films. [tM(pc)] thin films (ca. 40 nm in thickness) were prepared by the method described before.[11] Films were deposited onto indium-tin oxide (ITO) glass (10 Ω/□) previously cleaned by washing ultrasonically with dichloromethane and 2-propanol. The depositions were performed at 400—430 °C under ca. 10^{-5} Torr (1 Torr = 133.322 Pa) at a rate of 1—10 $\mathrm{nm\,min^{-1}}$, keeping the substrate temperature at 100 °C. 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.

To prepare different types of composite thin films of [tM(pc)], vapor deposition was performed both simultaneously and sequentially. In the case of sequentially evaporated thin films, the film thickness is ca. 20 nm for each phthalocyanine film. The molar ratio in simultaneously evaporated thin films was controlled by altering the evaporation temperature of the vessel containing each [tM(pc)].[22]

Analysis of the Structure of Phthalocyanine Thin Films. A Hitachi S-430 scanning electron microscope (SEM) and a Rigaku Rint-2400 X-ray diffractometer (XRD) were used to examine surface morphology and crystallinity of thin films, respectively. XRD was recorded by the θ–2θ scan at 40 kV, 100 mA with Cu $K\alpha$ radiation.

Voltammetric and Spectroelectrochemical Measurement. Electrochemical measurements of the thin films were carried out at room temperature in 0.1 $\mathrm{mol\,dm^{-3}}$ $NaNO_3$ aqueous solutions. Sodium nitrate was reagent grade and was used without further purification. Aqueous solutions were prepared using distilled water. The working electrode was the ITO glass covered with phthalocyanine thin film prepared by the vapor deposition. 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.[25] In order to measure the transient spectral change during the electrochemical process, a rapid scanning multichannel photodiode array spectrometer (Otsuka Electronics Co., MCPD-100A) was 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 2.5-s intervals with slow scanning (20 $\mathrm{mV\,s^{-1}}$) of the ITO potential. All potential values cited in this paper refer to Ag/AgCl.

Results and Discussion

Electrochromic Property of [tM(pc)] Thin Films. The oxidation and rereduction process of [Cu(pc)] thin film is governed by the scan range in the application of positive voltage and by the charge-compensating anion used as electrolyte.[11] When the scan range is controlled to admit the first oxidation peak and an appropriate anion is used as electrolyte, then the reversible electrochromism between sky blue and bluish purple is produced. As regards the scan range, the application of positive voltage from 0 to 1.1 V gives the reversible electrochromism in an appropriate electrolyte solution, since the first oxidation peak of [Cu(pc)] thin film appears at ca. 1.0 V. In the present experiments, electrochromism of [Cu(pc)], [Ni(pc)], [Zn(pc)], [Co(pc)], and [Fe(pc)] thin films are studied. Among these [tM(pc)]s, [Cu(pc)], and [Ni(pc)] have the highest oxidation potentials at ca. 1.0 V, as measured in solution[26] (cf. Table 1). Thus, in this experiment, the scan range is basically fixed from 0 to 1.1 V. On the other hand, as regards the electrolyte anion, nitrate anion provides almost Nernstian cyclic voltammogram (CV curve) and the quick color change of [Cu(pc)] thin film, since the Stokes radius of nitrate is rather small and the anion can go into and out from the film smoothly. Thus, sodium nitrate is used as the electrolyte in the present experiments.

(i) [Cu(pc)] Thin Film: As described before,[11] the reversible electrochromism between sky blue (original and rereduced) and bluish purple (oxidized) can be achieved. If the positive voltages are applied from 0 to 1.4 V, then [Cu(pc)] thin film exhibits two oxidation peaks in an aqueous electrolyte solution and the color of the film changes from sky blue to pale gray. This electrochromic process is irreversible. 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. The proposed structure is confirmed by examining the relationship between film thickness and the CV curves, and by using chronocoulometry under various positive voltages. Thus, when the scan range is controlled so as to admit the first oxidation peak, from 0 to 1.1 V, the reversible electrochromism between sky blue and bluish purple can be achieved.

(ii) [Ni(pc)] Thin Film : The [Ni(pc)] thin film shows

Table 1. The Reversibility of Electrochromism of Various [tM(pc)] Thin Films,[a)] Including the Oxidation Potentials in a Deposited Thin Film and in a Solution

	[Ni(pc)]	[Cu(pc)]	[Co(pc)]	[Zn(pc)]	[Fe(pc)]
Reversibility	++	++	±	±	−
Oxidation potential in a deposited thin film[b)]/V	0.94	0.92	0.60	0.55	—
Oxidation potential in a solution[c)]/V	1.05	0.98	0.77	0.68	0.19[d)]

a) ++ : reversible completely, ± : irreversible, and − : irreversible completely. The experiments were performed in a 0.1 $\mathrm{mol\,dm^{-3}}$ $NaNO_3$ aqueous solution. b) Estimated from CV curves. c) Ref. 26 (solvent: 1-chloronaphthalene). d) Oxidation of central metal.

reversible electrochromism. As shown in Fig. 1, the CV curve is more stable for repeated scan than that of [Cu(pc)] thin film and changes very little with more than 100 scans. The difference between oxidation and rereduction peak potentials, ΔE, is only 90 mV, indicating that this CV curve is almost Nernstian. In the visible spectral changes, two isosbestic points are observed at ca. 580 and 720 nm during the cyclic scanning. The color of the film changes from sky blue (original and rereduced) to bluish purple (oxidized). This electrochromic process is quite similar to that of [Cu(pc)] thin film. Accordingly, in this case the anions go into and out from the surface rough regions of a crystal grain smoothly with repeated scan.

(iii) [Zn(pc)] Thin Film : The [Zn(pc)] thin film shows irreversible electrochromism. As shown in Fig. 2, the CV curve decays gradually in height with repeated scan. No isosbestic points can be observed in the spectral change. The visible absorption spectrum after the first cycle does

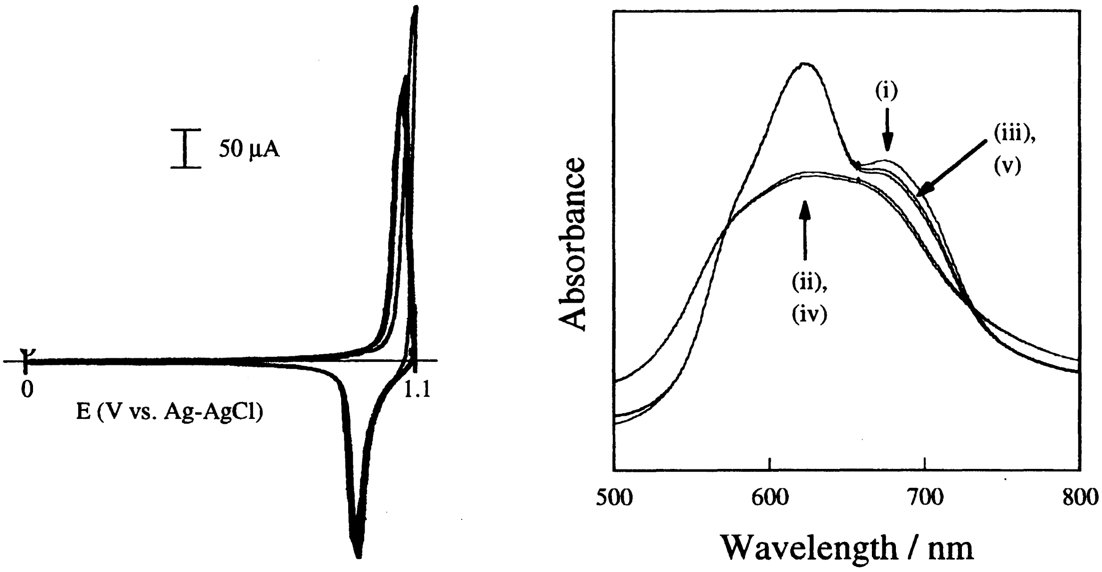

Fig. 1. Cyclic voltammograms (1st—10th) and visible absorption spectral changes ((i) original, (ii) 1st oxidation, (iii) 1st rereduction, (iv) 2nd oxidation, and (v) 2nd rereduction) of [Ni(pc)] films in 0.1 mol dm^{-3} NaNO$_3$ aqueous solutions at the scanning rate of 20 mV s^{-1}.

