

## Electrochemical Fabrication of a Polypyrrole–Polythiophene p–n Junction Diode

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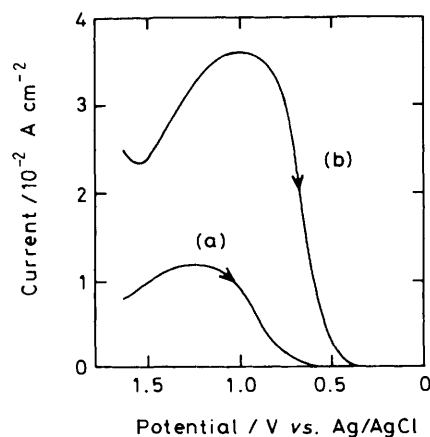
A p–n junction thin film was fabricated by sequential electrochemical polymerization of pyrrole and thiophene on a Pt substrate, followed by controlled-potential electrochemical doping to make the polypyrrole layer anion-doped and the polythiophene layer cation-doped.

Conjugated polymers such as polyacetylene have found promising application in electronic devices. Their conductivity can be controlled by either chemical or electrochemical doping from the insulating to the metallic region.<sup>1</sup> Furthermore, polypyrrole and polythiophene are easily synthesized in the form of thin films by electro-oxidative polymerization of pyrrole<sup>2</sup> and thiophene,<sup>3</sup> respectively. Electrosynthesis of these  $\pi$ -electron conjugated polymers may provide a route for the fabrication of organic thin film devices.

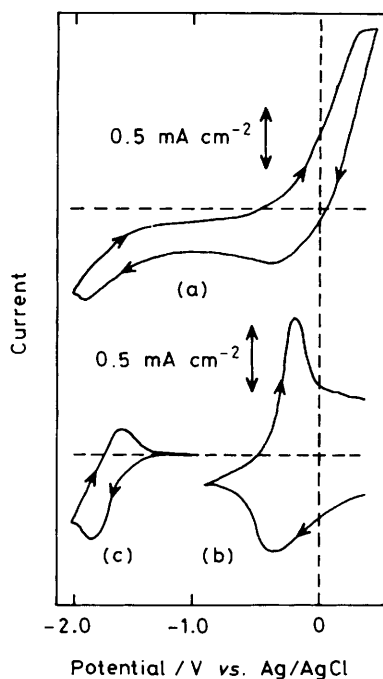
We first demonstrated that polythiophene can be electrochemically doped not only by electrolyte anions but also by cations.<sup>4</sup> However, the electrochemical cation doping of polypyrrole has not yet been observed. Anion-doped polypyrrole and polythiophene behave as p-type semiconductors and cation-doped polythiophene behaves as an n-type semiconductor. These results suggest the possibility of forming a p–n junction by heterocontact of p-type polypyrrole and n-type polythiophene. Chiang and his co-workers made a p–n junction device by pressure contact of a p-type polyacetylene film doped with Na with an n-type polyacetylene film doped with AsF<sub>5</sub>.<sup>5</sup>

We now propose a novel electrochemical method for making an organic heterojunction device. Polypyrrole and polythiophene films were sequentially fabricated on a Pt electrode by electropolymerization. The polypyrrole and polythiophene films are initially in the anion-doped state. A p–n junction interface may be formed by electrochemical cation doping of the polythiophene layer, if the polypyrrole remains anion-doped. However, the electrochemical cation doping of polythiophene is accomplished at a potential which would cause the polypyrrole layer to become undoped. We

expected that the dense microstructure of a polythiophene film on a polypyrrole film should suppress the undoping of anions from the polypyrrole film. Polythiophene films with various microstructures were synthesized by controlled electropolymerization conditions, and a polythiophene film with a dense microstructure was synthesized on a polypyrrole film in the presence of small anions. The two-layer films were electrochemically reduced resulting in an anion-doped p-type



**Figure 1.** Differential pulse voltammograms of polythiophene films, prepared in the presence of (a) BF<sub>4</sub><sup>-</sup> and (b) PF<sub>6</sub><sup>-</sup>; electrolyte: 0.1 M Me<sub>4</sub>NPF<sub>6</sub>–MeCN, scan rate: 5 mV s<sup>-1</sup>, pulse interval: 0.5 s, pulse amplitude: 50 mV.



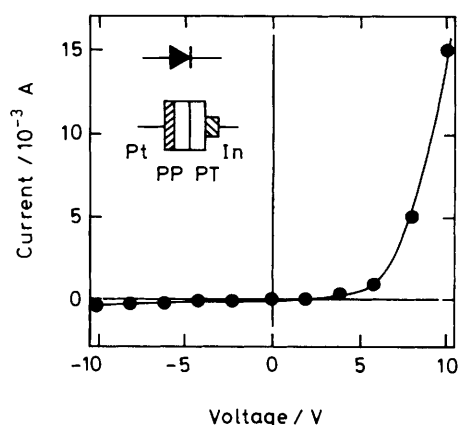
**Figure 2.** Cyclic voltammograms of (a) two-layer films of polypyrrole/polythiophene, (b) polypyrrole film, and (c) polythiophene film; electrolyte: 0.1 M  $\text{Me}_4\text{NPF}_6$ -MeCN, scan rate: 100  $\text{mV s}^{-1}$ .

polypyrrole layer and a cation-doped n-type polythiophene layer. The two-layer films of p-type polypyrrole and n-type polythiophene showed rectifying properties in a similar manner to a p-n junction diode.

