

## Electrosynthesis of Polythiophene and Poly(3-methylthiophene) Films by Oxidation of Thiophene and 3-Methylthiophene on an Iron Surface

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Electropolymerisation of thiophene and 3-methylthiophene was performed on iron, using a galvanostatic method; the structure of the films, analysed by IR and XPS spectroscopy, appeared to be similar to that of polythiophene and poly(3-methylthiophene) films obtained on a Pt electrode.

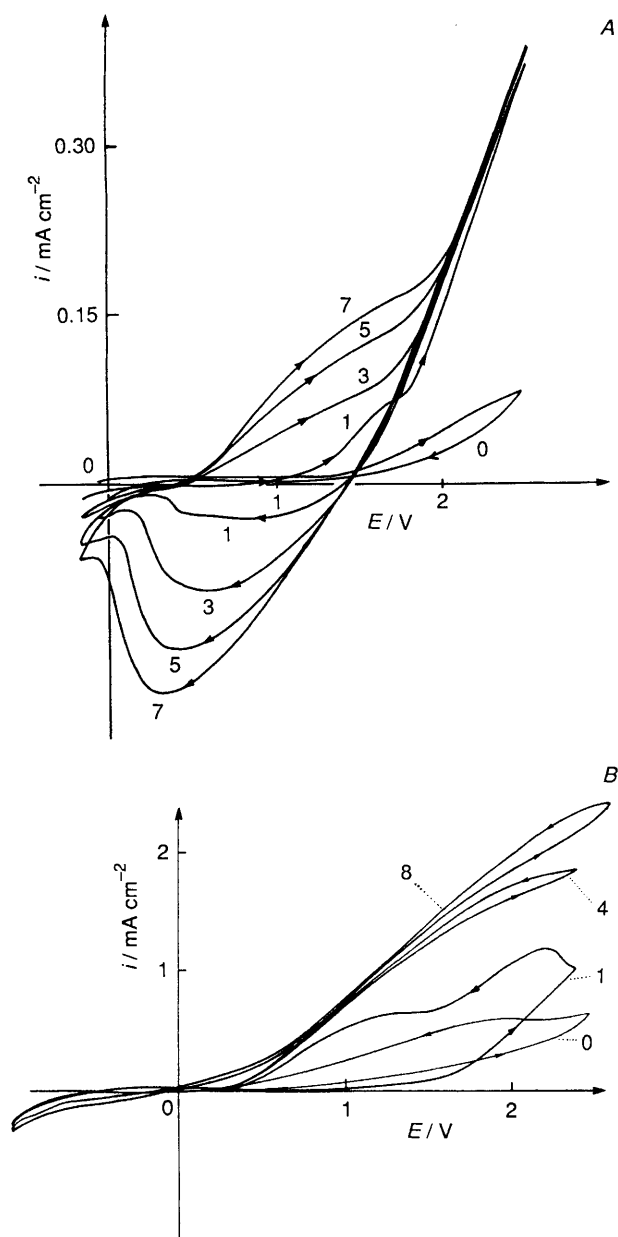
Over the past decade, the electrochemical preparation and structure characterisation of conducting polymer films deposited on noble metals (Pt, Au) have been extensively investigated.<sup>1-4</sup> In particular, polypyrrole<sup>1,5</sup> and polythiophene<sup>6-9</sup> have attracted considerable interest. However,

few studies have concerned the electropolymerisation of polypyrrole on oxidizable metals such as Fe, Ti, Cu and Al.<sup>10-14</sup> Cheng *et al.*<sup>10</sup> have shown that polypyrrole films could be obtained on sheets of Ti, Al and Fe, using propylene carbonate solutions. Beck *et al.*<sup>11,12</sup> found that well-adhering polypyrrole layers could be grown on iron electrodes in an aqueous medium containing partially-neutralized polyacrylates or NO<sub>3</sub><sup>-</sup> ions. The same behaviour was observed by Hülser and Beck<sup>14</sup> on aluminium, using HNO<sub>3</sub>, oxalic acid, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> as aqueous electrolytes. In our laboratory, we studied the effect of organic solvents and electrolytes on the structure of polypyrrole films deposited on iron electrodes, and found that electroactive films were obtained in tetrahydrofuran (THF) with N(Bu)<sub>4</sub>PF<sub>6</sub> as electrolyte.<sup>13</sup>

Until now, however, no study has concerned the electropolymerisation of thiophene on oxidizable metals. In this communication, we report, for the first time, on the growth of polythiophene (PT) and poly(3-methylthiophene) (PMT) films on an iron electrode, and we investigate the structure of these films by IR and XPS spectroscopy.