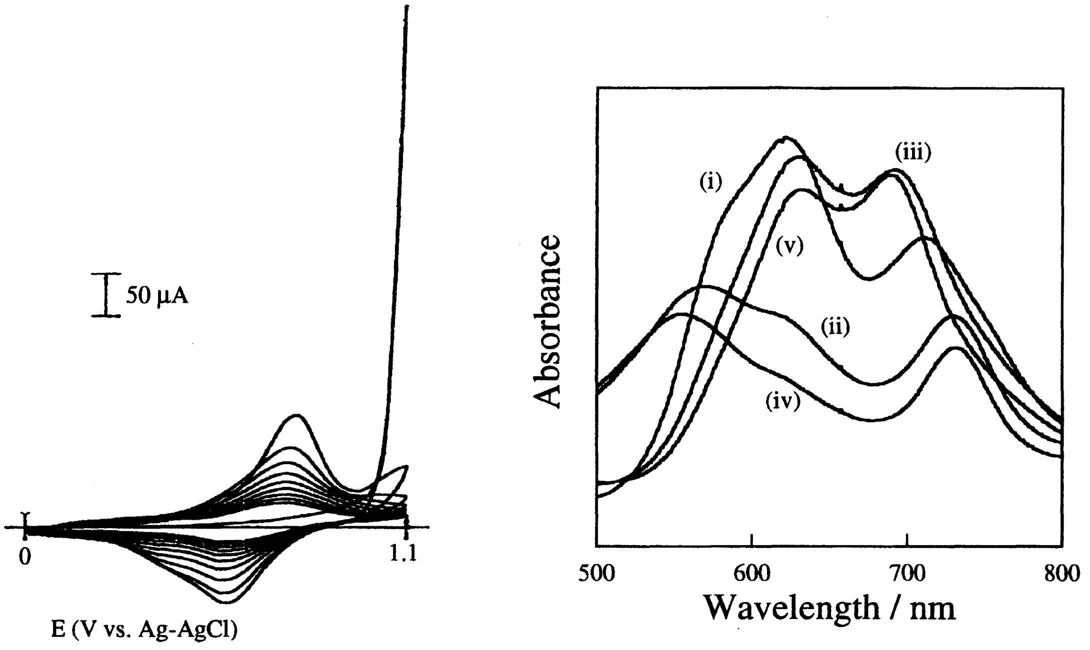

Fig. 2. Cyclic voltammograms (1st–10th) and visible absorption spectral changes ((i) original, (ii) 1st oxidation, (iii) 1st rereduction, (iv) 2nd oxidation, and (v) 2nd rereduction) of [Zn(pc)] films in 0.1 mol dm^{-3} NaNO$_3$ aqueous solutions at the scanning rate of 20 mV s^{-1}.

not match the original one. Furthermore, the spectrum at the rereduced state decays gradually with subsequent scans. The color of [Zn(pc)] thin film changes from sky blue (original) to pale purple (the first oxidation) and back to bluish green (the first rereduction). The electrochromism between bluish green and pale purple is attained when the cyclic oxidation and rereduction are repeatedly applied, although the color of the film gradually fades.

(iv) [Co(pc)] Thin Film : The [Co(pc)] thin film also shows irreversible electrochromism. This electrochromic process is quite similar to that of the [Zn(pc)] thin film except that two rereduction peaks appear at the first scan and that the CV curve of [Co(pc)] thin film decays more rapidly than that of [Zn(pc)] thin film.

(v) [Fe(pc)] Thin Film : The [Fe(pc)] thin film also shows irreversible electrochromism. As shown in Fig. 3, no isosbestic points can be observed in the spectral change and the absorption spectrum after the first cycle does not match the original one. Both the CV curve and the visible spectrum at the rereduced state decay dramatically in height with repeated scans and the current response cannot be observed at all after scanning only four times. The [Fe(pc)] thin film gives the color change from bluish purple (original) to pale gray/purple (the first oxidation) and back to pale gray/green (the first rereduction). The electrochromism between pale gray/green and pale gray/purple is observed during three- or four-times repeated scans.

Detailed Examination of Irreversible Electrochromism. Table 1 summarizes the results from the viewpoint of the reversibility of electrochromism of various [tM(pc)] thin films, including their oxidation potentials estimated from each CV curve. In the CV curves of [tM(pc)] thin films showing irreversible electrochromism, the oxidation peak in the first scan exhibits a significant overpotential, as compared to the peak position of all subsequent scans. The first oxidation peak appears at ca. 1.06 V irrespective of central metal. Thus, [tM(pc)] thin films with irreversible electrochromism seem to be fully oxidized with the application of positive voltage of 1.1 V.

In order to confirm this full oxidation, an *n* value, the number of electrons for the oxidation of each [tM(pc)] thin film, was determined by the same method as taken in the previous paper,[11] except that [Fe(pc)] is dissolved in *o*-dichlorobenezene instead of 1-chloronaphthalene and that the absorption coefficiency of [Zn(pc)]·bpy instead of [Zn(pc)] is adopted for the calculation.[27] (To our knowledge, there is no published data about the absorption coefficientry of [Zn(pc)].) The results are summarized in Table 2.

The resulting *n* values both for [Cu(pc)] and [Ni(pc)] are lower than 1, which means that only the parts of [Cu(pc)] and [Ni(pc)] molecules are oxidized by the application of 1.1 V. This result supports again the claim that, in the case of these films, the nitrate anions for charge compensation smoothly go into and out from the surface rough regions of a crystal grain with repeated scans, which leads to the reversible electrochromism between sky blue and bluish purple.

In the case of [Zn(pc)] thin film, only one pair of redox

Table 2. *n* Value for Initial Oxidation of [tM(pc)] Thin Film[a)]

	[Ni(pc)]	[Cu(pc)]	[Co(pc)]	[Zn(pc)]	[Fe(pc)]
n	0.26	0.63	1.41	1.01	1.96

a) Stepped potential at 1.1 V is applied to the films in a 0.1 mol dm^{-3} NaNO$_3$ aqueous solution.

