Spectroscopic and electrochemical study of conducting films of tetrathiotetracene iodides

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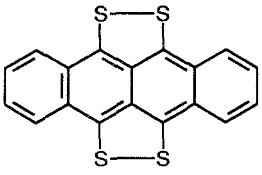
Films of tetrathiotetracene (TTT) iodides were prepared by electrochemical doping of deposited TTT films and were subjected to manyfold cycling in 0.2 mol L^{-1} aqueous KI solution in the range of potentials from +0.04 to +0.34 V relative to Ag/AgCl. The thus formed films were electrochromic: their color changed reversibly as the potential changed. The results of spectral and electrochemical studies show that radical-cation salts of $(TTT)I_x$ type are accounted for by the presence of several forms of such salts that differ in the content of iodine and reversibly transform into each other with potential changes. The formal compositions of the salts formed under high and low potentials can be approximately described as $(TTT)I_{0.9}$ and $(TTT)I_{0.5}$, correspondingly.

Key words: organic conductors, films, electrochemistry, absorption spectra.

Conducting organic films are promising materials for the production of highly conducting (and superconducting) coatings, various sensors, displays, and switchable light filters.[1,2] We have previously reported the preparation of conducting films of tetrathiotetracene (TTT) iodides by doping of vacuum-deposited TTT films with iodine from the gas phase.[3,4]



TTT

The present study is devoted to the preparation and investigation of films of the conducting salts $(TTT)I_x$ formed by electrochemical doping of vacuum-deposited TTT films from aqueous solutions containing I^- ions. It is established that no less than two forms of radical-cation TTT salts that differ in the content of iodine and in absorption spectra are sequentially formed in the electrochemical oxidation of these films. We discovered the possibility of manyfold reversible transformation of one form into another by changing the film potential; this opens a way for employing this material as an effective electrochromic coating.

Experimental

Original TTT films were deposited by thermal evaporation of TTT in vacuum ($7 \cdot 10^{-4}$ Pa) onto glass supports covered with a transparent layer of conducting tin oxide. The temperature of the evaporator was 300 °C, and that of the support was 20 °C. The thickness of the deposited films was about 0.03 μm. The samples obtained were stable in air and in a freshly prepared potassium iodide solution. The films were electrochemically oxidized in aqueous solution of KI (0.2 mol L^{-1}) by multiple cycling of their potential in the interval from +0.04 to +0.34 V relative to an Ag/AgCl reference electrode.

All the electrochemical studies were performed with the use of PI-50-1 potentiostat and PR-8 programmer. A three-electrode electrochemical cell could be installed in a correspondingly adapted cell compartment of SF-8 spectrophotometer so that visible transmission spectra of the films could be registered *in situ* during electrochemical measurements.

Infrared transmission spectra of the film material were obtained with Perkin-Elmer 325 spectrophotometer, X-ray photoelectron spectra were obtained with PHI-551 electron spectrometer.

TTT was purified by the method described elsewhere.[5] KI used was of "special purity" quality without additional purification. All the solutions were prepared with thrice-distilled water.

Results and Discussion

Cyclic voltammograms (CVA) of TTT film obtained in an aqueous solution of KI (0.2 mol L^{-1}) are shown in Fig. 1. CVA of a Pt electrode and of an SnO_2 sublayer (without TTT film) are given here for comparison. One may see that the current on the SnO_2 electrode is due purely to capacitance phenomena over the whole interval of working potentials, and the electrode may be considered as entirely polarizable. The Pt electrode exhibits current corresponding to the beginning of a reversible elimination of iodine at potentials higher than

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2400—2403, December, 1995.

1066-5285/95/4412-2295 $12.50

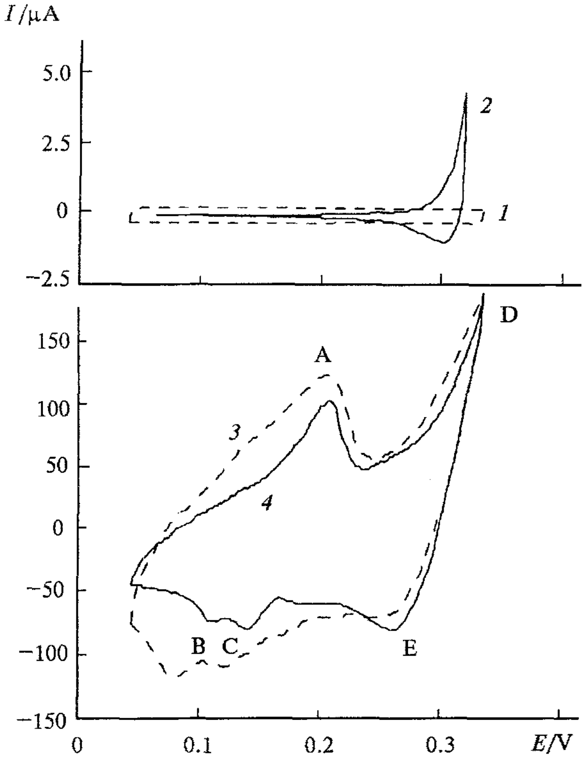


Fig. 1. Cyclic voltammograms (CVA) (aqueous solution of KI, 0.2 mol L^{-1}). Sweep rate is 4 mV s^{-1}, Ag/AgCl. *1*, SnO_2 sublayer; *2*, Pt electrode (surface area ~0.1 cm^2); *3*, fresh TTT film, *4*, TTT film after 2 h of continuous cycling.