PT and PMT films were electrochemically grown on Pt and on Fe electrodes from 0.3 mol dm<sup>-3</sup> thiophene and 3-methylthiophene propylene carbonate (PC) solutions, in the presence of 0.1 mol dm<sup>-3</sup> tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), using cyclic voltammetric or galvanostatic methods. The iron electrodes were prepared using 15 × 30 mm commercially-available iron sheets, which were polished with diamond paste by a polishing wheel (Struers model DP10), then cleaned in an ultrasonic acetone bath.

Fig. 1 shows typical cyclic voltammetric curves obtained for thiophene between -1.0 V and 2.5 V on Pt (A) and Fe (B) electrodes. There is a striking difference in shape between the voltammetric curves from the two metals, which may be attributed to the fact that a well adhering, conductive PT film was formed on Pt, whereas no film growth occurred on the iron surface. The study of the voltammetric curves recorded on iron indicates a complex electrochemical behaviour on this metal surface. The curves 0 and 1 [Fig. 1(B)], obtained respectively in the absence and in the presence of thiophene, are characterised by very weak oxidation current densities between 0 and about 1.8 V vs. Ag/AgCl, which demonstrates the inhibitive effect of the PC-TBAPF<sub>6</sub> medium as well as of thiophene itself on the oxidation process of iron. When performing more scans [curves 4 and 8, Fig. 1(B)], an



**Fig. 1** Cyclic voltammograms for thiophene (0.3 mol dm<sup>-3</sup>) recorded with a Pt electrode (A) and on Fe electrode (B) in propylene carbonate + TBAPF<sub>6</sub> (0.1 mol dm<sup>-3</sup>) solution. The numbers labelling the curves indicate successive potential cycles. Curves 0 are performed without thiophene. Scan rate 50 mV s<sup>-1</sup>.

**Table 1** Electropolymerisation of thiophene on an iron electrode at constant current densities in propylene carbonate<sup>a</sup>

<i>I</i> <sup>b</sup> /mA cm <sup>-2</sup>	<i>t</i> <sup>c</sup> /s	<i>Q</i> <sup>d</sup> /C cm <sup>-2</sup>	<i>E</i> <sup>e</sup> /V
4.2	600	2.5	3.7
4.8	600	2.9	4.1
6.9	500	3.45	4.8

<sup>a</sup> Monomer concentration = 0.3 mol dm<sup>-3</sup>. TBAPF<sub>6</sub> concentration = 0.1 mol dm<sup>-3</sup>. <sup>b</sup> Current density. <sup>c</sup> Time of electropolymerisation of PT. <sup>d</sup> Coulombic charge. <sup>e</sup> Potential corresponding to the applied *I* value, in V vs. Ag/AgCl.

