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Electrochemical and Electrochromic Properties of Polymer Complex Films Composed of Polytetramethyleneviologen and Poly-[*p*-Styrenesulfonic Acid] Containing a Conductive Powder

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ELECTROCHEMICAL AND ELECTROCHROMIC PROPERTIES OF POLYMER COMPLEX FILMS COMPOSED OF POLYTETRAMETHYLENEVIOLOGEN AND POLY-(*p*-STYRENESULFONIC ACID) CONTAINING A CONDUCTIVE POWDER

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ABSTRACT

The electrochemical and electrochromic properties of polymer films containing a conductive powder (SnO_2/TiO_2) have been investigated. The films are complexes of polytetramethyleneviologen and poly(*p*-styrenesulfonic acid). It was found that the coloration (purple) and bleaching rates of the composite films increase markedly with increasing conductive powder content(x). The coloring and bleaching of the composite film with x = 95 wt% were about 7 and 44 times faster, respectively, than those for an equivalent film without conductive powder. This increase in the rate of color change by introduction of a conductive powder was found to be correlated with the apparent diffusion coefficient (D_{app}) for the diffusionlike charge-transport process within

the composite films which increases with increasing x. The D_{app} for the reduction process of the film with x = 95 wt% was larger by about 3 orders of magnitude than that for the unfilled film.

INTRODUCTION

A large number of studies concern the application of bipyridinum compounds (better known as viologens) to electrochromic displays [1-11]. Electrochromic displays based on viologens have some characteristics, such as a memory effect, good perceived contrast, low switching voltage, low mean power consumption, and no viewing angular dependence, that are also common to other electrochromic materials (e.g., WO_3) [12-14]. However, they are not yet in practical use, mainly because 1) the response rate of the reversible color change induced by an electric field is slow compared with other display devices (e.g., those based on liquid crystals), 2) the chemical stability is inferior to that of other electrochromic materials (e.g., inorganic materials such as WO_3), and 3) a "residue" is produced on the electrode during the bleaching process [3, 9-14].

In the present paper the electrochemical and electrochromic properties of composite films consisting of a viologen polymer complex (i.e., a polyion complex composed of polytetramethyleneviologen and poly(*p*-styrenesulfonic acid)) and a conductive powder (SnO_2/TiO_2) will be examined, especially the effects of introducing conductive powder into the polymer complex films on the response rate. It will be demonstrated 1) that the response rates of the color change can be correlated with the apparent diffusion coefficients (D_{app}) for the diffusionlike charge-transport process within the composite films and 2) that the response rates and D_{app} values significantly increase with increasing content of the conductive powder in the polymer complex films.

EXPERIMENTAL

Reagents

Polytetramethyleneviologen (PTV, MW_{ave} 6000) was prepared from 4,4′-bipyridine and 1,4-tetramethylene bromide, as described previously [11]. Poly(*p*-styrenesulfonic acid) (PSS) was obtained commercially from Sanyo Kasei Co. The polymer complex (PTV-PSS), shown in Fig. 1, was prepared by adding PTV aqueous solution dropwise to PSS aqueous solution with

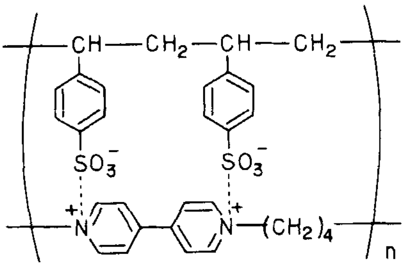

FIG. 1. The structure of the polytetramethyleneviologen (PTV)-poly(*p*-styrenesulfonic acid) (PSS) polymer complex.

stirring and then completely washing the resulting precipitate with distilled water and drying it. The conductive powder W-10 (TiO_2/SnO_2 doped with antimony oxide), obtained from Mitsubishi Kinzoku Co., Tokyo, had the following characteristics; specific resistance, 20-100 Ω•cm; color, white; shape, spherical; diameter, 0.2 μm; specific gravity, 4.4 g/cm^3. In-Sn oxide conducting glass (ITO, Matsuzaki Shinku Co., 10 Ω/□) was used as the electrode substrate. Aqueous solutions were prepared from doubly distilled water. All other chemicals were of reagent grade and used without further purification.