A polypyrrole film was synthesized on a Pt electrode ( $2 \times 1 \text{ cm}$ ) by electro-oxidative polymerization of pyrrole at a controlled potential of 1.0 V vs. Ag/AgCl in an acetonitrile solution containing 0.1 M pyrrole and 0.1 M  $\text{Et}_4\text{NPF}_6$ . The electro-oxidation charge was controlled at  $0.5 \text{ C cm}^{-2}$ . The polypyrrole/Pt produced was thoroughly washed with acetonitrile and immersed in 0.1 M  $\text{Me}_4\text{NPF}_6$  in MeCN. The potential of the polypyrrole film was then increased from the rest potential to 1.4 V for 1 min for doping with  $\text{PF}_6^-$ . The polypyrrole/Pt was thoroughly washed with acetonitrile and nitromethane and immersed in nitromethane containing 0.1 M thiophene and 0.1 M  $\text{Et}_4\text{NBF}_4$ . Electro-oxidative polymerization of thiophene on the polypyrrole/Pt was carried out at a potential of 1.8 V, the polymerization charge being controlled at  $0.5 \text{ C cm}^{-2}$ . After washing, the two-layer films of polypyrrole and polythiophene were placed in 0.1 M  $\text{Me}_4\text{NPF}_6$  in MeCN and electrochemically doped at a controlled potential. A p-n junction was formed by a potential step from 0 to -2.0 V to dope the polythiophene layer with cations, while preventing the polypyrrole layer from anion-undoping. In all electrochemical measurements, a Pt plate and an Ag/AgCl electrode were used as counter and reference electrodes, respectively.

After drying *in vacuo*, an indium wire was simply pressed onto the polythiophene surface of the two-layer film to form an ohmic contact. Current-voltage curves of the In/polythiophene/polypyrrole/Pt junction were measured.

Ion mobility was first measured for polythiophene films with different microstructures. Polythiophene films were prepared on a Pt electrode in the presence of  $\text{Et}_4\text{NPF}_6$  and  $\text{Et}_4\text{NBF}_4$  at the same charge. Figure 1 shows the differential



**Figure 3.** I-V curve for the In/polythiophene (PT)/polypyrrole (PP)/Pt junction.

pulse voltammograms of these polythiophene films in an acetonitrile solution containing 0.1 M  $\text{Me}_4\text{NPF}_6$ . The cathodic current is attributed to the reduction of the polythiophene, which is accompanied by  $\text{PF}_6^-$  undoping from the film. It is notable that the cathodic current depended significantly on the electrolyte anion species for electropolymerization. The anion-undoping rate for the polythiophene film prepared in the presence of  $\text{BF}_4^-$  was lower than that prepared in the presence of  $\text{PF}_6^-$ . These results indicated that the ion mobility in the film could be controlled by the electropolymerization conditions.

Two-layer films of polypyrrole and polythiophene were electrochemically synthesized. A polythiophene film was synthesized on polypyrrole/Pt in the presence of  $\text{Et}_4\text{NBF}_4$  under conditions to make its microstructure dense. Figure 2(a) shows the cyclic voltammogram of the polythiophene/polypyrrole two-layer films on a Pt electrode in acetonitrile containing 0.1 M  $\text{Me}_4\text{NPF}_6$ . Two cathodic current peaks were observed at potentials of -0.3 and -1.9 V. Cyclic voltammograms of polypyrrole/Pt and polythiophene/Pt films are shown in Figures 2(b) and 2(c) respectively. Figure 2(b) shows the electrochemical anion doping-undoping of the polypyrrole film. The polythiophene film was oxidized at potentials  $>0.4 \text{ V}$  and reduced at potentials  $<-1.5 \text{ V}$ . Figure 2(c) shows the electrochemical cation doping and undoping of the polythiophene film. Figures 2(a) and 2(b) indicate that the cathodic peak at -0.3 V may be attributed to neutralization and partial anion-undoping of the polypyrrole layer. Figures 2(a) and 2(c) indicate that the cathodic peak at -1.9 V may be attributed to reduction and cation-doping of the polythiophene layer. We consider that electroreductive cation-doping of the polythiophene layer was performed because of the electroconduction of the partially anion-maintained polypyrrole layer on the Pt substrate. These results suggest that the polypyrrole film remained slightly anion-doped and the polythiophene film remained cation-doped under the conditions. Anion undoping from the polypyrrole layer was effectively prevented by the dense microstructure of the outer polythiophene layer.

The p-n junction interface in the two-layer films was formed by a potential step from 0 to -2.0 V for about 5 min. The charge passed was controlled at  $25 \text{ mC cm}^{-2}$ , attributed to the partial anion-undoping of the polypyrrole layer and the cation-doping of the polythiophene layer. The thermoelectric motive force of the dried two-layer films was measured.

Measurements indicated that the polypyrrole film was a p-type semiconductor and the polythiophene film an n-type semiconductor. Figure 3 shows the current-voltage characteristics of the In/polythiophene/polypyrrole/Pt junction. A positive current started to flow at about +0.2 V, and a small ohmic current was observed in the negative voltage region. These results indicate that the electrochemically synthesized two-layer films of polypyrrole and polythiophene should work as a p-n junction diode.

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