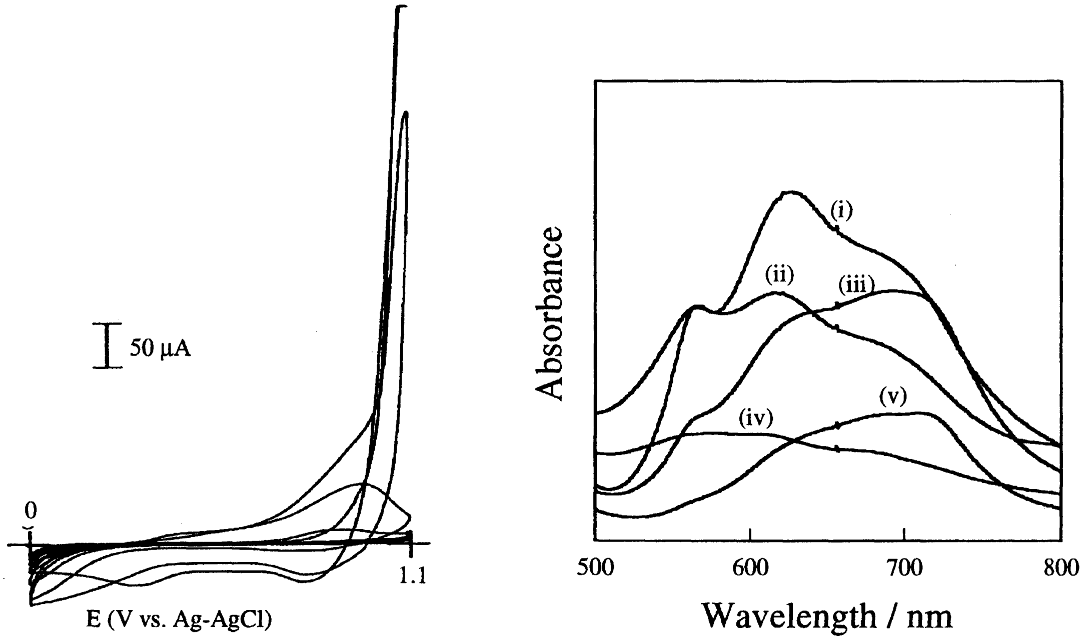

Fig. 3. Cyclic voltammograms (1st—10th) and visible absorption spectral changes ((i) original, (ii) 1st oxidation, (iii) 1st rereduction, (iv) 2nd oxidation, and (v) 2nd rereduction) of [Fe(pc)] films in 0.1 mol dm^{-3} NaNO$_3$ aqueous solutions at the scanning rate of 20 mV s^{-1}.

peaks is observed in the CV curve and *n* value is 1.0, which means that in the [Zn(pc)] thin film an exact one-electron oxidation fully proceeds. In the case of [Co(pc)] thin film, the CV curve is similar to that of [Zn(pc)] thin film. However, two rereduction peaks clearly appear only at the first cathodic scan and the *n* value is 1.41. These results suggest that, in the [Co(pc)] thin film, full one-electron oxidation and partial two-electron oxidation proceed. In the case of [Fe(pc)], at last, two rereduction peaks appear at the first scan, followed by the appearance of two oxidation peaks at the second anodic scan, and the *n* value at 1.1 V is 2.0, which shows that two-electron oxidation proceeds in the [Fe(pc)] film. Thus, it is clear that [tM(pc)] thin films with irreversible electrochromism completely undergo one or two-electron oxidation by the application of 1.1 V.

In order to improve the electrochromic property of these [tM(pc)] thin films, the scan range should be controlled, since [Cu(pc)] thin film can be reversibly oxidized and rereduced by this method. The positive voltage is applied from 0 V to the voltage where each [tM(pc)] thin film shows an oxidation peak from the second scan (cf. Table 1). However, little current response is exhibited and no peaks can be observed in spite of more than 20 repeated cycles. This means that nitrate anions require the application of 1.1 V for the charge-compensation in the first oxidation of the fresh compact [tM(pc)] thin film, which could not have affinity yet for hydrated anions.[11]

From these results, the CV curves of [tM(pc)] thin films with irreversible electrochromism can be interpreted as follows. The intrinsic oxidation potentials of these [tM(pc)] thin films are much lower than the first oxidation peak potential, which means that the nitrate anions require higher potential for the first charge compensation. The intrinsic oxidation peak does not appear at the first anodic scan, but appears from the second anodic scan. In the first anodic scan from 0 to 1.1 V, these [tM(pc)] thin films are completely oxidized and nitrate anions fully go into crystal grains of the film irrespective of the structure of the crystal grains. This behavior of nitrate anions leads to the expansion of crystal grains, so that the anions find it easier to go into and out from this film in the subsequent scans than in the first scan. After the first cycle, the core regions of crystal grains seem to be destroyed, resulting in the rough structure.

This behavior of the anions during the first cycle is well-reflected in the change of the visible absorption spectrum. As shown in Fig. 2, the spectrum of the rereduced [Zn(pc)] film has the narrower splitting (between major two peaks in the visible region) than that of the original film, which coincides with Faulkner's report.[12] According to this report, this fact indicates that the rereduced film involves decreased interaction between adjacent [Zn(pc)] molecules in comparison with the original one,[12] which means that the first oxidation causes the expansion of the lattice within crystal grains. Taking this into consideration, the big restructuring of the film should take place in the case of [tM(pc)] with irreversible electrochromism.

Strictly speaking, in the case of [Cu(pc)] and [Ni(pc)] thin films, the restructuring of the films may also occur, since the slight overpotential is observed in the first scan of the CV. However, [Cu(pc)] and [Ni(pc)] show reversible electrochromism, and the anions go into and out from the surface region under this scan range as mentioned above. Thus, this slight restructuring will occur only in this region, which does not affect the reversibility.

Thus, the repeated scan was performed as follows. The 1.1 V positive voltage was applied to the film only at the first anodic; in subsequent scans, the voltage which gives the oxidation peak was applied to the film. The resulting CV curves of [Zn(pc)] film are shown in Fig. 4, as an example. Both the oxidation and the rereduction peaks decay gradually with repeated scans, as in the case of the scan range from 0 to 1.1 V (Fig. 2).

These results suggest that, in the case of [tM(pc)] thin films, which show virtually irreversible electrochromism, the reversible electrochromism cannot be achieved even though the scan range is well-controlled, and that the dependence of central metal on electrochromism of [tM(pc)] thin films can be attributed to the way of the oxidation, in other words, the way of charge compensation for each oxidized [tM(pc)] thin film by electrolyte anions.

Charge Compensation of Oxidized [tM(pc)] Thin Film by Electrolyte Anions. The structure, to be precise, the crystallinity and the morphology of [tM(pc)] thin films, have been well-investigated.[28—34] Those of composite [tM(pc)] thin films, i.e., codeposited and sequentially deposited films have also been investigated by SEM and XRD measurements.[22] These measurements make it clear not only

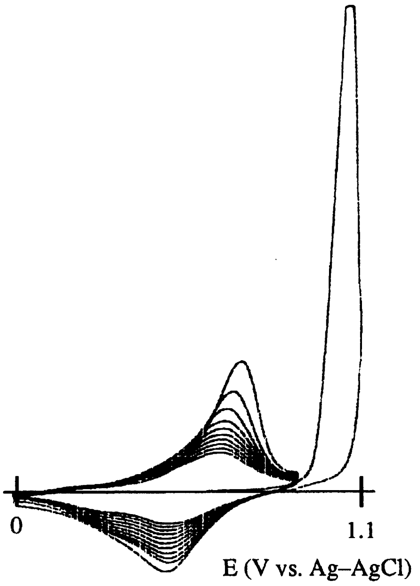

Fig. 4. Cyclic voltammograms (1st—10th) of [Zn(pc)] films in a 0.1 mol dm^{-3} $NaNO_3$ aqueous solution under the well controlled scan range at the scanning rate of 20 mV s^{-1}.

that the structure of [tM(pc)] films is independent from the kinds of central metal of [tM(pc)] but also that the structure of composite [tM(pc)] films is the same as the single [tM(pc)] film and independent of the composition way. The SEM photographs show that the vapor-deposited [tM(pc)] thin film has rod-like crystalline form; the XRD pattern of this film on an ITO glass exhibits a single peak located at ca. $2\theta = 7.0°$, indicating that the [tM(pc)] molecules are aligned in crystal grains with the molecular plane nearly perpendicular to the surface of the ITO substrates.[31,33] Thus the structural changes of [tM(pc)] thin films after repeated scans could give some information on the reversibility.