Preparation of Composite Film-Coated ITO Electrodes

The polymer complex (PTV-PSS) (e.g., 0.5 g) was dissolved in dioxane/12 *N* HCl/H_2O (volume ratio 10/9/1) mixed solvent (10 mL), and then the conductive powder W-10 (e.g., 5 g) was added to it. After that, the PTV-PSS complex and the conductive powder were mixed thoroughly in a mortar. A further 5 mL of mixed solvent was added to the PTV-PSS/W-10 mixture. Aliquots of the PTV-PSS/W-10 suspension solution thus prepared were spray-coated onto ITO electrodes, and then the solvent was evaporated as quickly as possible. By changing the ratio of PTV-PSS complex to W-10, composite film-coated ITO disk electrodes (area: 0.16 cm^2) of various conductive powder contents (x: 0, 67, 75, 83, 91, and 95 wt%) were prepared.

Apparatus and Procedures

A standard three-electrode, two-compartment electrochemical cell was used for all the electrochemical experiments. The electrode assembly consisted of composite film-coated ITO as the working electrode, a sodium chloride/saturated calomel electrode (SSCE) as the reference electrode, and a spiral platinum electrode as the counterelectrode. The cyclic voltammetric and potential-step chronoamperometric (and chronocoulometric) measurements were carried out according to the procedure described previously [15, 16]. The surface concentrations (Γ in mol/cm^2) of electroactive viologen sites in the PTV-PSS/W-10 composite films on electrodes and their thickness (ϕ) were estimated as described previously [15, 16], and the molar concentrations were calculated from the Γ and ϕ values.

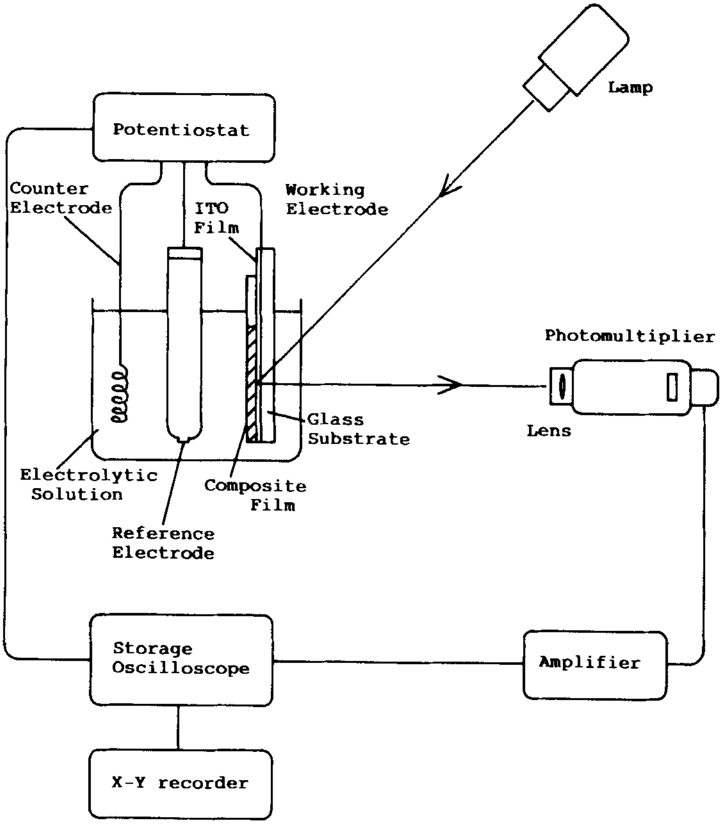

FIG. 2. Schematic representation of the apparatus for the electrooptic measurements.

The electrooptical measurements were made with the assembly shown in Fig. 2. In a typical potential-step chronoabsorbance experiment, the reflectance was monitored at the maximum absorption peak (λ_{max} = 550 nm) for the radical cation of the viologen site in the composite film as a function of the time when the electrode potential was stepped repeatedly between 0 and -0.65 V vs SSCE.

Nitrogen gas was passed through the solutions to remove dissolved oxygen before the measurements and over the solutions during the measurements. All experiments were conducted at laboratory temperature (25 ± 1°C). The potentials were measured and are quoted with respect to the SSCE.

RESULTS AND DISCUSSION

Cyclic Voltammetry

The typical cyclic voltammograms for oxidation-reduction of the filled and unfilled films of almost the same thickness in Fig. 3 display several features.

