Fig. 3 - Behaviour of nickel for electroless metal deposition in
0.1 M NiSO$_4$ + 0.1 M DMAB + 0.2 M (C$_2$H$_2$NaO$_2$)$_2$ (a)
0.1 M CoSO$_4$ + 0.1 M DMAB + 0.2 M (C$_2$H$_2$NaO$_2$)$_2$ (b)
pH = 4.5, T = 25 °C

The catalytic ability of Co for the electrooxidation of DMAB and subsequent deposition of Co-B in complete solution is illustrated by figure 3b. Short and similar transition times for both substrates - Co specpure and electroless Co-B - were expected from the known catalytic behaviour of that metal for hydrogenation / dehydrogenation processes [2].

CONCLUSION

The onset of electroless metal deposition, using DMAB as reducing agent can be strongly influenced by the substrate morphology. The effect is more pronounced for metals presenting weak interaction with the reductant, being nickel a typical example. Although the catalytic effect of the metalic ions in solution on the electrooxidation of DMAB must be taken into account, differences in structure and non-metallic content between first and subsequent electroless deposited layers are to be expected for platings occurring on the electrodeposited or the bare metal.

For substrates with high catalytic activity for EMD, as is the case of Cobalt, the influence of the underlaying morphology on the deposited layers properties is more difficult to establish. It will justify a detailled investigationon the voltammetric behaviour, since the DMAB oxidation process was seen to be well descriminated by measurements carried out on electrodes under rotation.

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ON THE ELECTROCHEMICAL SYNTHESIS OF POLY - 3 - METHYLTHIOPHENE

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Electronic polymers such as polypirrole, polyaniline and polythiophene, have been under active study [1-3] due to the interest in the numerous applications of these materials and to enhance the understanding of fundamental aspects.

Although considerable literature exists on the charge transport in polymeric systems [4] only recently emphasis has been given to the influence of the preparation conditions on the properties exhibited by these materials [5,6].

Conducting polymers can be synthesized easily by electrochemical oxidation of respective monomers / olygomers in solution. The deposition mechanism is poorly understood likely due to different growth processes imparted by certain potential / current conditions.

With the aim of correlating morphological and redox behaviour differences with the potentiostatic and galvanostatic conditions used to grow conducting polymer films on metal electrodes, in the present work poly-3-methylthiophene films have been synthesized by electrochemical oxidation of the monomer in a three electrode two compartment cell consisting on a specpure Pt working disk electrode (Ø = 670 μm), a Pt foil counter electrode and a saturated calomel reference. The solution was 0.6 mol dm^{-3} 3-methylthiophene in 0.2 M LiClO$_4$/acetonitrile, deaerated before each experiment by purified nitrogen bubbling for, at least, 15 min. The growth has been carried out either potentiostatically, in the range 1.24 - 1.29V (vs SCE) with a resolution of 10 mV, and galvanostatically, imposing a current density in the range 0.4 - 1.2 mA cm^{-2} with a resolution of 0.2 mA cm^{-2}. In all experiments it was used 60 mC cm^{-2} total charge density.

Current evolution during the growth under potentiostatic control is displayed in figure 1. Besides the effect of potential on the rate, the results clearly show two growth regimes, and the transients main features are summarized in table 1. The time lapse to reach the current minimum, which is probably related with the onset of film formation after some olygomerization in solution [7], decreases with the increase of potential. The same trend have the transition time between the two regimes and the charge involved in the first stage of growth.
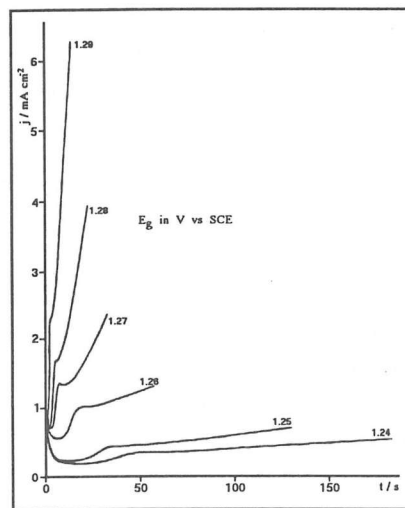

Fig. 1 - Current transients of P-3-Meth growth under potentiostatic control at different potential values.