The SEM photographs of [Ni(pc)] and [Zn(pc)] thin films after electrochemical measurements are shown in Fig. 5. In the case of [Ni(pc)], which shows reversible electrochromism, there is no remarkable difference in morphology between the original film[22] and the cycled one. This is true for the case of [Cu(pc)] as well. In contrast, [Zn(pc)] film, whose electrochromism is irreversible, is partly fissured after repeated scans. The formation of the partial cracks with repeated scans (Fig. 5b) leads to the decay of both the CV curves and the visible absorption spectrum of [Zn(pc)] film. The [Co(pc)] film exhibits the same phenomena. In the case of [Fe(pc)], SEM photographs after spectroelectrochemical measurements cannot be obtained, because the film deteriorates almost completely.

Consequently, in the case of [tM(pc)] thin films with irreversible electrochromism, the movement of electrolyte anions for charge-compensation with repeated scans leads to the deterioration of the film. The crack parts, as observed in [Zn(pc)] thin films after repeated scans, may show the electrically isolated domains.[12] This was described in the consideration about the electrochromism of [Cu(pc)] thin film in Cl^- electrolyte in the previous paper.[11] And such electrically isolated domains seem to be caused by electrolyte anions remaining after rereduction.

In connection with the way of charge-compensating by anions, Ashida and co-workers reported about electrochromism of (octacyanophthalocyaninato)metal–metal complex ($[\text{M}\{\text{pc(CN)}_8\}]$–M, M = Cu, Co) thin films.[15—17] According to these reports, the reduced $[\text{Cu}\{\text{pc(CN)}_8\}]$–M film shows a new absorption peak in the NIR region, which is attributed to the protonated pc ring formed by the attack of charge-compensating cation, H^+.[17]

In order to examine whether the same behavior as this can be observed in the present experiments, the spectral changes of various [tM(pc)] in the NIR region were measured during the electrochemical process. The results are shown in Fig. 6. In the case of [Ni(pc)], there is no remarkable change, except that the absorbance decreases with the oxidation relative to the original one. The same is the case for [Cu(pc)] film. In these cases, no remarkable change also occur, although 1.4 V is applied to these films in order to oxidize them completely. In contrast, the [Zn(pc)] film exhibits a new peak at 850 nm with the oxidation, which is also observed for a [Co(pc)] film. In the case of [Fe(pc)], too, a small broad peak was observed

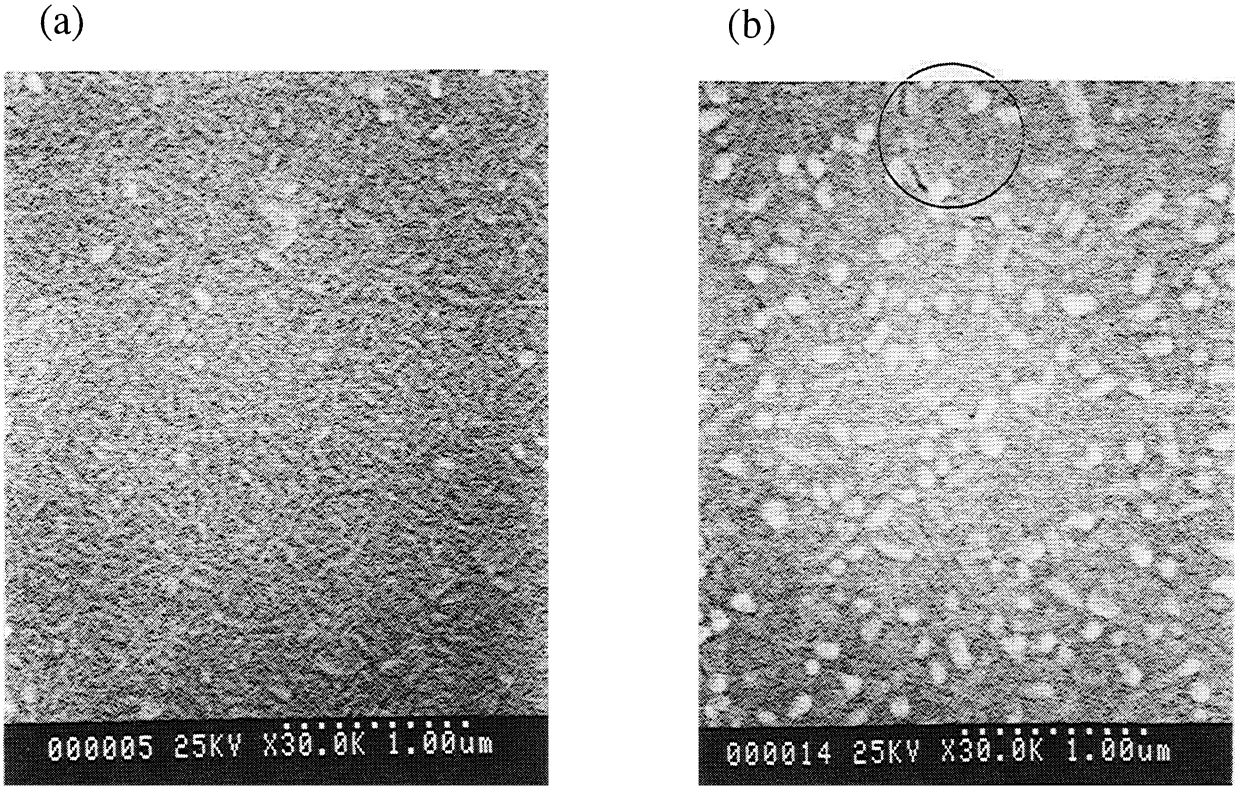

Fig. 5. SEM photographs of (a) [Ni(pc)] and (b) [Zn(pc)] films after electrochemical measurements. A crack part can be found in the circle.

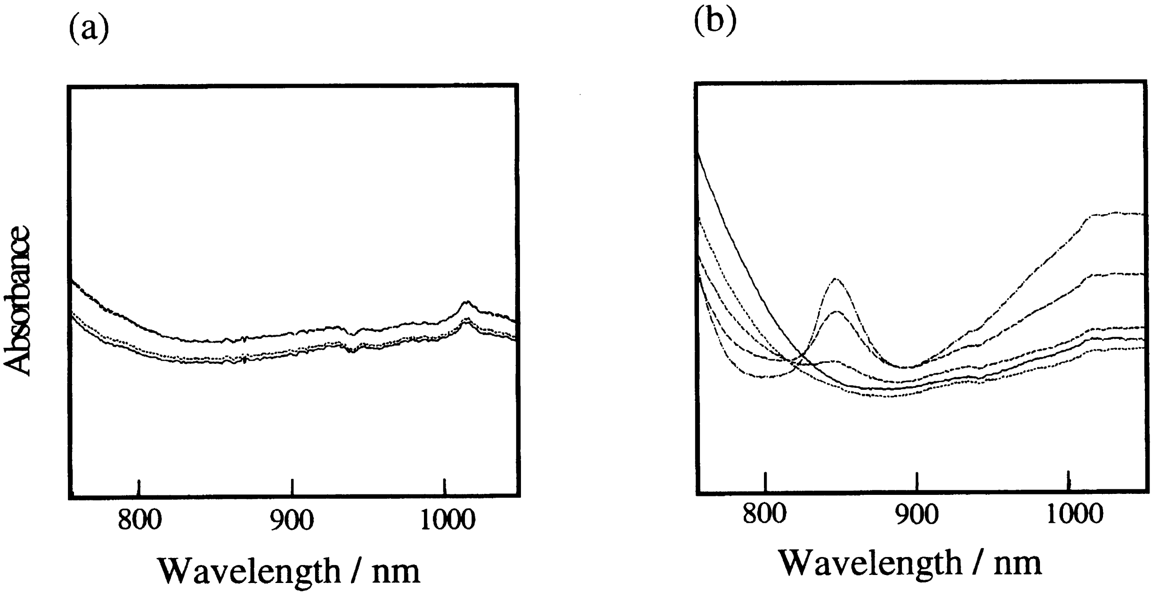

Fig. 6. Absorption spectral changes of (a) [Ni(pc)] and (b) [Zn(pc)] films measured under the scanning from 0 to 1.1 V in 0.1 mol dm^{-3} NaNO$_3$ solutions.

at rather longer wavelength than the case of [Zn(pc)] and [Co(pc)], and the absorbance decreases with the oxidation relative to the original one.