First, the formal redox potential ($E^{\circ\prime}$ = -0.516 V vs SSCE), estimated as the average of the anodic and cathodic peak potentials, for the composite film is more positive by about 100 mV than that (-0.633 V) for the unfilled film. Thus, the reduced form (i.e., the radical monocation) of the viologen site is considered to be stabler in the filled film than in the unfilled one. In the latter, the peak currents decrease, though slightly, with successive potential scans in the potential region where the redox reaction between the dication and the monocation radical states occurs. Similar but more striking behavior has sometimes been observed for redox reactions of solution-phase viologen compounds [3, 8]. This may be due to the fact that most viologen monocation radical salts show "aging effects" caused by the crystallization of the radicals [3, 8, 17]. This crystallization causes incomplete erasure in electrochromic displays since the crystallized radicals are not completely reoxidized during the oxidation step. It seems likely that such aging effects are suppressed to a certain extent in polyviologen systems, especially for polymer complex films composed of cationic polyviologens and anionic polyelectrolytes (such as PSS used in this study) [6, 16]. For the PTV-PSS/conductive powder film, the aging effects under consideration were found to be suppressed much more markedly. The peak currents remained substantially unchanged even after the potential cyclings for several hours in the potential region where only the first reduction and oxidation steps occur.

Second, the separation (ΔE_p) between the anodic and cathodic peak potentials for the filled film is only several mV at a scan rate of 2 mV/s, while ΔE_p

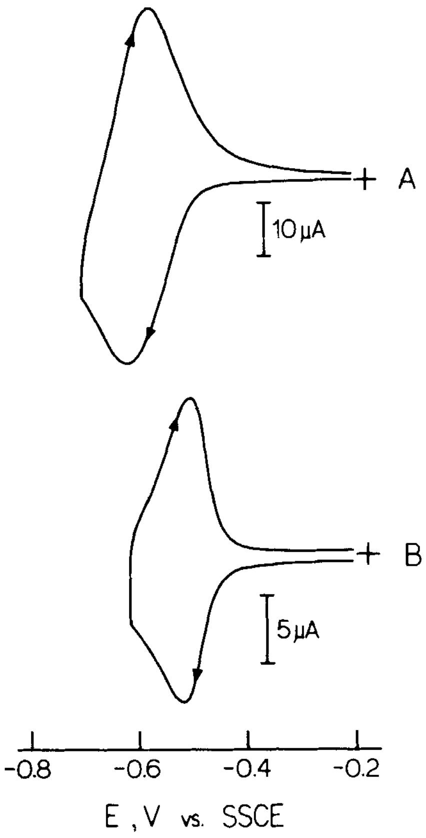

FIG. 3. Typical cyclic voltammograms for the oxidation-reduction reaction of (A) unfilled PTV-PSS complex film and (B) PTV-PSS/conductive powder composite film (x = 91 wt%) coated onto ITO electrodes in 0.5 M Na_2SO_4 aqueous solution. Scan rate, 2 mV/s; electrode area, 0.16 cm^2; film thickness, 4.0 µm.

for the unfilled film is about 60 mV at the same scan rate. The cyclic voltammogram for the latter film has a so-called diffusion tail and the shape is unsymmetric, whereas for the composite film such a diffusion tail cannot be seen, and the shape of the voltammogram is symmetrical. As a whole, we can see that the cyclic voltammogram (Fig. 3A) of the unfilled film resembles that obtained for a "diffusion-controlled" reaction of a dissolved redox species [18, 19], and on the other hand, the voltammogram (Fig. 3B) of the filled film is very similar to that expected for a surface-confined redox species [20].

Previously, we [11] examined the dependence of the peak current (i_p) on the potential scan rate (v) for the composite films of various powder contents (x). That is, the n values in the $i_p \propto v^n$ relation were determined for composite films of various x. It was found that the n value is equal to 0.5 at $x = 0$, and that it increases almost linearly from 0.53 to 0.94 with x increasing from 37 to 86%. In this experiment, composite films with almost the same thickness (4.0 ± 0.7 μm) were used. It is apparent from this result that as x is increased, the cyclic voltammetric behavior of the composite films comes close to that expected for a surface-confined redox species [20] although the films used correspond to several hundreds of monolayers (estimated from the surface concentrations (~0.038-0.08 μmol/cm^2) of viologen sites in the films and a monolayer coverage of about 10^{-10} mol/cm^2). A similar i_p vs v relation has also been observed for electroactive electropolymerized films (e.g., pyrrolo-[3,2-*b*] pyrrole polymers) [21]. The present and previous data [11] may suggest that there is a significant contribution of "electronic conduction" to the overall charge transport within the films. The theoretical treatment of this problem still remains to be developed.

