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A New Preparation Method of Electrochromic Prussian Blue Films by Casting a Solution and Their Electrochemical Properties

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A novel method for preparing Prussian Blue (PB) films cast from a PB solution of organic solvent containing cationic surfactants is reported. The cyclic voltammogram for the oxidation of the film is much simpler than that of an electrochemically deposited PB film. The electrochromic behavior was investigated by in-situ UV-VIS spectroscopy.

The modification of electrode surfaces by electroactive Prussian Blue (PB) has been accomplished in a variety of ways.[1-3] As thin films, the area of current interests includes application of these modifications to catalysts,[2,4] electrochromic materials,[5] photovoltaic materials,[6] and secondary battery.[3,7] The techniques for the preparation of PB-modified electrodes have been limited to dip coating,[1,3] and electrochemical deposition[4,5] from an aqueous solution of $FeCl_3$ and $K_3Fe(CN)_6$, because of the insolubility of PB in most of organic solvents. It is not so easy to manufacture a uniform PB film of large area by the above methods. The casting of PB colloids from a non-aqueous solvent is considered to be an effective way to overcome this problem. However, such a film has not been developed yet. In this letter, we first report the results on a novel method for preparing a PB film cast from a solution of organic solvent containing surfactants, and its characteristic redox property.

In the present investigation, the surfactants were used to dissolve the PB colloids into an organic solvent resulting in a homogeneous solution. Among cationic, anionic, and nonionic surfactants examined in a chloroform solution, only cationic surfactants can extract the PB colloids from an aqueous solution prepared by dissolving equimolar amount of $FeCl_3$ (20 mmol dm^{-3}) and $K_4Fe(CN)_6$ (20 mmol dm^{-3}) in a 0.01 mol dm^{-3} HCl solution. The extracted PB solution, hereafter denoted as PB-surfactant, was cast onto an indium tin oxide electrode (ITO, 10 Ω/□) to prepare a cast PB-surfactant film. The cationic surfactants with a longer alkyl chain than C_{14} were effective to form in a stable PB-surfactant film.

Electrochemical measurements for the cast PB-surfactant film were carried out at 25 ℃ by using a 0.1 mol dm^{-3} $KClO_4$ (pH 4.0) aqueous solution. A platinum wire and Ag/AgCl saturated KCl electrode were used as a counter and a reference electrode, respectively. The electrochromic properties of the PB-surfactant-modified electrode was investigated by the in-situ UV-VIS spectroscopy as mentioned in the previous paper,[8] and the results were compared with those of an electrochemically deposited PB film.[9]

Figure 1a shows the absorption spectral changes of the PB-hexadecyltrimethylammonium chloride (HTAC)-modified electrode measured under repeated cyclic scanning between -0.3 V and +1.4 V vs. Ag/AgCl with the scan rate of 50 mV s^{-1}. The color changes of the PB-HTAC film at various potentials are not clear (Fig. 1a) in comparison with those of the electrochemically deposited PB film for which the so-called Berlin Brown (at +1.4 V vs. Ag/AgCl), and Prussian White (at -0.3 V vs. Ag/AgCl) are well-known.[10] This may be due to the low conductivity of the PB-HTAC film. To improve the conductivity of the PB-HTAC film, $LiClO_4$ in acetone was added to the extracted PB-HTAC solution of chloroform as a promoter for ionic conductivity.[11] In the PB-HTAC-$LiClO_4$ film, the UV-VIS

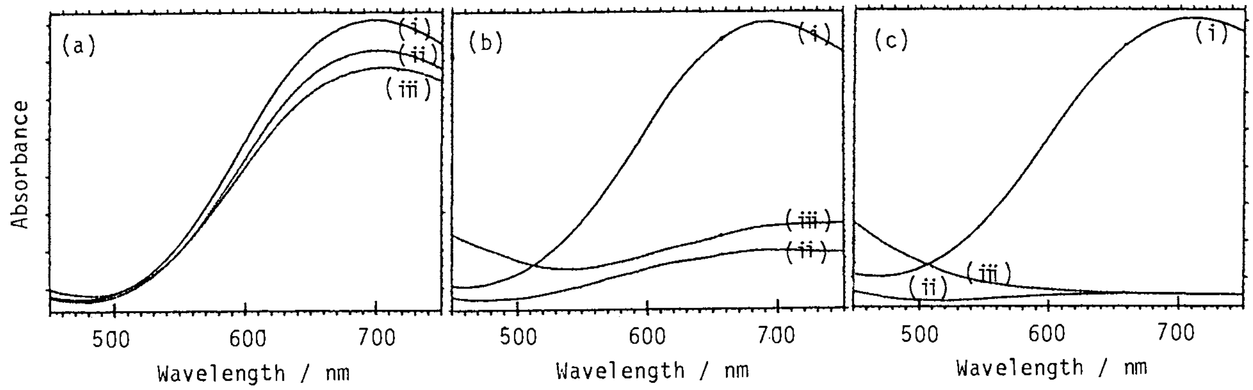

Fig. 1. Absorption spectral changes of the (a) PB-HTAC, (b) PB-HTAC-$LiClO_4$, and c) electrochemically deposited PB films measured under repeated cyclic scanning. The curves show spectra at (ⅰ) +0.5 V, (ⅱ) -0.3 V, and (ⅲ) +1.4 V vs. Ag/AgCl.

spectra of the oxidized and reduced states show a clear and rapid electrochromic behavior as shown in Fig. 1b. The oxidized and reduced films are yellow and colorless at +1.4 V and -0.3 V vs. Ag/AgCl, respectively. The transient spectral changes are similar to those of the electrochemically deposited PB film present in liquid electrolyte (Fig. 1c).