In the present experiments, the anodic scan is applied, which is reverse to the case in Ashida's report,$^{17)}$ so that the species which go into the film for charge compensation are not cations but anions, i.e., NO$_3^-$ and/or OH$^-$. Figure 6 clearly shows that some chemical changes of the molecular structure like the reduced [Cu{pc(CN)$_8$}] film occur with the oxidation in the case of [Zn(pc)] and [Co(pc)] films, indicating that positive charge is localized in the pc ring and that NO$_3^-$ and/or OH$^-$ link with this pc cation strongly. This behavior seems to lead to the formation of electrically isolated domains, because the anions strongly linked with the pc cations can easily remain within the film after rereduction. This is supported by Fig. 7, which demonstrates that the absorbance changes at 675 nm (λ_{max} of the [Zn(pc)] film after the first scan) and 850 nm. With the repeated scans, the absorbance at 675 nm of the rereduced [Zn(pc)] film decreases, while the peak at 850 nm appears at the same intensities with each oxidation. Furthermore, the color of [Zn(pc)] film after rereduction changes from sky blue to bluish green, which resembles that of (substituted phthalocyaninato)metal complexes, for example (octahalophthalocynaninato)metals complexes.$^{35)}$ Thus, once these [tM(pc)]s are oxidized, charge-compensating anions are linked strongly with pc cations, some of which remain within the film after rereduction and form electrically isolated domains. This behavior leads to the decay of current responses of these [tM(pc)] film with repeated scans, although the scan range is controlled.

On the other hand, [Cu(pc)] and [Ni(pc)] do not change significantly, indicating that a weak charge compensation by anions takes place in these [tM(pc)] cations. Thus, anions can go out from the film smoothly with rereduction, leading to the reversible electrochromism.

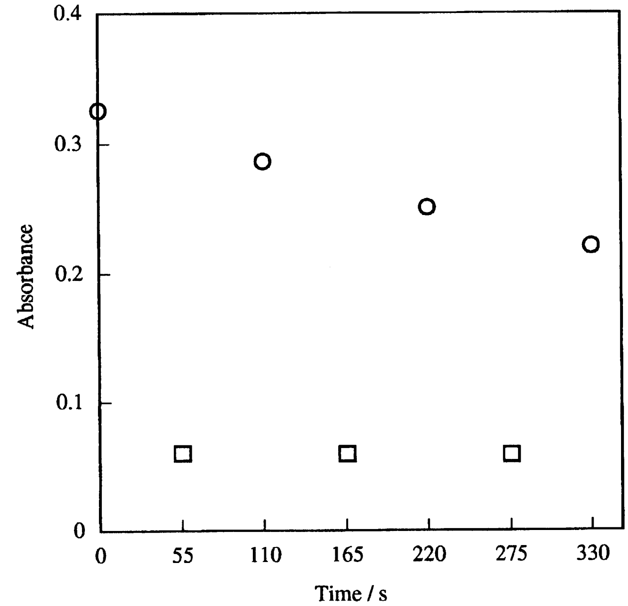

Fig. 7. Absorbance changes of [Zn(pc)] film at (○) 675 nm (λ_{max} after the first oxidation) and (□) 850 nm measured under the repeated scanning from 0 to 1.1 V in a 0.1 mol dm^{-3} NaNO$_3$ solution.

In the case of [Fe(pc)] film, which shows much worse irreversible electrochromism than [Zn(pc)] and [Co(pc)], a new peak appears in the NIR region, but it is weaker and broader than the case for [Zn(pc)], indicating that other factor(s) may be related to the irreversible electrochromism of [Fe(pc)] film. The facts that the n value at 1.1 V is 2.0 and that two rereduction peaks appear at the first scan, followed by the appearance of two oxidation peaks at the second anodic scan, show that [Fe(pc)] film undergoes two-electron oxidation in the present experiments. Taking it into consideration that the oxidation of central metal is reported in the references about electronic spectra,[6,7] electrochromism of thin films,[18] and reduction of oxygen by [tM(pc)] thin film,[8,9] we think two-electron oxidation to mean that both pc ring and central metal are oxidized by the application of 1.1 V. Because of the oxidation of the central metal, Fe^{2+}, charge-compensating anions go into the columns of [Fe(pc)] molecules in crystal grains in order to coordinate to the central metal, which promotes the more rapid deterioration of [Fe(pc)] film than [Zn(pc)] and [Co(pc)] films.

The oxidation of the central metal could occur partly on the [Co(pc)] film, too, because the n value is 1.41 and a small rereduction peak appears in addition to the main peak at the first scan. Indeed, the possibility of the oxidation at the central metal was demonstrated for the electronic reduction of oxygen on the [Co(pc)] film.[9]

It follows from what has been examined that the dependence of electrochromism of [tM(pc)] thin film on central metal is attributed to the way of the oxidation, in other words, the way of charge compensating by electrolyte anions for each [tM(pc)]. In the case of [tM(pc)] with irreversible electrochromism, electrolyte anions compensate the charge of [tM(pc)] cation, independent from the applied voltage, in the way that anions link strongly with pc cations, leading to the formation of electrically isolated domains after rereduction and to the decay of CV current and UV-vis absorbance. On the other hand, in the case of [tM(pc)] with reversible electrochromism, the way of charge compensating by electrolyte anions can be controlled by the scan range.

Dependence of Electrochromic Behavior of [tM(pc)] Thin Films on the Central Metal. Phthalocyanine has the characteristic absorptions, so-called Soret-band, located at ca. 350 nm and Q-band in the visible region.[6] The former originates from many conjugated double bonds of the porphyrin ring and the latter is the characteristic forbidden transition. In the case of the oxidation like the present experiments, an electron is removed from the $a_{1\pi}$ orbital, which causes the change of character of Q-band, and consequently, electrochromism is observed.

The coordination of central metal to the pc ring may change the redox ability of [M(pc)] because charge transfer occurs between the central metal and the pc ring, depending on the character of central metal. Thus, the coordination of various metals changes the electron state of pc ring, which causes the different way of oxidation of the pc ring. Furthermore, because the oxidation of central metal itself is also possible, the electrochromic behavior may remarkably depend on the central metal.

Table 1 presents the oxidation potentials of various [tM(pc)] thin films, as well as those measured in solutions. The order of the oxidation potential of [tM(pc)]s, measured by CVs for thin films, is [Ni(pc)] $\geq$ [Cu(pc)] > [Zn(pc)] $\geq$ [Co(pc)] > [Fe(pc)], which is the same as that measured in solutions.[26] It is noteworthy that there is a marked tendency that [tM(pc)] thin films having high oxidation potentials show good reversibility, as shown in Table 1. Moreover, the electronegativities of central metals of [tM(pc)]s studied in the present experiments are Ni, Cu = 1.75 > Co = 1.70 > Zn = 1.66 > Fe = 1.64.[36] This order is also in good agreement with that of the oxidation potentials of [tM(pc)] films. These results suggest that the dependence of electrochromism of [tM(pc)] films on the central metal can be explained by the consideration about their electronegativity.

When the central metal with high electronegativity coordinates to the pc ring, the electron density of pc ring decreases and consequently, the pc ring becomes difficult to be oxidized. This means more precisely that the oxidation potential of the pc ring becomes higher. [Ni(pc)] and [Cu(pc)] thin films are examples. Furthermore, the positive charge of the oxidized [Cu(pc)] and [Ni(pc)] cations tends to delocalize on the pc rings, since only a weak interaction between electrolyte anion and [tM(pc)] cation can occur with oxidation. Thus, both [Cu(pc)] and [Ni(pc)] thin films show reversible electrochromism under the controlled scan range.

