

Proceedings of the IV International Seminar on Organic Materials for Molecular Electronics,
Zajęczkowo 1994

ELECTROCHEMICAL PROPERTIES AND ABSORPTION SPECTRA OF CONDUCTING FILMS OF TETRATHYOTETRACENE IODIDS

M.G. KAPLUNOV AND S.N. SHAMAEV

Institute of Chemical Physics, Chernogolovka, Moscow Distr., 142432 Russia

Films of tetrathyotetracene (TTT) iodides were obtained by doping of evaporated TTT films with iodine from I-containing solutions. TTT was evaporated onto a conducting substrate which then was used as an anode in KI solution. As a result of electrochemical reaction, iodine penetrated into the TTT film forming conducting TTT iodides. Cyclic voltamogrammes and absorption spectra show at least two stable forms of TTT-I_x, differing by iodine contents.

PACS numbers: 82.45.+z, 78.40.Kc

1. Introduction

Conducting organic films attract a considerable attention as promising materials for molecular electronics [1, 2]. In our previous works, we reported the investigation of spectral and electrical properties of tetrathyotetracene (TTT) iodides films prepared by vacuum deposition of TTT followed by doping with iodine from the gas phase [3, 4].

The present study is devoted to the investigation of TTT iodides films prepared by electrochemical doping of vacuum deposited TTT from the aqueous solutions.

2. Experimental

Original TTT films were deposited by thermal evaporation of TTT in vacuum onto glass supports covered with a transparent conducting layer of tin dioxide. The obtained samples with the thickness of about 0.03 μm were stable in air and in the potassium iodide solution. These films were electrochemically oxidized in 0.2 M aqueous solution of KI by multiple cycling of their potential in the interval +0.04 to +0.34 V relative to a Ag/AgCl reference electrode. Visible spectra were registered *in situ* during the electrochemical reaction.

3. Results and discussion

Cyclic voltamgrammes (CVA) of typical TTT films in 0.2 M aqueous solution are shown in Fig. 1. CVA of Pt electrode and of SnO_2 sublayer are given here for comparison. The current on SnO_2 electrode is purely due to capacitance phenomena and the electrode may be considered as entirely polarizable. The Pt electrode exhibits current corresponding to a reversible extracting of iodine. From the CVA of TTT film, one may suppose the existence of complex oxidation-reduction processes in this material.

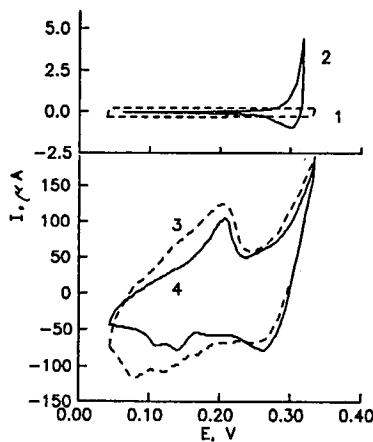


Fig. 1. Cyclic voltamgrammes (CVA) of a typical TTT film in 0.2 M aqueous KI solution. Sweep rate is 4 mV/s, potential vs. Ag/AgCl . (1) SnO_2 sublayer, (2) Pt electrode with a surface area of about 0.1 cm^2 , (3) new TTT film, (4) TTT film after 2 hours of continuous cycling.

The original TTT film was of light green color. After several tens of cycles, the CVA stopped to change from cycle to cycle and the film acquired a uniform color. An electrochromic effect was observed: the color of the film depended on its potential and changes reversibly from red to blue during the cycle. Visible spectra of such a film for different potentials are shown in Fig. 2. The time dependence of its transmittance at fixed wavelength caused by steplike changing of potential is given in Fig. 3. It must be noted that the original green color could not be recovered at any potential. This is an evidence of irreversible changes in the TTT film after an electrochemical treatment.

The films being formed reveal rather high conductivity and can exist in different stable forms (two forms as minimum) transferring from one to another by changing of electrode potential. One may suppose the formation of conducting salts of the composition $\text{TTT}-\text{I}_x$, similar to the previously observed in the films doped from the gas phase [3, 4]. The formation of $\text{TTT}-\text{I}_x$ salts is confirmed by the IR spectroscopy data. The appearance of wide bands in the region of $1000-1400 \text{ cm}^{-1}$ typical for conducting TTT salts [3-5] in the spectra of electrochemically treated films is an evidence of generation of such salts in the material of the film.

