

## Electrochemical Polymerization of Pyrrole

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**Summary** The electrochemical polymerization of pyrrole on platinum produces a strongly adhered, durable film with enhanced conductivity and good electrode properties.

MANY workers have been interested in the modification of electrode surfaces by covalently attaching organic monolayers or depositing polymer films.<sup>1</sup> While the electrochemical preparation of films on a surface could conceivably produce superior material, this approach has not been pursued rigorously. Our interest in the preparation of durable, conducting organic electrode surfaces led us to this approach. We now present the preliminary results on the electrochemical polymerization of pyrrole<sup>2</sup> under controlled conditions.

The polypyrrole films were synthesized galvanostatically on a platinum surface in a two-electrode cell containing 0.1 M  $\text{Et}_4\text{NBF}_4$  and 0.06 M pyrrole in 99% aqueous MeCN. The films strongly adhere to the surface. These films can

be prepared in a variety of aprotic solvents. The yield of deposited film is 0.5 mol  $\text{F}^{-1}$  but can be less if the nucleophilic character of the solvent or electrolyte is enhanced. For example, no film is produced in the presence of 0.1 M  $\text{Et}_4\text{NBr}$  in MeCN.

A polypyrrole film (0.8  $\mu\text{m}$  thick) on platinum was used as an electrode in cyclic voltammetry measurements. In MeCN and  $\text{Me}_2\text{SO}$  containing  $\text{Et}_4\text{NBF}_4$ , only a broad background current is observed in the range +1.0 to -2.0 V. The voltammogram of  $10^{-3}$  M ferrocene in MeCN resembles that obtained on platinum. The  $E^\circ$  value equals +0.450 V vs. NaCE (sodium chloride calomel electrode) (0.450 V on Pt<sup>3</sup>),  $i_{\text{pc}}/i_{\text{pa}}$  equals unity, and  $|E_{\text{pa}} - E_{\text{pc}}|$  equals 90 mV at 20  $\text{mV s}^{-1}$  scan rate, with ca. 70%  $iR$  compensation. For the reduction of tetracyanoquinodimethane (TCNQ) the signals appear at +0.260 and -0.290 V vs. NaCE (+0.265 and -0.300 V on Pt). The  $|E_{\text{pa}} - E_{\text{pc}}|$  values equal 70 mV at 20  $\text{mV s}^{-1}$  scan rate and  $i_{\text{pa}}/i_{\text{pc}}$  values equal unity for both reaction steps.

Alternating current techniques were used to discriminate against the broad background signal. Using  $0.5 \mu\text{m}$  polypyrrole film on platinum,  $5 \times 10^{-4} \text{ M}$  TCNQ in MeCN was examined at a frequency of  $12.5 \text{ Hz}$ . The amplitude, phase, and widths of the fundamental and second harmonic currents were consistent with those of the completely reversible one-electron reduction of TCNQ. These results are qualitatively consistent with the cyclic voltammograms. Except for the broad background signals, the responses on the pyrrole electrode were indistinguishable from those on a clean platinum electrode of equal area.

Elemental analysis of this material indicates that it is primarily polymerized pyrrole units plus  $\text{BF}_4$  anions in the ratio of *ca.* 4:1 with the formula  $\text{C}_{4.00} \text{H}_{3.44} \text{N}_{0.87} (\text{BF}_4)_{0.26-0.30}$ .<sup>2,4†</sup>

The electrical conductivity of thicker films ( $5\text{--}50 \mu\text{m}$ ) stripped from the electrode was examined using four-probe techniques. The lateral conductivity was measured using current densities  $<5 \text{ A cm}^{-2}$ . The room tempera-

ture conductivities ranged from  $10\text{--}100 \Omega^{-1} \text{ cm}^{-1}$ , where the higher values can be consistently obtained. This compares to the value  $8 \Omega^{-1} \text{ cm}^{-1}$  previously reported.<sup>2</sup> Assuming similar conductivities in the transverse direction, the film resistance of a micron film is negligible, being  $<10 \mu\Omega \text{ cm}^{-2}$ .

The exposed surface of the film on platinum can be further modified. For example, it is nitrated with  $\text{HNO}_3$  and the nitro groups can be subsequently reduced electrochemically. The broad irreversible signal in the  $i\text{-}V$  plot has  $E_{\text{pc}}$  at  $-0.35 \text{ V}^5$  and corresponds to  $1 \times 10^{-9} \text{ F cm}^{-2}$ .

In conclusion, polypyrrole films prepared under controlled electrochemical conditions produce material with improved conductivity, strong adhesion to the metal surface, and good stability under electrochemical conditions making it attractive as an organic electrode material.

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† Found: C, 55.4; H, 4.0; N, 14.0; B, 3.2—3.6; F, 16.9. The fluorine analyses were consistently low even for compounds of known composition.

<sup>1</sup> See papers by A. F. Diaz and R. W. Murray in Proceedings from 'Symposium on Silylated Surfaces,' Midland, Michigan, May 1978.

<sup>2</sup> A. Dall'Olio, Y. Dascola, V. Varacca, and V. Bocchi, *Compt. rend.*, 1968, C 267, 433.

<sup>3</sup> C. K. Mann and K. K. Barnes, 'Electrochemical Reactions in Nonaqueous Systems,' Marcel Dekker, New York, 1970.

<sup>4</sup> G. P. Gardini, *Adv. Heterocyclic Chem.*, 1973, 15, 67.

<sup>5</sup> J. Tirouflet and P. Fournari, *Bull. Soc. chim. France*, 1963, 1651.