0.25 V. On the CVA of TTT film, D and E peaks correspond, as for Pt, to a reversible liberation of iodine on the surface of the electrode. Currents at lower potentials point to the occurrence of oxidation-reduction processes in the material of the film. In this region of potentials, peaks of anodic (A) and cathodic (B and C) currents are observed. The shape and location of the current peaks are affected by many factors, such as the ohmic drop of voltage on the film material between the support and the reaction zone propagating through the film, different conductivity of the oxidized and reduced forms of the material, possible kinetic problems, finite film thickness, *etc.* However, from the location of peaks A, B, and C one can conclude that the oxidation potential of the film material falls in the interval 0.14—0.21 V.

Original TTT films were of light-green color in transmitted light. After several tens cycles, the CVA virtually did not change any more from cycle to cycle, and the films acquired a uniform saturated color. An electrochromic effect was observed: the color of the film depended on its potential and changed reversibly from purple-red to blue during the cycle. Blue color corresponded to higher and red color to lower potentials. Optical transmission spectra of such a film for different electrode potentials are shown in Fig. 2. The time required for optical density to reach its constant value after the stepwise change in the potential was somewhat different for different wavelengths, but did not exceed two minutes.

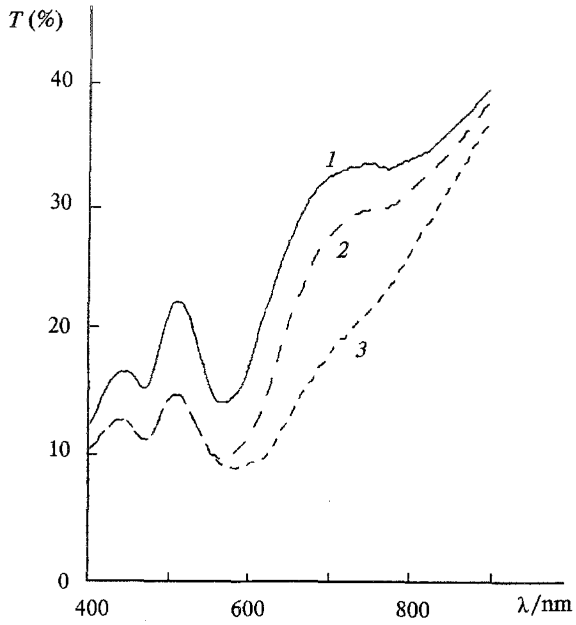


Fig. 2. Visible transmission spectra of $(TTT)I_x$ film at electrode potentials: +0.05 (*1*), +0.15 (*2*), +0.2 (*3*) V (*vs.* Ag/AgCl in 0.5 mol L^{-1} KI).

It must be noted that the original light-green color of the sample could not be restored at any potential accessible in the given electrolyte. This points to irreversible changes in TTT film in the electrochemical treatment of the electrode.

The presence of the oxidation and reduction peaks on CVA and of electrochromic effect give an evidence for the existence of at least two stable forms of film material which is converted into one another with the change of the electrode potential. One may suppose that the formation of conducting salts of the composition $(TTT)I_x$ occurs in the films in the course of their treament like in the films doped with iodine from the gas phase.[3,4]

TTT is known to form iodides of different compositions. Three iodides were obtained in crystalline form: $(TTT)_4I_4$, $(TTT)_2I_3$ and $(TTT)I_{2.8}$, the charge state for which can be expressed as $(TTT)_4^{2+}I_3^-I^-$, $(TTT)_2^+I_3^-$ and $(TTT)^{0.93+}(I_3^-)_{0.93}$ (Refs. 5 and 6). TTT cation radicals in the crystals of these salts are packed in linear stacks and anions of iodine (or of polyiodides) are placed in channels between the stacks. Similar stacks exist in the crystals of neutral TTT.[6] Here, channels between stacks are free and may be filled with iodine atoms from environment. In the case of formation of iodides by doping of TTT films with iodine from the gas phase,[3,4] I_2 molecules penetrate between TTT stacks, then electron transfer occurs between TTT and iodine