On the other hand, in the case of a central metal having low electronegativity, the pc ring becomes easy to be oxidized and the oxidation potential of the pc ring becomes lower. [Zn(pc)], [Co(pc)], and [Fe(pc)] thin films correspond to this case. In this case, the positive charge of the oxidized [Zn(pc)] and [Co(pc)] cations tends to localize on a special position of the pc ring, since a strong linkage between electrolyte anions and these [tM(pc)] cations can occur with oxidation. This behavior leads to the formation of electrically isolated domains within the film after rereduction, resulting in irreversible electrochromism. Furthermore, the lower the electronegativity is, the higher the energy level becomes and consequently the higher the oxidation probability of the central metal becomes. Thus, [Fe(pc)], whose central metal has the lowest electronegativity among [tM(pc)] used in the present experiment, shows the most irreversible electrochromism.

On the basis of these considerations, the dependence of electrochromism of [tM(pc)] thin films on the central metal can be reasonably explained by the electronic states of pc rings and the central metals. In the case of [tM(pc)]s with reversible electromism, when the film is oxidized, the positive charge is delocalized in the [tM(pc)] molecule and the anions do not attack any specific position of [tM(pc)] molecule. It prevents the thin film from deterioration. In the case of [tM(pc)]s with irreversible electrochromism, in contrast, the positive charge is localized at some positions of pc ring or the central metal, which the anions can attack, resulting in the formation of electrically isolated domains within thin films, and then in the deterioration of films with repeated scans, although the scan range is well controlled.

Electrochromism of Codeposited Phthalocyanine Thin Films. The present investigations have indicated that the electrochromic property of [tM(pc)] thin films greatly depends on the central metal. Thus, composite thin films composed of various [tM(pc)]s having different electron and/or hole transferring properties are expected to produce a unique property, unlike simple [tM(pc)] thin films.

We have already studied in detail about the structure of composite [tM(pc)] thin films, i.e., the codeposited and sequentially deposited thin films consisting of two kinds of [tM(pc)]s.[22] The structures of composite films were analyzed by SEM, XRD, and ESR measurements. Composite [tM(pc)] films maintain the same morphology and crystallinity as simple [tM(pc)] films, having sharp peaks at ca. $2\theta = 7.0°$ in the XRD patterns and narrow rod-like crystal grains in SEM photographs. The important point to be noted is that [tM(pc)] molecules disperse very well in the codeposited thin films in a molecular level, by comparison with the physical mixture of [tM(pc)] powders. For example, as shown in Fig. 8, the ESR spectrum of [Cu(pc)] : H_2pc = 1 : 1 composite film clearly shows the hyperfine structure (hfs) attributed to nitrogen of the pc ring, although the hfs cannot be detected in that of the 1 : 1 physical mixture. Thus, codeposition of organic semiconductor molecules can accomplish high dispersibility, and this is thought to be one of the important techniques to construct new organic advanced solid devices.

The electrochromic properties of both simultaneously and sequentially deposited composite thin films are also compared in various pairs of [tM(pc)]s. One of the pair of the composite film is the [tM(pc)] showing reversible electrochromism, and the other is that showing irreversible electrochromism.[22] In the case of the codeposited film, high dispersibility of [tM(pc)] molecules in the film can play a role to improve the reversibility in the electrochromism of [tM(pc)] which is irreversible in a simple film form.

The [Ni(pc)]–[Zn(pc)] composite film is taken as an example. The simple [Ni(pc)] film can be oxidized and rereduced reversibly (Fig. 1). In contrast to [Ni(pc)], simple [Zn(pc)] film is oxidized and rereduced irreversibly. The oxidation (ca. 0.8 V) and rereduction (ca. 0.6 V) peaks mostly decay with ten repeated scans (Fig. 2). The composite film prepared by codeposition of [Ni(pc)] and [Zn(pc)] revealed a quite different result. The CV curves of the [Ni(pc)]–[Zn(pc)] composite films ([Ni(pc)] : [Zn(pc)]= 5 : 4) are shown in Fig. 9. It is noteworthy that the oxidation peak, which corresponds to that gradually decaying in a simple [Zn(pc)] film, does not decay in the composite thin films. Although the spectra

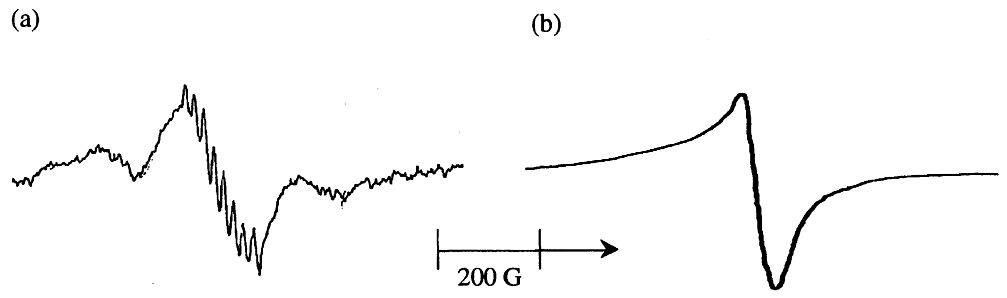

Fig. 8. ESR spectra of [Cu(pc)]–H_2pc ([Cu(pc)] : H_2pc = 1 : 1) composite; (a) codeposited thin film and (b) physical mixture of pc powder.

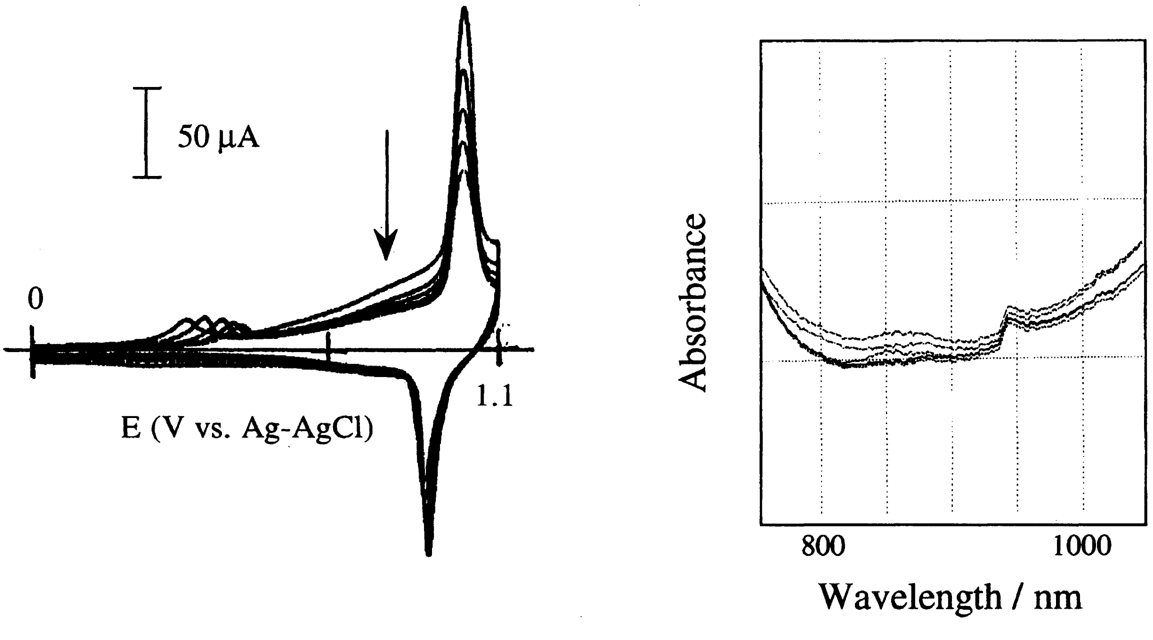

Fig. 9. Cyclic voltammograms (1st—10th) and absorption spectral changes (at the first oxidation) of [Ni(pc)]–[Zn(pc)] codeposited films ([Ni(pc)] : [Zn(pc)] = 5 : 4) in a 0.1 mol dm^{-3} $NaNO_3$ solution at the scanning rate of 20 mV s^{-1}.

at the reduced state decay compared to the original one, the shape of the spectra is kept after the repeated scan. (The visible spectral change of composite film is shown in Fig. 7 in Ref. 22.) From the viewpoint of reversible electrochromism, the electrochromic property is actually improved by codeposition.