By using the known average diameter of the conductive powder, 0.2 μm, and on the assumption that the PTV-PSS complex films coat the surfaces of the conductive powders uniformly, the thicknesses of the PTV-PSS complex films on the conductive powder were estimated from the amounts of the polymer and the powder blended. For example, the film thicknesses on the powders in the films of $x = 86$ and 37% were ~50 and 500 Å, respectively [11]. In both cases the actually measured thickness of the composite films on the electrodes was ~4 μm. Based on these calculations and measured data, the cross-sectional views of the composite films are shown schematically in Fig. 4.

Potential-Step Chronoamperometry and Chronocoulometry

In order to estimate the kinetic parameters characterizing the charge-transport process within the films, the potential-step chronoamperometric and chronocoulometric responses for the reduction and oxidation of the viologen site in the films were examined. Typical examples are shown in Figs. 5 and 6. For the film without conductive powder, Cottrell plots (i.e., i-$t^{-1/2}$ and Q-$t^{1/2}$ plots), which passed through the origin, were found to be linear in the examined range of times (~1-40 ms). This indicates that the charge-transport process within the film follows Fick's diffusion laws, and thus the slopes of the linear plots shown in Figs. 5(A) and 6(A) yield the apparent diffusion

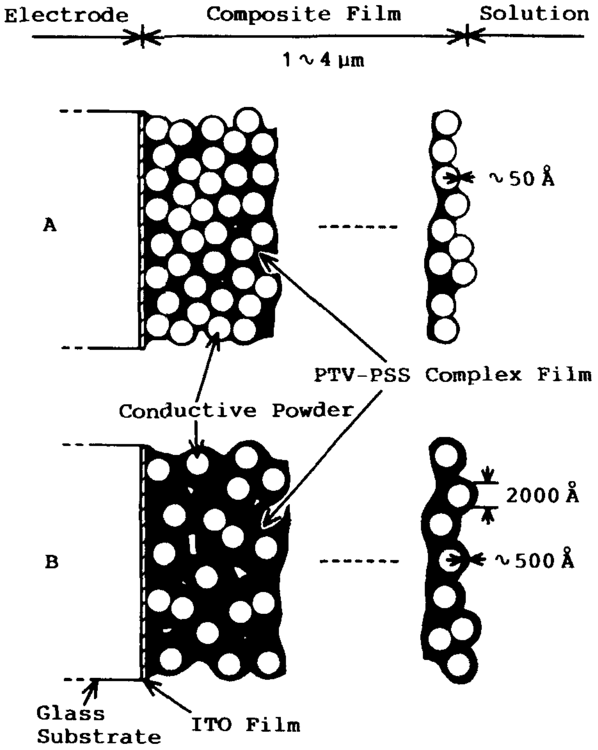

FIG. 4. A schematic cross-sectional view of PTV-PSS/conductive powder composite film-coated ITO electrodes. Conductive powder content: (A) high (x= 86 wt%); (B) low (x = 37 wt%).

coefficients (D_{app}) for the diffusionlike charge-transport process within the film.

In the case of the composite films, on the other hand, the situation seems to be different. That is, the chronoamperometric Cottrell plots (Figs. 5B, C, and D) are not linear and are curved, more for the films of higher x. This suggests that the charge-transport processes within these films do not simply obey Fick's diffusion laws. However, we obtained almost linear chronocoulometric Cottrell plots (see Figs. 6B, C. and D). The time range shown in Figs. 5 and 6 is the same and, for each composite film-coated electrode, the chronoamperometric and chronocoulometric measurements were conducted together. At the present stage we have no reasonable explanation why nonlinear Cottrell

