

Electrochemical Cation Doping of a Polythienylene Film

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Electrochemical doping and undoping by cations such as tetraethylammonium was first performed with a polythienylene thin film, which was synthesized by the electrochemical oxidative polymerization of thiophene in an acetonitrile solution in the potential range below -1.5 V vs. Ag/AgCl.

Electrochemically synthesized polythienylene is a conducting polymer of great interest for its properties, particularly its stability. It can be electrochemically doped by anions to give it an electrical conductivity of the order of 10^2 S cm^{-1} .

Electrochemical doping not only by anions but also by cations has been observed with π -electron conjugating polymers such as polyacetylene.¹ Neutral polyacetylene can be electrochemically oxidized to incorporate anions in an electrolyte solution and neutralized to release the doped anions, whereas cation doping can be performed by electrochemical reduction. Electrochemical anion doping has been observed with electrosynthesized polypyrrole² and polythienylene³ films. However, these polymers have not hitherto been electrochemically doped by cations. We report here the first example of the electrochemical reductive doping of an electrosynthesized polythienylene film with cations.

Polythienylene films were prepared on a working electrode by the electrochemical oxidative polymerization of thiophene at a controlled potential in acetonitrile solution containing Et_4NClO_4 . Either platinum wire or platinum deposited on glass was used as the working electrode. A Pt plate and an Ag/AgCl electrode were used as the counter and reference electrode, respectively. The electrosynthesized polythienylene film was thoroughly rinsed with acetonitrile and immersed in an acetonitrile solution containing an electrolyte such as Et_4NPF_6 for electrochemical measurements, which were carried out under nitrogen.

The current-potential curve is shown in Figure 1 for the electrochemical oxidation of thiophene on a Pt electrode. The onset potential of electrochemical polymerization was about 1.7 V vs. Ag/AgCl. A 0.2 μm black-green polythienylene film was prepared at a controlled potential of 1.8 V with a steady anodic current.

The polythienylene film, which had been doped by perchlorate anions during the electro-oxidative polymerization,

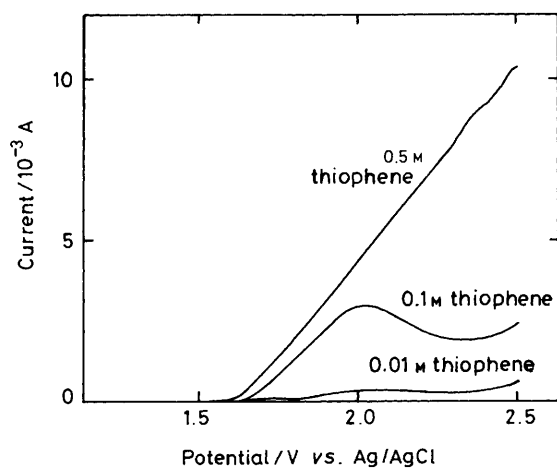


Figure 1. Electrochemical oxidation of thiophene in an acetonitrile solution containing 0.1 M Et_4NClO_4 on a Pt electrode. Scan rate 100 mV s^{-1} .

was fully undoped at 0 V in an acetonitrile solution containing 0.1 M Et_4NClO_4 . Cyclic voltammetry was carried out with the neutralized polythienylene film in the potential range 0 – 1.5 V. The polythienylene film was oxidized and doped by perchlorate anion above about 0.3 V, which resulted in an increase of the anodic current. The reverse potential scanning caused the film to be neutralized, which was accompanied by undoping of the film. The electrochemical doping and

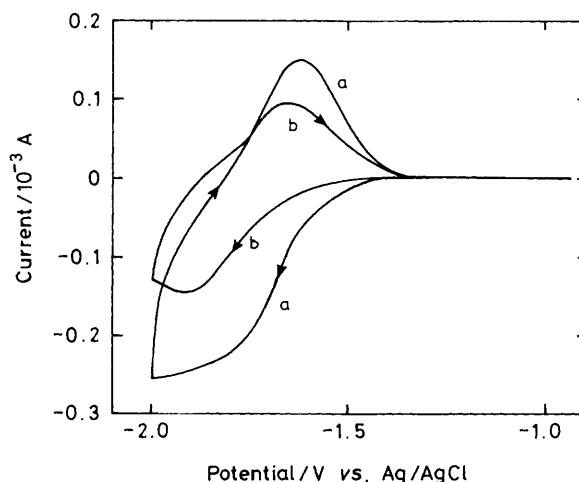


Figure 2. Electrochemical cation doping and undoping of a polythienylene film in acetonitrile solution. Electrolyte (a): 0.1 M Et_4NPF_6 , (b): 0.1 M Bu_4NPF_6 , scan rate 100 mV s^{-1} .

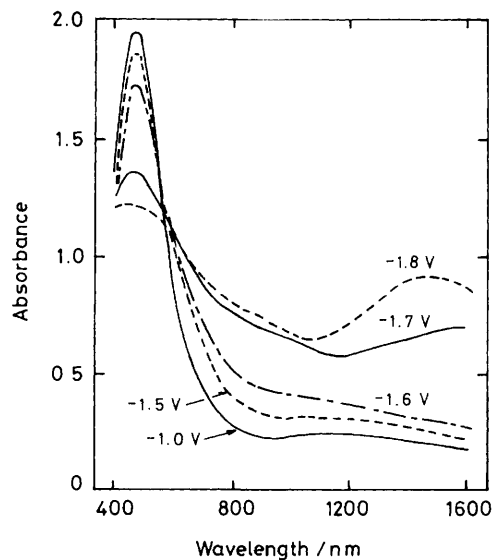


Figure 3. Absorption spectra of a polythienylene film at various cathodic potentials in an acetonitrile solution containing 0.1 M Et_4NClO_4 .

undoping showed excellent reversibility, consistent with the results of Tourillon *et al.*^{3,4}

Figure 2 shows the cyclic voltammograms of the electrosynthesized polythienylene film in the potential range -0.5 to -2.0 V in an acetonitrile solution containing 0.1 M Et_4NPF_6 and 0.1 M Bu_4NPF_6 . A cathodic current due to the reduction of polythienylene and the cation doping was observed below about -1.5 V on the cathodic scan. Reverse potential scanning resulted in the neutralization of the reduced polythienylene, which was accompanied by undoping of the film. The polythienylene film had been doped by Et_4N^+ and Bu_4N^+ cations during electrochemical reduction. However, the doping current depended on the cation species partly because of the difference in ionic radius.

It is noted that electrochromism from red to green occurs due to the electrochemical cation doping. Absorption spectra were measured for a polythienylene film deposited on an optically transparent Pt electrode at various controlled potentials, as shown in Figure 3. The absorption peak at about 480 nm, by which the neutral state of polythienylene is

characterized, may be attributed to the π - π^* transition. The potential step to below -1.5 V caused the absorption at 480 nm to decrease, and was followed by an increase of absorption in the near i.r. region. The absorption spectra start to vary at the onset potential of the cathodic current, indicating that the electrochemical cation doping is responsible for the chromism.

In conclusion, the cation doping of a polythienylene film by electrochemical reduction occurs in association with chromism.

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