

Electrochemical Formation of an Organic Thin Film Based on Dyeing with Vat Dye

Tetsuo SAJI,* Yukie YAMADA, and Hisanao TANI

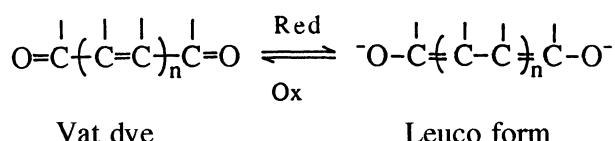
Department of Chemical Engineering, Tokyo Institute of Technology,
Ohokayama, Meguro-ku, Tokyo 152

A bluish green thin film of 16,17-dimethoxy-anthra[9,1,2-cde]-benzo-[rst]pentaphene-5,10-dione(1) was prepared on an indium tin oxide electrode by controlled potential electrolysis (oxidation) of an aqueous solution containing a leuco form of the vat dye (1^{2-}), $\text{Na}_2\text{S}_2\text{O}_4$, and 0.1 M NaOH. Higher concentration of 1^{2-} , less positive electrolysis potential, and shorter electrolysis time produced a more transparent film.

Recently, thin films of dyes and pigments are important subject due to their potential application to optics, electrochromism, solar energy conversion, etc. However, the technique for the preparation of these thin films is limited to a few methods,¹⁾ e.g., cast method vacuum sublimation,²⁾ and the micelle disruption method.³⁾

Vat dyes, such as indigo, are known to be one of the most important group of dyes at the present time.^{4a)} Vat dyes are usually water-insoluble, and must be chemically reduced to form a water-soluble leuco form of the dye. In the case of dyeing fabric with vat dye, after application of the leuco form of the vat dye, the dye is reoxidized on the fabric by oxygen in the air.

A characteristic of the chemical structure of these dyes is a chain of conjugated double bonds with two keto groups in the end positions. After reduction, the structure of these dyes changes to diol derivatives;^{4b)}



As diols, these leuco derivatives are very sparingly soluble in water. However, they are acidic and dissociate in alkaline media to form soluble enolates.

In this paper, we report a new method for the preparation of a thin film of vat dye by electrochemical oxidation of a leuco form of the vat dye, which is based on dyeing fabric with vat dyes.

Indanthren Brilliant green FFB was purchased from Tokyo Kasei Kogyo Co. Ltd. This sample was received as fine powders containing unspecified dispersing agents and

diluents. This sample contained 34% of **1** was checked by absorbance of the chlorobenzene solution at 648 nm ($\epsilon = 38600$).⁵⁾ This sample was purified by recrystallization with chlorobenzene.

Results of the voltammetric behavior and film formation were the same regardless of the purification of the sample.

The cyclic voltammogram of an aqueous solution containing 0.034 mM **1**²⁻, 1 mM Na₂S₂O₄, and 0.1 M NaOH at the ITO electrode shows an oxidation step with a peak potential at -0.69 V vs. SCE, which starts at -0.75 V and accompanies a re-reduction peak at -0.76 V (Fig. 1). The oxidation peak current was proportional to the square root of the scan rate.⁶⁾ These two peak potentials did not vary with scan rate. This step is reversible and may be assigned to the redox system, **1**²⁻/**1**. This redox potential is close to that previously reported.⁷⁾ The cyclic voltammogram of an aqueous solution containing 10 mM Na₂S₂O₄ and 0.1 M NaOH does not show any peak corresponding to the oxidation of Na₂S₂O₄ in the potential range of -1.0 to -0.4 V vs. SCE in spite of the fairly negative redox potential for oxidation of Na₂S₂O₄ (-1.21 V vs. SCE).⁸⁾ Large over potential of the ITO electrode for the oxidation of Na₂S₂O₄ may account for this result.