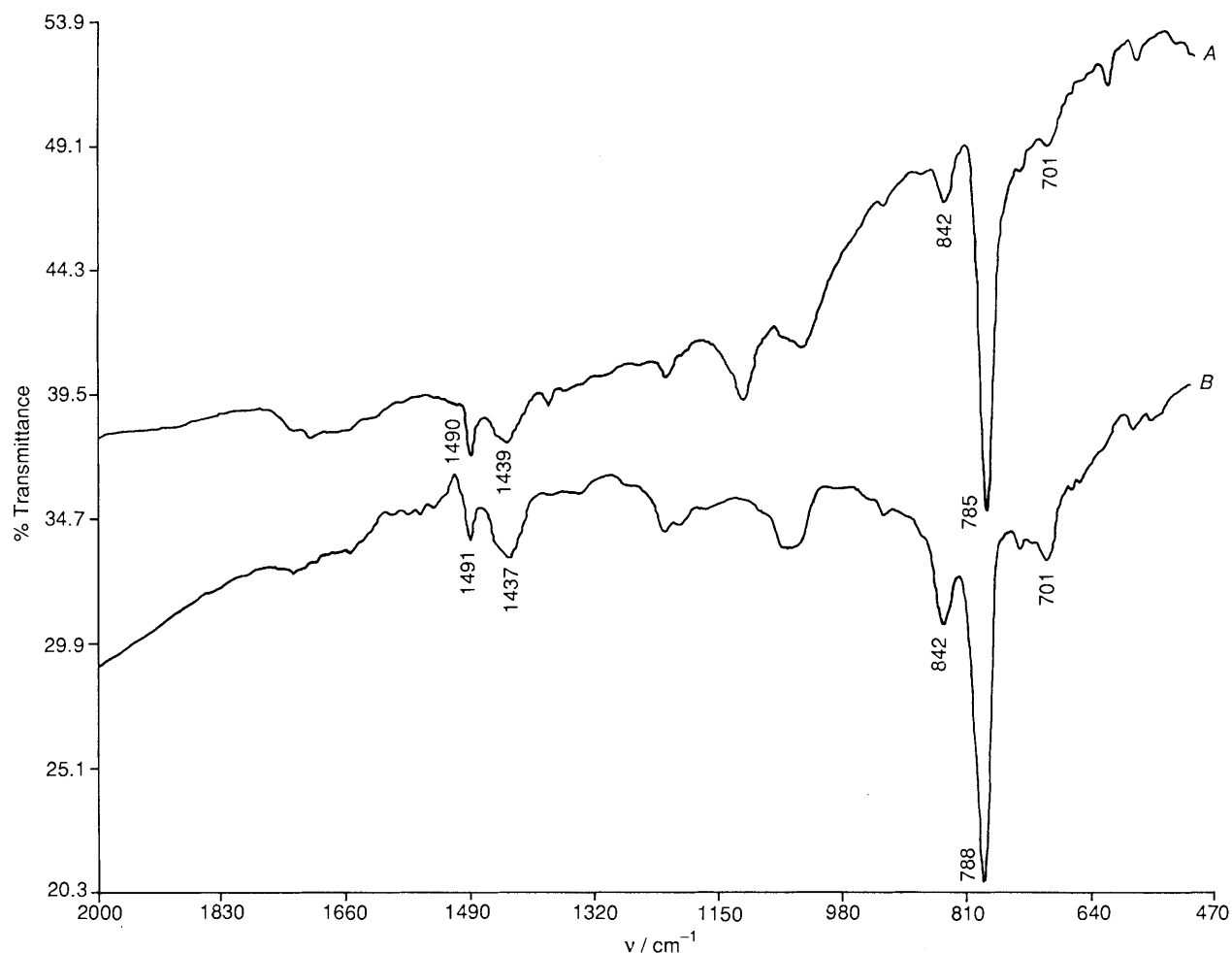


Fig. 2 IR transmission spectra of polythiophene films obtained by galvanostatic electrooxidation of thiophene ( $0.3 \text{ mol dm}^{-3}$ ) in propylene carbonate +  $\text{TBAPF}_6$  ( $0.1 \text{ mol dm}^{-3}$ ) solution. A: undoped polythiophene film prepared on an iron electrode. B: undoped polythiophene film prepared on a Pt electrode.

oxidation wave with a stronger current density occurred, beginning at only 0.4 V, which shows that the iron surface becomes oxidised whereas the oxidation of thiophene is slowed down. As may be seen from the results obtained on Pt and Fe electrodes, the anodic peak potential values,  $E_{\text{ox}}$ , for thiophene oxidation are *ca.* 1.7–1.9 V *vs.* Ag/AgCl, in both cases. A similar behaviour was observed for the cyclic voltammetric curves of 3-methylthiophene, with  $E_{\text{ox}}$  values of about 1.6–1.7 V *vs.* Ag/AgCl. Again, a PMT conductive film was formed on Pt, whereas no film was obtained on Fe.