Examining this CV curve in detail, we recognize that the oxidation current continues to appear between oxidation peak potentials of the corresponding simple [tM(pc)], i.e., [Ni(pc)] and [Zn(pc)] films. This behavior is quite different from that of the double-layered thin films prepared by sequential deposition (see below), indicating that charge-transfer complexes between two kinds of [tM(pc)] could be generated within the composite film because the oxidation potentials of these simple [tM(pc)]s are quite different each other. Such charge-transfer complexes must have the different electronic states from the corresponding simple [tM(pc)]s, resulting in the observation of the oxidation peak between the oxidation peaks of the corresponding [tM(pc)]s. Although the codeposition film has the good dispersibility, two kinds of [tM(pc)] do not have the completely alternative alignment within the crystal grains of the film. It is quite possible that some parts within a crystal grain consist of one kind of [tM(pc)]. These parts contribute to the same oxidation peak currents as the corresponding [tM(pc)] film. These results suggest that the codeposition technique can alter the oxidation potential by generating charge transfer complexes. Thus, perfect codeposition technique is thought to control the oxidation potential of organic molecules artificially, which leads to a novel technique of "molecular doping".

Codeposition with [Ni(pc)] having reversible electrochromism can improve the reversibility of electrochromism of [Zn(pc)], which originally shows irreversible electrochromism. The irreversibility of [Zn(pc)] films is due to some chemical change of molecular structure, which is revealed by the spectral change in an NIR region as demonstrated above. Then, the similar measurement was also examined on the [Ni(pc)]–[Zn(pc)] composite thin film. As shown in Fig. 9, a new peak at 850 nm characteristic for the oxidized [Zn(pc)] is very faint, which is quite different from the case of [Zn(pc)] simple films. In addition, there is no remarkable difference in SEM photographs between the original film and the cycled one, which a simple [Zn(pc)] film was partly fissured after repeated scans. These results clearly show that codeposition with [tM(pc)], showing reversible electrochromism, prevents the pc molecules showing irreversible electrochromism from the chemical change of molecular structure. This prevention may be due to the high dispersibility of codeposited thin film and to the change of electron state of [tM(pc)] molecules by molecular doping.

Electrochromism of Double-Layered Phthalocyanine Thin Films. Figure 10 shows the CV curves of [Ni(pc)]–[Zn(pc)] sequentially deposited double-layered thin films, including the band diagrams of each film. In the CV

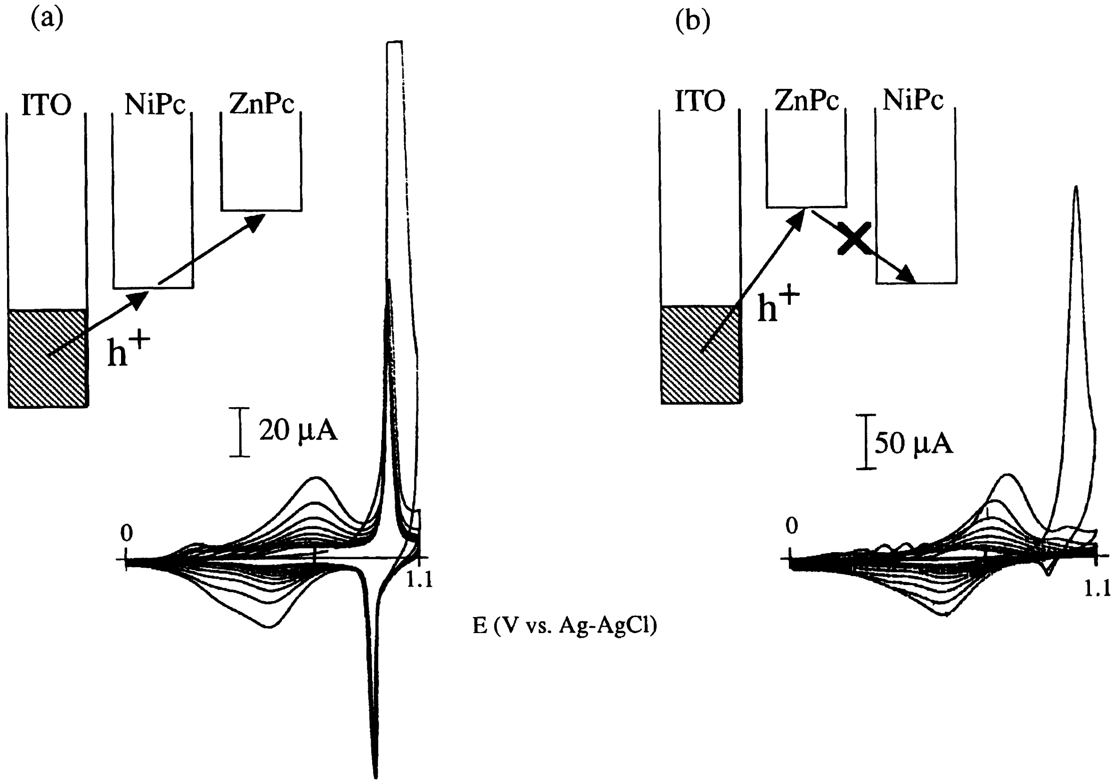

Fig. 10. Cyclic voltammograms of [Ni(pc)]–[Zn(pc)] sequentially deposited double-layered films; (a) ITO/[Ni(pc)]/[Zn(pc)], (b) ITO/[Zn(pc)]/[Ni(pc)] films in 0.1 mol dm^{-3} $NaNO_3$ solutions at the scanning rate of 20mV s^{-1}, including the schematic band diagrams.

curve of the ITO/[Ni(pc)]/[Zn(pc)] film, which is prepared by sequential deposition of [Ni(pc)] and then [Zn(pc)] on the ITO electrode, both peaks originated from [Ni(pc)] and [Zn(pc)] are observed, while, in that of ITO/[Zn(pc)]/[Ni(pc)], which is prepared by the reverse way, only one broad peak originated from [Zn(pc)] is observed.[22] This big difference can be explained by the diagrams demonstrated in Fig. 10. In the case of the ITO/[Ni(pc)]/[Zn(pc)] film, [Ni(pc)] layer, which contacts with the ITO substrate, has the higher oxidation potential than that of [Zn(pc)]. When enough positive voltage is applied to the ITO substrate, a hole transfers from ITO to [Ni(pc)] layer and this layers oxidized, resulting in the generation of holes in [Ni(pc)] layer. These holes easily transfer to [Zn(pc)] layer because the oxidation potential of [Zn(pc)] is lower then that of [Ni(pc)]. Consequently, [Zn(pc)] is fully oxidized together with the first [Ni(pc)] layer. Thus, this order of the oxidation potentials makes it easy for electron or hole to transfer through the layers in the repeated oxidation and rereduction scan. Furthermore, the first layer, [Ni(pc)] shows reversible electrochromism, so that both [Ni(pc)] and [Zn(pc)], i.e., the first and second layers can be oxidized and rereduced continuously.