The cyclic voltammogram of an aqueous solution containing 3.4 mM **1**²⁻, 100 mM Na₂S₂O₄, and 0.1 M NaOH shows oxidation step which starts at -0.84 V. However, this step does not show a clear peak. The magnitude of this current increased as increasing the concentration of Na₂S₂O₄. The gradual increase in the current, and lack of a peak may be due to the deposition of **1** and following catalytic current for oxidation of Na₂S₂O₄ through **1**. At a higher

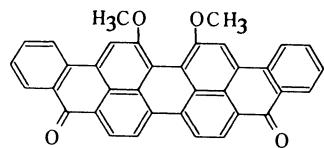
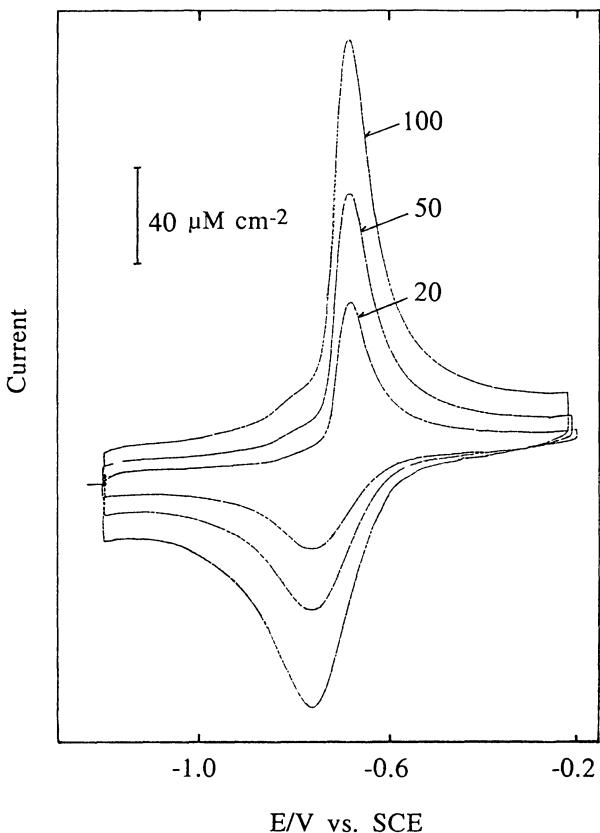
**1**

Fig. 1. Cyclic voltammogram of an aqueous solution containing 0.034 mM **1**²⁻, 1 mM Na₂S₂O₄, 0.1 M NaOH. Numbers in the figure show scan rate in mV. Working electrode: ITO.

concentration of $\text{Na}_2\text{S}_2\text{O}_4$, **1** on the surface of the electrode may be effectively reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in the solution and **1**²⁻ may be re-oxidized at the electrode.

Film formations of **1** were tried by controlled-potential electrolysis at the ITO electrode maintained at -0.70 V in an aqueous solutions of various **1**²⁻ concentrations in 0.1 M NaOH. Solutions of 0.034 (1.0), 0.14 (5.0), 0.27 (8.0), 0.34 (10), 1.7 (50), and 3.4 mM **1**²⁻ (20, 100 mM $\text{Na}_2\text{S}_2\text{O}_4$) concentrations were used for film forming. Bluish green films were obtained except for the 0.034 mM **1**²⁻ solution. These films were smooth and adhered well to the electrode. A low concentration and re-reduction of **1** may account for the failure of film formation in the 0.034 mM **1**²⁻ solution. More than 20 minutes was necessary for the cases of 0.14, 0.27, and 0.34 mM **1**²⁻. Higher concentration of **1**²⁻, less positive electrolysis potential, and shorter electrolysis time produced a more transparent film. The films from 1.7 and 3.4 mM **1**²⁻ solutions were transparent. A short electrolysis time was enough for the latter film formation (5 and 2 min for the 1.7 and 3.4 mM **1**²⁻ solutions, respectively). Using an aqueous solution of 3.4 mM **1**²⁻, films obtained at -0.55 and -0.40 V, and that for 8 min electrolysis at -0.70 V were less transparent. The SEM micrographs showed that a particle of the film grows as the electrolysis proceeds. These photographs also showed that the transparent films are uniform and are composed of 0.2-0.4 μm particles (Fig. 2), while the less transparent films are composed of larger particles and are not uniform. The SEM analysis of the cross section of these films show that the transparent films have a uniform thickness.

