

A Polymer Electrode with Variable Conductivity: Polypyrrole

By ART F. DIAZ* and JUAN I. CASTILLO

(IBM Research Laboratory, San Jose, California 95193)

Summary Thin films of the 'metallic' polymer, polypyrrole, when adhered to a platinum electrode surface, can be repeatedly driven between the conducting and insulating state with E° near -220 mV vs. the sodium chloride calomel electrode.

PREVIOUS reports concerning polypyrrole have pointed to the importance of an electrochemical approach for the preparation of stable organic polymers with metallic properties.^{1,2} We can now demonstrate that thin films of polypyrrole, when attached to an electrode surface, can be repeatedly driven between the conducting and insulating state. With these results, we report for the first time the electroactive properties of an organic polymer which can have metallic properties.

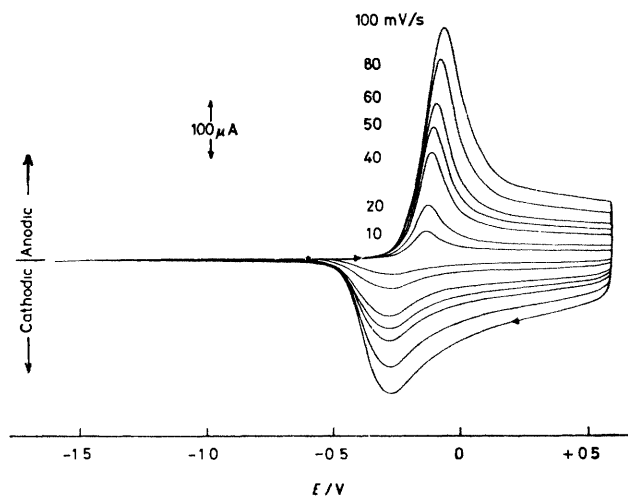


FIGURE 1. Cyclic voltammogram of a $0.1 \mu\text{m}$ polypyrrole film on Pt (0.5 cm^2) in MeCN.

The black films of polypyrrole (*ca.* $0.1 \mu\text{m}$ thick) were grown on a platinum surface by passing 24 mC/cm^2 of charge. As seen in Figure 1, the cyclic voltammogram of this film in MeCN containing only $0.1 \text{ M Et}_4\text{NBF}_4$ shows broad current peaks for the redox reaction of the film centred at -0.22 V vs. NaCE (sodium chloride calomel electrode). All measurements were made in the absence of oxygen and with iR compensation. The i_{pa} values vary linearly with sweep rate (within 10%) between 10 and 100 mV/s as expected for the reaction of surface localized material. The broad reduction peak is more difficult to analyse. Although the redox reaction must involve the electrons in the extended π -system of the polymer, the broadness of the peaks together with the fact that E_{pa} does not equal E_{pc} suggest that the reaction has some kinetic limitations.³ The limitations must arise in part from the motion of solvent

and ions in the film since the E_{pa} values shift when the electrolyte is changed to Bu_4NBF_4 , Me_4NPF_6 , or Et_4NCIO_4 . The film is quite stable and can be cycled repeatedly without evidence of decomposition. As expected, the reaction is slow with thicker films and the peaks broaden considerably.

The integrated current for the oxidation peak (1.5 mC/cm^2) appears equal to that for the reduction peak, and is 6% of the total charge involved in the preparation of the film (24 mC/cm^2). Thus the number of cation centres affected by this reaction is less than expected considering that the polymerization reaction required 2.25 F/mol where the charge in excess of 2.0 F/mol (11%) is associated with the oxidation of the film.²

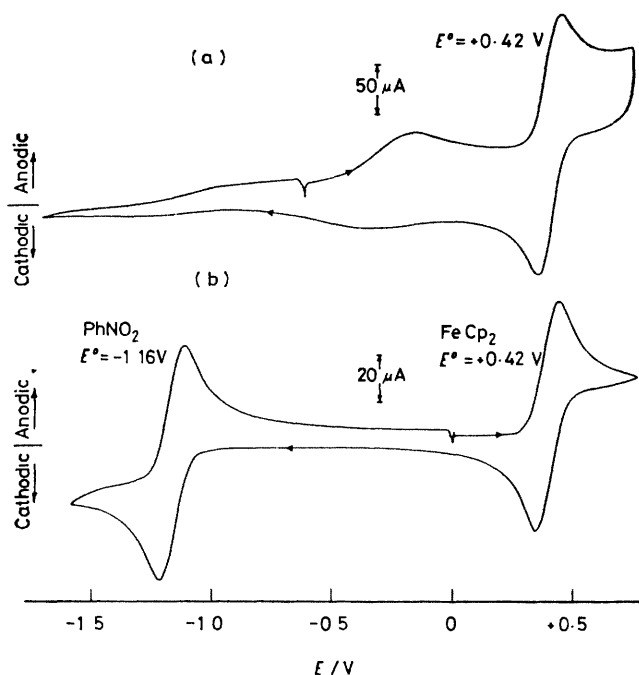


FIGURE 2. Cyclic voltammograms measured in MeCN containing $0.1 \text{ M Et}_4\text{NBF}_4$, 10^{-3} M FeCp_2 , and 10^{-3} M nitrobenzene at 50 mV/s using a sodium chloride calomel reference electrode: (a) Pt (0.2 cm^2); (b) $0.1 \mu\text{m}$ polypyrrole film on Pt (0.6 cm^2).

Evidence that the film is insulating when in the neutral form is provided in Figure 2. The electrochemistry of ferrocene (FeCp_2) is readily accomplished on the oxidized film with no change in E° and with nearly equal i_{pa} and i_{pc} values. The i_p values vary linearly with $\nu^{1/2}$, the ΔE_p value equals 70 mV , and the area under the curve is consistent with the geometric surface area of the film. Thus the oxidized film acts like a metal showing rapid electron transfer to the solution species which must occur at the film surface-solution interface. In contrast with the reaction of the film itself, the ferrocene reaction is not influenced by

varying the electrolyte. On the other hand, the film is an insulator when reduced to the neutral form and it inhibits the reduction of nitrobenzene which must now occur on the platinum surface. The peak is reduced 100-fold, reflecting the slow diffusion process across the film.

We believe that the electrochemical approach will prove

important for the development of new materials with voltage-dependent conductivities.

We thank K. Kanazawa, J. Bargon, and J. Torrance for many interesting discussions.

(Received, 18th January 1980; Com. 094.)

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² A. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 635; K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *ibid.*, p 854; K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, *Synthetic Metals*, 1980, **3**, in the press; A. Diaz, W. Lee, A. Logan, and D. C. Green, *J. Electroanal. Chem. Interfacial Electrochem.*, 1980, in the press.

³ For reports on this effect see F. B. Kaufman, A. H. Schroeder, E. M. Engler, and J. Q. Chambers (abstract 301), and L. L. Miller, M. R. Van de Mark, G. Hostetter, and J. Kerr (abstract 299) in Chemically Modified Electrodes Symposium, 155th Electrochemical Society Meeting, May, 1979.