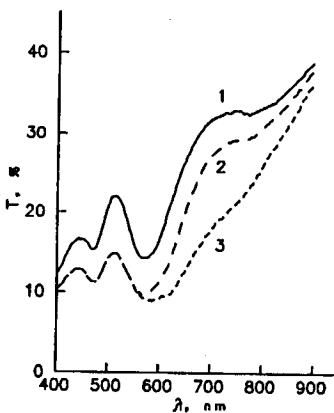


Fig. 2. Visible transmittance spectra of TTT-I_x film at potentials (vs. Ag/AgCl) in 0.5 M KI: (1) + 0.05 V, (2) + 0.15 V, (3) + 0.2 V.

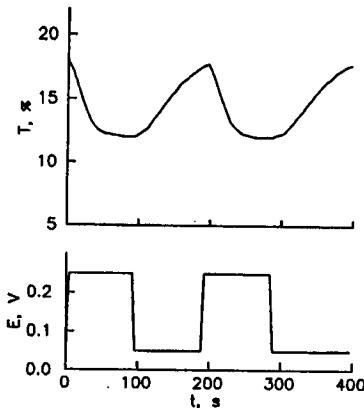


Fig. 3. The time dependence of TTT-I_x film transmittance at fixed wavelength 620 nm after steplike changing of potential in 0.5 M KI.

Different iodine contents in the films prepared at different potentials may be seen from different intensities of the two components of 1600 cm^{-1} band which is a characteristic of the composition of TTT-I_x salts [3, 5]. For a film taken from the solution at low potential (≈ 0.05 V), the low frequency component is less intense than for a high-potential (≈ 0.25 V) film which is an evidence of lower iodine contents.

A change of the oxidation degree in the process of reversible transition of the film material from the "red" to "blue" form was evaluated from the data of chronopotentiometry (Fig. 4). For a typical curve, parts I and III correspond to charging a double electric layer, part II — to reversible transition of one form to another and part IV — to oxidation of iodine ions on the electrode. In the assumption of an oxidation of the total width of the film, the number of electrons lost by one TTT molecule was evaluated to be about 0.5.

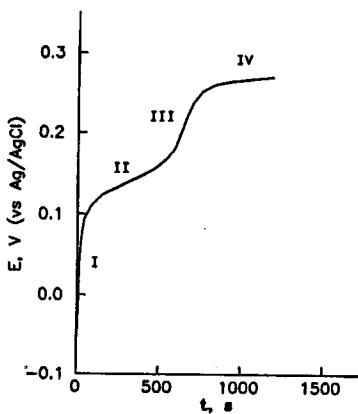


Fig. 4. Chronopotentiogram of TTT- I_x film in 0.5 M aqueous KI solution. Current density on the electrode is $5 \mu\text{A}/\text{cm}^2$.

Thus, the possibility of preparing conducting electrochromic films with a different composition by electrochemical doping of TTT films from aqueous iodides solutions is shown.

Acknowledgment

This work is supported by the Russian Foundation of Fundamental Investigations, project No. 93-03-4531.

References

- [1] V.F. Ivanov, O.L. Gribnova, A.V. Vannikov, *Elektrokhimiya* **30**, 378 (1994).
- [2] K. Kawabata, K. Tanaka, M. Mizutani, *Synth. Met.* **32**, 191 (1990).
- [3] M.G. Kaplunov, E.A. Buzyurkin, in: *Electronics of Organic Materials*, Ed. A.A. Ovchinnikov, Nauka, Moscow 1985, p. 17.
- [4] M.G. Kaplunov, E.A. Buzyurkin, Yu.G. Borodko, *Khim. Fiz.* **6**, 1398 (1987).
- [5] L.M. Kachapina, M.G. Kaplunov, A.I. Kotov, O.N. Eremenko, E.B. Yagubskii, Yu.G. Borodko, *Zh. Prikl. Spektrosk.* **30**, 84 (1979).