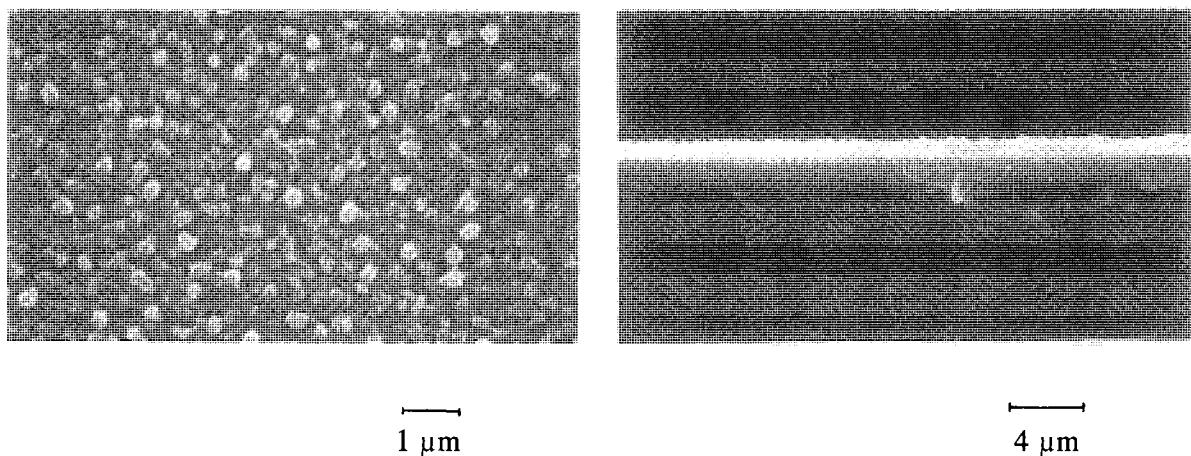


Fig. 2. Scanning electron micrographs of surface and cross sections of the film prepared by the electrolysis of an aqueous solution containing 3.4 mM **1**²⁻, 20 mM $\text{Na}_2\text{S}_2\text{O}_4$, and 0.1 M NaOH at ITO electrode maintained at -0.70 V vs. SCE for 3 min.

The absorption spectrum of the chlorobenzene solution obtained by dissolution of the film obtained above was the same as that of 1, which showed that these films are composed mainly of 1.

The deposition amount of 1 versus electrolysis time was independent of $\text{Na}_2\text{S}_2\text{O}_4$ concentration. Current efficiency of the deposition of 1 after a 2 min electrolysis was 19, 9, and 7% for 20, 30, and 50 mM $\text{Na}_2\text{S}_2\text{O}_4$ (1.7 mM I^{2-}) solutions, respectively. Such a low current efficiency may be due to the catakytic current of $\text{Na}_2\text{S}_2\text{O}_4$. A higher concentration of $\text{Na}_2\text{S}_2\text{O}_4$ effectively brings about this catalytic current, and leads to lower current efficiency. The amount of the film depended approximately on root of the electrolysis time. This behavior is the same as the diffusion controlled case in chronoamperometry where current is replaced by the deposition amount, which suggests that the rate of film growth is controlled by the diffusion of I^{2-} .⁶⁾

A new electrochemical procedure was used to prepare the thin films of a vat dye by the oxidation of the reduced form (leuco form) of a vat dye. These films were smooth and adhered well to the ITO electrode. We are currently extending this method to preparing thin films of other vat dyes, e.g., indigo. Present experiments show that such a electrochemical method serves as a technique for preparing thin films of a wide variety of vat dyes.

This was partially supported by a Grant-in-Aid for Scientific Research (C) and on Priority Areas from the Ministry of Education, Science and Culture (Nos. 02650578 and 03205046), and Shorai Science Foundation.

References

- 1) For a review, see: P.S. Vincett and G. G. Roberts, *Thin Solid Films*, **68**, 135(1980).
- 2) K. L. Chopra, "Thin Film Phenomena," McGraw-Hill, New York(1969), pp.10-76.
- 3) T. Saji, K. Hoshino, Y. Ishii, and M. Goto, *J. Am. Chem. Soc.*, **113**, 450(1991).
- 4) a) "Senryo Binran," ed by The Society of Organic Chemistry (Japan), Maruzen Ltd., Publishers, Tokyo (1970); b) H. Zollinger, "Color Chemistry," VCH Publishers, Weinheim (1987), Chap. 8.
- 5) R. A. Durie and J. S. Shannon, *Aust. J. Chem.*, **11**, 168(1958).
- 6) A. J. Bard and L. Faulkner, "Electrochemical Methods," Wiley, New York (1980).
- 7) U. Baumgart, *Colorage, Annual 1987-1988*, 67(1988).
- 8) V. Cermak, *Collect. Czech. Chem. Commun.*, **23**, 1471(1958).

(Received July 18, 1992)