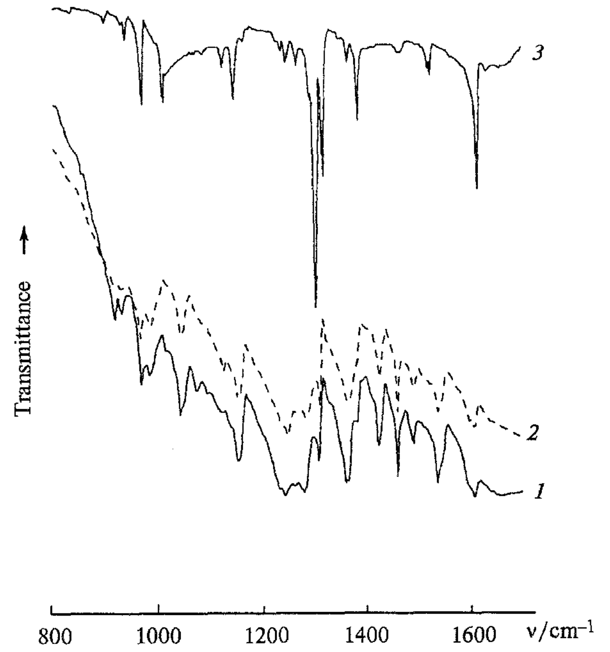


Fig. 3. IR spectra (in KBr pellets) of: the material of $(TTT)I_x$ film exposed to 0.2 mol L^{-1} KI solution at 0.25 V potential (*vs.* Ag/AgCl) (*1*), stoichiometric salt $(TTT)_4I_4$ (*2*), neutral TTT (*3*).

with the formation of TTT$^{+\cdot}$ radical cations and of anions such as I^-, I_3^-, *etc.* Coexistence of the phases with different composition is possible in the film.

In the case of TTT film doping from a solution, I^- anions penetrate into channels between TTT molecules. Then TTT molecules loose electrons which go to the external circuit. This process is possible only at sufficiently high positive electrode potential. As the result, iodides of variable composition $(TTT)I_x$ are also formed with possible coexistence of several such phases in the film.

The appearance of widened vibrational bands (typical for conducting TTT salts[3,4]) in the IR spectra (Fig. 3) points to the generation of $(TTT)I_x$ salts in the electrochemical treatment of TTT films.

Change in the TTT oxidation degree upon reversible transition of the film material from "red" to "blue" form was evaluated from the data of chronopotentiometry. In a typical curve (Fig. 4), regions I and III correspond to charging of double electric layer, region II, to reversible transition of one form to another, and region IV is associated with elimination of iodine on the electrode. In the assumption of the oxidation of the total width of the film[7] occurs on the region II of the curve, the number of electrons lost by one TTT molecule was estimated as about 0.5, on transition from one form to another.

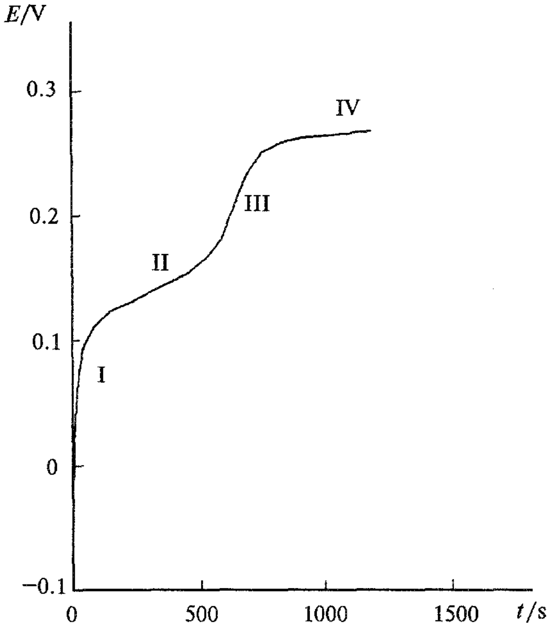


Fig. 4. Chronopotentiogram of $(TTT)I_x$ film in 0.5 mol L^{-1} aqueous KI solution. Current density on the electrode is 5 μA cm^{-2}, reference electrode Ag/AgCl.

The data of X-ray photoelectron spectroscopy of the film material are in good agreement with this estimation. The atomic relation of the concentrations of iodine and sulfur in the films of "red" and "blue" forms is about 1 : 8 and 1 : 4.5, respectively which corresponds to formal compositions $(TTT)I_{0.5}$ and $(TTT)I_{0.9}$.

The results given above are in qualitative agreement with those obtained by us for the electrochemical behavior of the films $(TTT)I_x$ prepared by doping of TTT films with molecular iodine from the gas phase.[3,4] Such films also exhibit electrochromic effect due to the reversible electrochemical oxidation and reduction of their material.

Thus, the possibility of preparing of conducting electrochromic films with different composition by electrochemical doping of TTT films from aqueous solutions of iodides is shown in the present work. The formation of ion radical salts of the form $(TTT)I_x$ in films is established, and their composition is determined. The explanation of the observed electrochromic effect in the obtained films is given.

The authors thank G. M. Mikhailov for measuring XPS and G. A. Krasochka for assistance in electrochemical experiments.

This work is supported by the Russian Foundation for Basic Research, Project No. 93-03-4531.

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Received January 10, 1995;
in revised form June 8, 1995