In contrast, the use of a galvanostatic method with high current densities led to the formation of relatively thick PT or PMT films on iron electrodes. Thus, by using anodic current density values ranging between 4.2 and 6.9  $\text{mA cm}^{-2}$ , homogeneous and well adhering films to the iron surface were obtained. The Pt and PMT films could be grown continuously, and film thicknesses of the order of 10–20  $\mu\text{m}$  could be reached (Table 1). That the galvanostatic method enables thick PT and PMT films to be deposited is probably due to the fact that, at the high current densities and oxidation potentials used, optimal concentrations of thiophene and 3-methylthiophene radical-cations are produced, resulting in an increase of the rate of electropolymerisation relative to that of iron oxidation.

The PT films were removed from the iron (or Pt) substrate after undoping with a 5% ammoniacal aqueous solution, and their IR spectra determined in the transmission mode, using NaCl plates (Fig. 2). Similar bands, typical of polythiophene, are observed in the spectra obtained from the iron electrode [Fig. 2(A)] and on the Pt electrode [Fig. 2(B)]. Those at 842 (medium), 785–788 (strong) and 701  $\text{cm}^{-1}$  (weak) are

attributed to C–H out-of-plane vibrations. The strong intensity of the 785–788  $\text{cm}^{-1}$  band, which is characteristic of 2,5-disubstituted thiophene rings, indicates that the electrochemical coupling of thiophene rings occurs preferentially at the 2,5 positions.<sup>9</sup> Two medium bands at 1490–1491 and 1437–1439  $\text{cm}^{-1}$  are assigned to stretching vibrational modes of the thiophene ring.<sup>9</sup> For the IR spectrum of Pt film electropolymerised on iron a wide band occurs at 3460  $\text{cm}^{-1}$ , which is probably due to O–H stretching vibrations resulting from the presence of iron oxide.

The degree of polymerization (DP) of the PT films was evaluated using the procedure given by Furukawa *et al.*<sup>15</sup> and Sauvaziol *et al.*,<sup>16</sup> according to the expression, see eqn. (1),

$$\text{DP} = 2 (R_0/R + 2) \quad (1)$$

where  $R$  is the ratio of integrated intensity of the two IR bands at 701 and 788  $\text{cm}^{-1}$  assigned to the C–H out-of-plane vibration of monosubstituted and bisubstituted thiophenes respectively,  $R_0 = 1.07$  is the value of  $R$  evaluated for the  $\alpha$ -sexithiophene.<sup>16</sup> We found DP values of 32 and 25 for PT films electrodeposited on Fe and Pt, respectively.

XPS spectra of PT films deposited on iron were also investigated, and compared to those of terthiophene. S  $2p_{3/2}$  and S  $2p_{1/2}$  were located at 163.87 and 165.27 eV, and 163.97 and 165.17 eV, for PT films and terthiophene sample, respectively. The S:C atomic ratios calculated from the peak areas were of 0.20 for PT films, and 0.25 for terthiophene. This difference in S:C between the two samples can be attributed to carbon contamination of the PT films resulting from some residual amount of propylene carbonate. The O 1s

peak in the XPS spectrum of PT film contains two components at 530.2 and 531.8 eV, which can be assigned to iron oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  . . .), and to iron hydroxide or oxyhydroxide ( $\text{FeOOH}$ ). This is confirmed by the presence of a broad Fe 2p peak located between 711 and 715 eV. These results indicate the probable formation of a  $\text{Fe}_x\text{O}_y$ -Pt or  $\text{FeOOH}$ -PT composite on the surface of the Fe electrode.

In conclusion, the present investigation demonstrates the possibility of thiophene electropolymerisation on iron surfaces. The PT films obtained were homogeneous, relatively thick, adherent to the iron surface and they were characterised by a relatively high degree of polymerisation. The polythiophene deposition on Fe may have important industrial applications for the protection of oxidizable metals, which is currently under study in our laboratory.

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