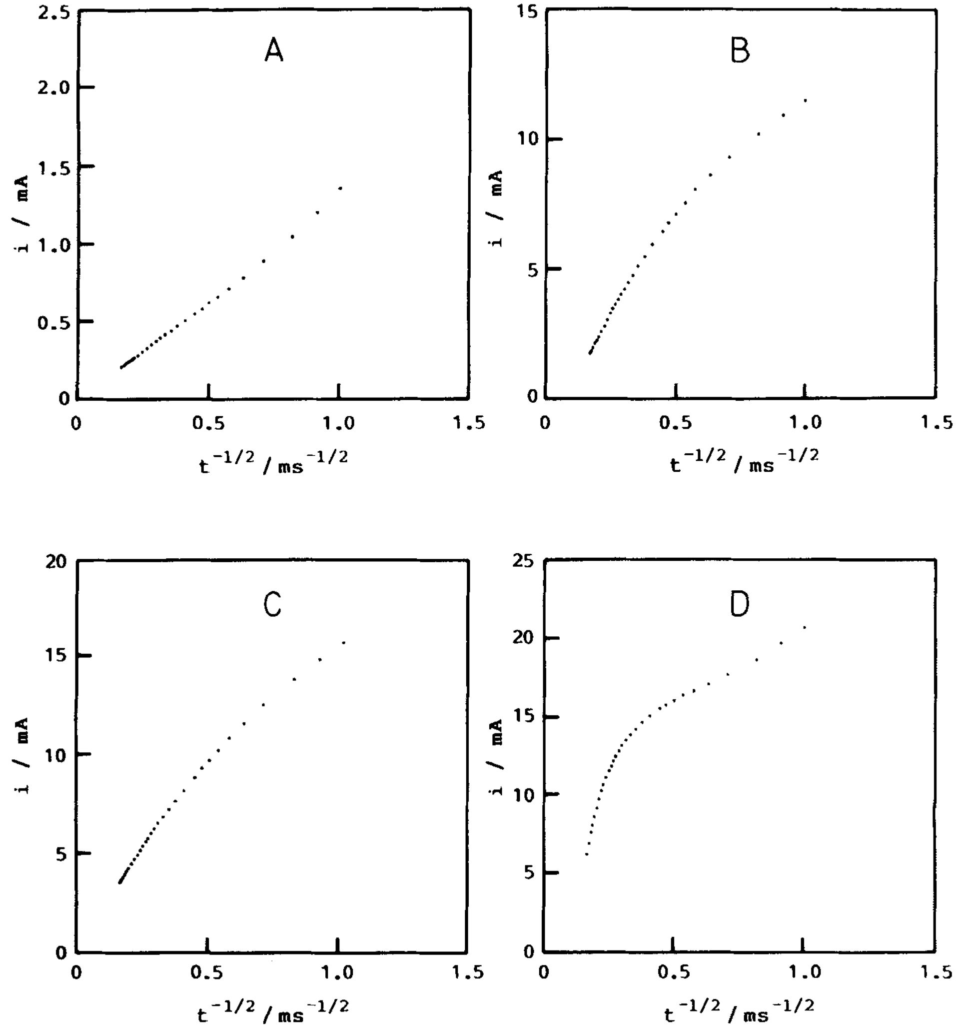

FIG. 5. Typical potential-step chronoamperometric Cottrell plots for the reduction of (A) unfilled PTV-PSS complex film and (B, C, D) PTV-PSS/ conductive powder composite films coated on ITO electrodes in 0.5 *M* Na_2SO_4 solution. Conductive powder content (*x*): (A) 0, (B) 67, (C) 83, and (D) 91 wt%. Electrode areas: (A) 0.25, (B, C, D) 0.16 cm^2. Film thicknesses: (A) 1.7, (B) 3.3, (C) 3.9, and (D) 3.7 μm. Concentrations of viologen sites: (A) 0.19, (B) 0.17, (C) 0.22, and (D) 0.083 mol/L. The electrode potential was stepped from -0.2 to -0.9 V vs SSCE.