Figure 2 illustrates the change of the absorbance at 700 nm (λ_{max} of PB) in the PB-HTAC, PB-HTAC-$LiClO_4$, and the electrochemically deposited PB films, for which the applied potential is stepped between +0.5 V and +1.4 V vs. Ag/AgCl. It is observed that the electrochromic response of the PB-HTAC-$LiClO_4$ film (ii) is remarkably faster than that of the PB-HTAC film (iii), and close to that of the electrochemically deposited PB film (i). This would be due to the difference of conductivity between the PB-HTAC-$LiClO_4$ and PB-HTAC films.

The typical examples of the cyclic voltammograms (CV) of the electrochemically deposited PB and the PB-HTAC-$LiClO_4$ films in 0.1 mol dm^{-3} $KClO_4$ are shown in Fig.3. The electrochemical reduction and re-oxidation peaks of the PB-HTAC-$LiClO_4$ are sharp, simple, and entirely reversible as those of an

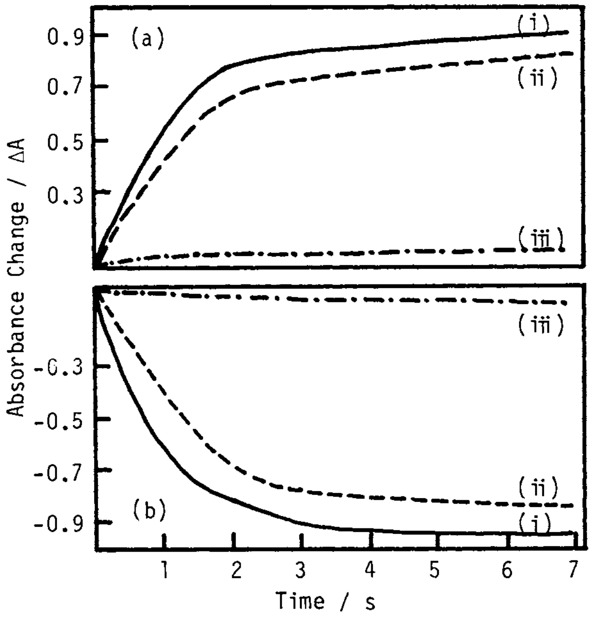

Fig. 2. Absorbance changes at 700 nm with time for (i) electrochemically deposited PB, (ii) PB-HTAC-$LiClO_4$, and (iii) PB-HTAC films when the potentials are stepped (a) from 1.4 V to 0.5 V and (b) from 0.5 V to 1.4 V in a 0.1 mol dm^{-3} $KClO_4$ aqueous solution.

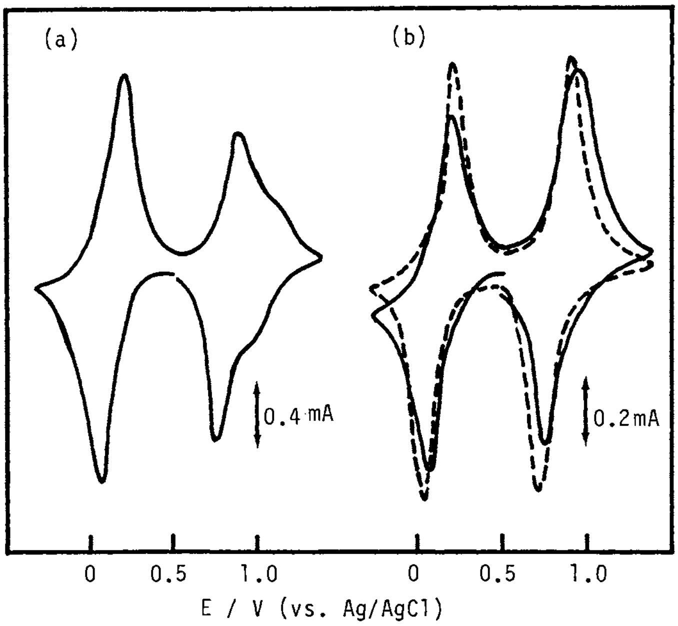

Fig. 3. Cyclic voltammograms of (a) the electrochemically deposited PB and (b) PB-HTAC-$LiClO_4$ films coated on ITO electrode, measured in a 0.1 mol dm^{-3} $KClO_4$ solution. The dashed line in (b) shows the cyclic voltammgram obtained as the tenth scanning.

electrochemically deposited PB. In the electrochemical oxidation and re-reduction, symmetrical main redox peaks were observed for the PB-HTAC-$LiClO_4$ film, while two separate shoulder waves were observed at the electrode potentials higher than 0.8 V for the electrochemically deposited PB film in addition to the main redox peaks. This indicates that the oxidation of the PB-HTAC-$LiClO_4$ is much more simple than that of the electrochemically deposited PB.

The PB-HTAC-$LiClO_4$ film is stable; no decomposition of the film was observed after the repeated cyclic scanning in CV. The stability of the PB-HTAC-$LiClO_4$ film is estimated by repeated CV scanning in 0.1 mol dm^{-3} $KClO_4$ (pH 4.0) between -0.3 V and +1.4 V vs. Ag/AgCl at a scan rate of 50 mV s^{-1}. After the initial scan, an increase in the peak current was observed at the second scan, resulting in stable, reproducible and more symmetrical CV peaks after the 10th cycle as shown with a dashed line in Fig. 3b. A more detailed investigation of these behaviors are currently under way.

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