In contrast, in the case of the ITO/[Zn(pc)]/[Ni(pc)] film, the order of the depositions is reverse to that in the ITO/[Ni(pc)]/[Zn(pc)] film. In this case, it is difficult for both hole and electron to transfer through the layers because there is a potential barrier between [Zn(pc)] and [Ni(pc)] layers for the transfer. Consequently, only the first [Zn(pc)] layer is oxidized and rereduced and the CV curve is quite similar with that of the [Zn(pc)] single layered film.

Recently, Pietro reported about rectifying junctions based on [Ni(pc)] and [Cu(pcF$_8$)] double-layered thin film.[24] According to his report, this rectification in a junction is non-Shottky type. In the [Ni(pc)]–[Zn(pc)] double-layer system, the similar rectifying junction forms between [Ni(pc)] and [Zn(pc)] layers, although the difference of the oxidation potentials between these [tM(pc)]s is smaller than between [Ni(pc)] and [Cu(pc)F$_8$]. Holes can transfer from [Ni(pc)] layer to [Zn(pc)] one, while they cannot from [Zn(pc)] to [Ni(pc)]. Thus, the electrohromism of double-layered [tM(pc)] thin films depends on the order of the depositions on the ITO substrate. The double-layer system of [tM(pc)] thin film makes it possible to control hole transfer through the film, which is the first important step to construct a so-called "sequential potential field".[23] Now, we are trying to apply this concept to solid devices using double-layered [tM(pc)] thin films.

Conclusions

Among single transition-metal phthalocyanine thin films ([tM(pc)], M = Ni, Cu, Co, Zn, Fe), [Cu(pc)] and [Ni(pc)] thin films show reversible electrochromism under the designed experimental conditions, while [Zn(pc)], [Co(pc)], and [Fe(pc)] thin films show irreversible type even though the experimental conditions are well-designed.

The dependence of the behavior on central metal may be attributed to the difference of electron states of pc rings and central metals. In the case of [Cu(pc)] and [Ni(pc)], whose oxidation potentials are high, chemical changes of molecular structure never happen by oxidation, while in the case of [Zn(pc)], [Co(pc)], and [Fe(pc)], this chemical change is clearly observed by oxidation. This difference may decide the reversibility of electrochromism.

In the simultaneously deposited thin film, two kinds of pc molecules disperse each other well, and consequently, the electrochromic property is improved, focusing attention on the [tM(pc)] with irreversible electrochromism. The interaction between two kinds of [tM(pc)] changes the way of charge compensation by electrolyte anions with oxidation, and prevents these anions from remaining inside the film after rereduction. These results suggest the possibility of "molecular doping" by using codeposition of organic molecules.

In the case of the sequentially deposited double-layered [tM(pc)] thin film, the eletrochromism depends on the order of the deposition in the order of the oxidation potential to the substrate. The double-layer system of [tM(pc)] can control the hole transfer in the organic thin film, which is a good experimental achievement of the novel concept of the so-called "sequential potential field".

The authors wish to express their sincere thanks to Dr. Mitsuhito Adachi for measurement of SEM. One of the authors (T. T) also acknowledges the Research Fellowships for Young Scientists of the Japan Society for the Promotion of Science. This research was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas "Molecular Superstructures" No. 07241214 and a Grant-in-Aid for Encouragement of Young Scientists No. 3610 from the Ministry of Education, Science, Sports and Culture.

References

1) F. H. Moser and A. L. Thomas, "The Phthalocyanines," CRC Press, Boca Raton (1983).

2) M. Tanaka and S. Koma, "Phthalocyanine," Bunshin Pub., Tokyo (1991).

3) D. Wöhrle and D. Meissner, *Adv. Mater.*, **30**, 129 (1991).

4) R. O. Loufty, A. M. Hor, and A. Rucklidge, *J. Imaging Sci.*, **31**, 31 (1987).

5) G. C. S. Collins and D. J. Schiffrin, *J. Electrochem. Soc.*, **132**, 1835 (1985).

6) A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswamy, and K. Magnell, *J. Am. Chem. Soc.*, **103**, 6800 (1981).

7) P. C. Minor, M. Gouterman, and A. B. P. Lever, *Inorg. Chem.*, **24**, 1894 (1985).

8) A. Putten, A. Elzing, W. Visscher, and E. Barendrecht, *J. Electroanal. Chem.*, **214**, 523 (1986).

9) D. Ham, C. Hinnen, G. Magner, and M. Savy, *J. Phys. Chem.*, **91**, 4743 (1987).

10) N. Toshima, S. Kawamura, and T. Tominaga, *Chem. Lett.*, **1993**, 1299 (1993).

11) N. Toshima, T. Tominaga, and S. Kawamura, *Bull. Chem. Soc. Jpn.*, **69**, 245 (1996).

12) J. M. Green and L. R. Faulknr, *J. Am. Chem. Soc.*, **105**, 2950

(1983).

13) J. L. Kahl, L. R. Faulkner, K. Dwarakanath, and H. Tachikawa, *J. Am. Chem. Soc.*, **108**, 5434 (1986).

14) D. Schlettwein, D. Wöhrle, and N. I. Jaeger, *J. Electrochem. Soc.*, **136**, 2882 (1989).

15) K. Takeshita, Y. Aoyama, and M. Ashida, *Bull. Chem. Soc. Jpn.*, **64**, 1167 (1991).

16) K. Takeshita and M. Ashida, *J. Electrochem. Soc.*, **138**, 2617 (1991).

17) K. Takeshita and M. Ashida, *J. Electrochem. Soc.*, **139**, 285 (1992).

18) J. Silver, P. Lukes, A. Houlton, S. Howe, P. Hey, and M. T. Ahmet, *J. Mater. Chem.*, **2**, 849 (1992).

19) J. Silver, P. Lukes, P. K. Hey, and M. Ahmet, *J. Mater. Chem.*, **2**, 841 (1992).

20) M. Shimura, K. Sato, T. Okumura, Y. Shimura, and K. Ozawa, *Denki Kagaku*, **61**, 922 (1993).

21) H. Yanagi and M. Toriida, *J. Electrochem. Soc.*, **141**, 64 (1994).

22) T. Tominaga and N. Toshima, *Polym. Adv. Technol.*, **6**, 9 (1995).

23) N. Toshima,"Macromolecular Complexes: Dynamic Interacrions and Electronic Processes," ed by E. Tsuchida, VCH, New York (1991), pp. 331—352.

24) W. J. Pietro, *Adv. Mater.*, **6**, 239 (1994).

25) R. -J. Lin and N. Toshima, *Bull. Chem. Soc. Jpn.*, **64**, 136 (1991).

26) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).

27) M. Whalley, *J. Chem. Soc.*, **1961**, 866 (1961).

28) M. Ashida, *Bull. Chem. Soc. Jpn.*, **39**, 2625 (1966).

29) M. Ashida, *Bull. Chem. Soc. Jpn.*, **39**, 2632 (1966).

30) M. Hara, H. Sasabe, A. Yamada, and A. F. Garito, *Jpn. J. Appl. Phys.*, **28**, L306 (1989).

31) M. Komiyama, Y. Sakakibara, and H. Hirai, *Thin Solid Films*, **151**, L109 (1987).

32) H. Ozaki and Y. Harada, *J. Chem. Phys.*, **92**, 3184 (1990).

33) S. Tanishima, K. Ohno, Y. Sakakibara, and N. Toshima, *Chem. Express*, **5**, 153 (1990).

34) P. S. Vincett, Z. D. Popovic, and L. Mcintyre, *Thin Solid Films*, **82**, 357 (1981).

35) J. M. Birchall, R. N. Haszeldine, and J. O. Morley, *J. Chem. Soc. C*, **1970**, 2667.

36) "Handbook of Chemistry," Maruzen Pub., Tokyo (1984).