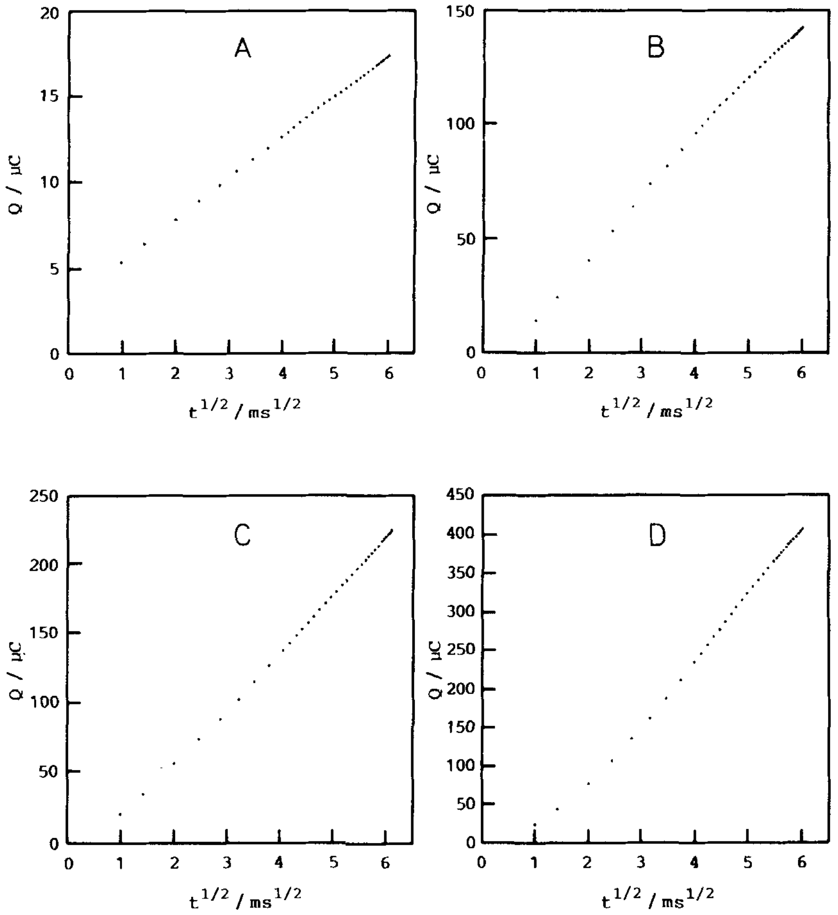

FIG. 6. Chronocoulometric Cottrell plots for the data of Fig. 5.

plots were obtained for the chronoamperograms but linear ones for the chronocoulograms.

At any rate, from the linear Cottrell plots such as those shown in Figs. 6(B), (C), and (D), we obtained the D_{app} values (Fig. 7). At a given x, the D_{app} value for the reduction process was larger by about 1-2 orders of magnitude than that for the oxidation process, and both these values increased greatly with increasing x. For example, the reduction value for the compos-

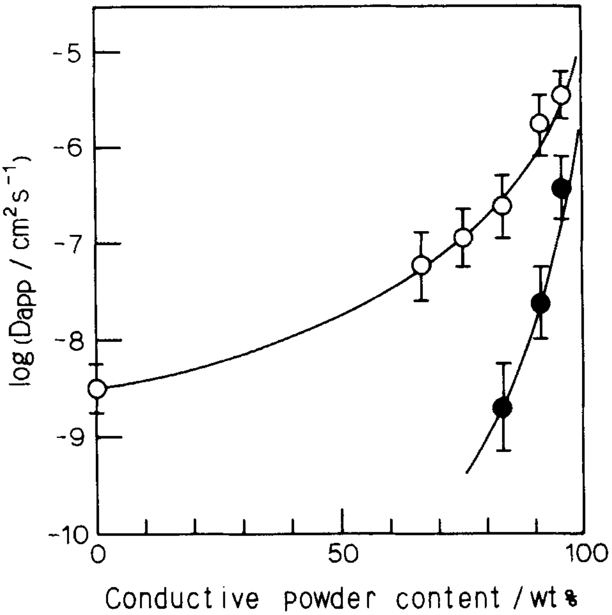

FIG. 7. Correlation between D_{app} and conductive powder content (x). (○) Reduction process; (●) oxidation process. The D_{app} values were estimated by potential-step chronocoulometry (see text).

ite film with x = 95 wt% is larger by about three orders of magnitude than that for x = 0 wt%.

As mentioned above, it should be kept in mind that the D_{app} values, except those for the unfilled film, may not necessarily reflect the true charge-transport rates within the films. Thus, the exact explanation of the D_{app} values obtained seems to be impossible at present. A probable explanation for the data of Fig. 7 is that as the conductive powder content (x) is increased, the effective electrode area and/or D_{app} itself might increase. The effective electrode area might increase with increasing x if the conductive powders make contact directly with the electrode and, in addition, are in contact with each other, since the powders are electronically conductive. In the estimation of the D_{app} values in Fig. 7, the geometric areas of the electrode substrates were used. Murray et al. [22] reported that incorporation of small carbon particles in poly(N-vinylbenzyl-N'-methyl-4,4'-bipyridinum hexafluorophosphate) film raises the apparent diffusion coefficient. They explained this by inserting a "roughness factor" into the Cottrell equation to represent the increased area of electrode/polymer interface or the decreased distance over which the charge has to diffuse.

The D_{app} values reflect the apparent charge-transport rates within the films. In the present system, electrons are considered to be transported through the polymer layers by an electron-hopping reaction between neighboring viologen sites, because the viologen sites are fixed covalently in the polymeric backbones [15, 16]. The intrinsic electron-transfer reaction is followed by the charge-compensating counterion motion which is necessarily coupled to electron transfer (for charge neutrality), the motion of solvent, and/or the segmental motion of polymeric chains [15, 16, 23, 24]. As x is increased, the films can be expected to become more porous. As a result,the rates of the charge-compensating counterion motion, the motion of solvent, and the segmental motion of polymeric chains might increase and, consequently, larger D_{app} values are obtained. For the films examined here, it was found that the concentrations (C^0) of the electroactive viologen site in the films decrease slightly with increasing x: C^0 was 0.19, 0.17, 0.17, 0.22, 0.083, and 0.075 mol/L for the films of x = 0, 67, 75, 83, 91, and 95 wt%, respectively. This may be attributed to the increasing volume occupied by the conductive powder with increasing x. Such a decrease of C^0 is considered to lead to a decrease in the contribution of the intrinsic electron-transfer reaction between the viologen sites to the overall charge transport rate [15]. However, the increase in x also leads to an alternative effect, as mentioned above (i.e., the increases in the effective electrode area, the film porosity, and the contribution of "electronic conduction" to the overall charge transport). Consequently, as x increases, larger D_{app} values are obtained.

Electrochromic Properties

Figure 8 shows the absorption spectra of the oxidized and reduced forms of the PTV-PSS complex film coated on ITO electrodes. The oxidized form (dicationic form, MV^{2+}) is colorless and the singly reduced cation radical form ($MV^{\cdot+}$) is purple. The λ_{max} of the $MV^{\cdot+}$ form is 550 nm, which is similar to those of viologen cation radicals in water [25-27]. Using 550 nm, so as to be optically selective toward the $MV^{\cdot+}$ form, reflectance-time curves were observed to track potential stepping between the MV^{2+} and $MV^{\cdot+}$ states, as shown in Fig. 9. The reflectance change during the $MV^{\cdot+} \rightarrow MV^{2+}$ oxidation (i.e., bleaching) reaction occurs more slowly than the reduction transient (i.e., coloration; $MV^{2+} \rightarrow MV^{\cdot+}$). This means that the charge-transport rates of the composite films differ in the oxidation and reduction directions, as supported by

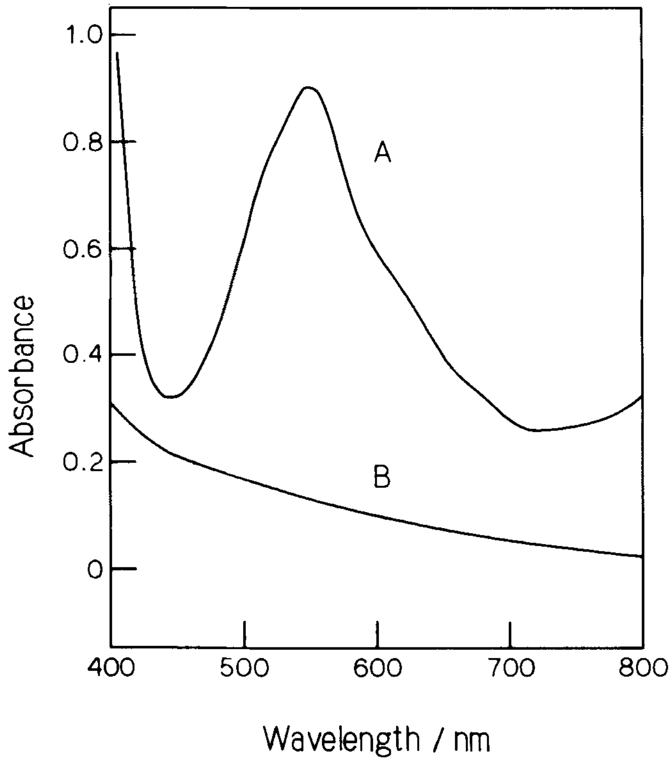

FIG. 8. Absorption spectra of (A) reduced and (B) oxidized forms of the unfilled PTV-PSS complex film coated onto ITO electrode in 0.5 *M* Na_2SO_4 aqueous solution. Film thickness: 1.7 μm.

the data in Fig. 7. Similar differences have been reported for benzyl-viologen-silane polymer [7], polymeric ferrocene [28], tetrathiafulvalene [29], and electropolymerized poly(*o*-phenylenediamine) [30] films. We can also see that the coloration and bleaching rates depend on the conductive powder content (x).

Figure 10 shows the correlation between the response times of the color change (i.e., colorless $\rightleftharpoons$ purple) corresponding to the $MV^{2+} \rightleftharpoons MV^{+\cdot}$ states and the conductive powder content. At a given x, the response time (t_c) for the coloration process is shorter than that (t_b) for the bleaching process, and the difference between t_c and t_b decreases as x is increased. For example, t_b/t_c =

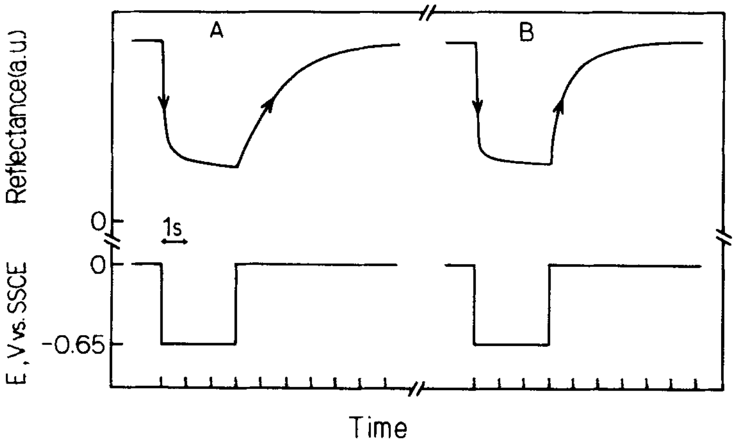

FIG. 9. Typical reflectance-time curves of PTV-PSS/conductive powder composite film-coated ITO electrodes during potential stepping between -0.65 and 0 V vs SSCE in 0.5 *M* Na_2SO_4 solution. The reflectance was measured at 550 nm. Conductive powder content: (A) 83 wt% and (B) 91 wt%.

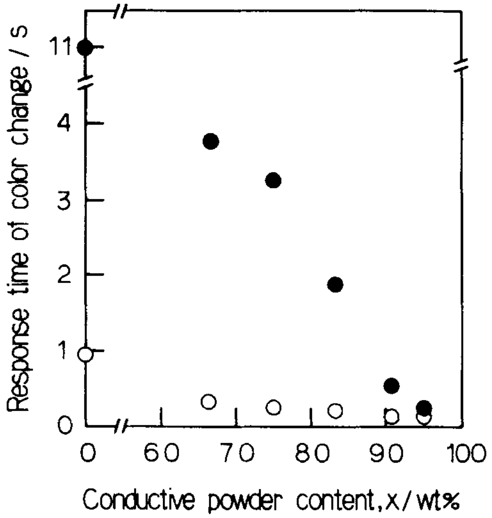

FIG. 10. Correlation between the response times of the color change and the conductive powder content. (○) Coloration process; (●) bleaching process. The response times were measured from reflectance-time curves (at 550 nm) such as those shown in Fig. 9.

11.5 and 1.9 for $x = 0$ and 95%, respectively. In this case, both t_c and t_b shorten with increasing x.

Both response rates (Fig. 10) and D_{app} values (Fig. 7) increase with increasing x. This is a very interesting result, especially from the viewpoint of practical application of the PTV-PSS/conductive powder composite film-coated electrodes to an electrochromic display. However, increasing the conductive powder content weakened the contrast in color. Thus, the optimum conditions should be sought for their practical use as electrochromic materials.

CONCLUSIONS

The composite viologen polymer films consisting of PTV-PSS polymer complexes and conductive powders showed electrochromic character: the MV^{2+} form is colorless and the $MV^{\cdot +}$ form is purple. It became apparent that both the response rates of the color change and the apparent diffusion coefficients for the diffusionlike charge-transport process within the composite films increase significantly with increasing conductive powder content. An introduction of small particles (or powders) into "polymer film-coated electrodes" can be expected to improve (or generally change) their various functions and further to develop new applications for them [31].

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