Table 1 - Involved charge and time needed to reach the minimum current value and the inflexion point for P-3-Meth grew under potentiostatic control.

E_g /V vs SCE	t_{min} /s	$Q_{t_{min}}$ / mC cm^{-2}	t_{inf} /s	$Q_{t_{inf}-t_{min}}$ / mC cm^{-2}
1.24	20.0	5.2	50.0	8.9
1.25	14.0	4.6	36.0	6.8
1.26	7.5	4.6	18.5	9.3
1.27	3.5	2.7	8.5	6.2
1.28	2.3	1.9	5.5	4.7
1.29	1.0	0.9	3.5	3.6

The slope analysis of the j vs t curves after the minimum - figure 2 - shows that there is an increase in the rate of growth during the film formation which is potential dependent (in both regimes). This suggests that films of different structural / morphological properties are being formed at each potential.

The redox behaviour of the films so obtained has been characterized by cyclic voltammetry in a monomer free solution within the potential range 0.0 - 1.0V (vs SCE) at a sweep rate of 0.05 Vs^{-1}. Complete polymer discharge has been achieved by holding the potential at 0.0 V during 12 min before the potential scan. The cyclic voltammograms in
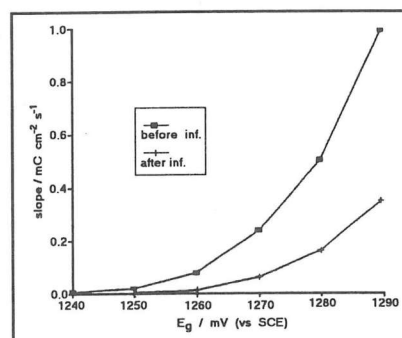

Fig. 2 - Evolution of the rate of growth during film formation under potentiostatic control.

figure 3 and their characteristics summarized in table 2 are illustrative of the influence of the growth conditions on the polymer properties. In terms of number of active sites formed by unit charge of growth, better efficiency is observed at higher growth potentials. The non-complete discharge during the cathodic sweep, which must be correlated with polymer structure reorganization and ability for retention of doping anions and evaluated by Q_O/Q_R ratio, is also dependent of the growth potential although non-monotonically.
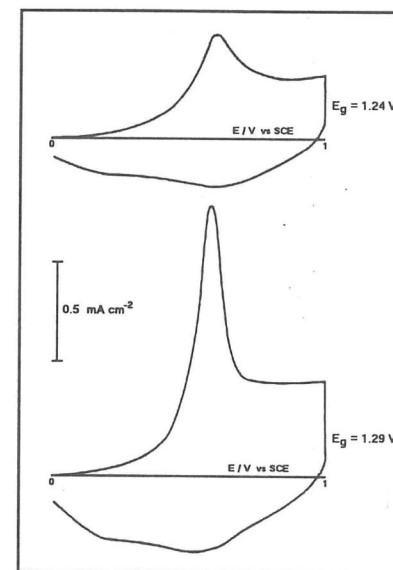

Fig. 3 - Redox behaviour of polymer films obtained potentiostatically.

Table 2 - Ratio between the oxidation charge measured in the redox characterization of polymer (Q_O) and the growing charge (Q_g) and the ratio between the anodic and cathodic charge (Q_R) during the redox of the polymer grew under potentiostatic control.

E_g / V vs SCE	Q_O/Q_g (%)	Q_O/Q_R
1.24	6.6	1.2
1.25	8.3	1.2
1.26	10.9	1.4
1.27	11.9	1.6
1.28	12.1	1.4
1.29	13.1	1.3

The potential-time profiles obtained when the electropolymerization has been carried out under galvanostatic control are shown in figure 4. After an initial period, which decreases as j_g increases, the electrode potential tends to a plateau, which is likely to be indicative of an homogeneous film formation.

The data on table 3 shows that all plateau potential values are close and those to be expected from the potentiostatic current transients; notwithstanding the redox behaviour of the films (figure 5) present marked dissimilarities. Poor conductive films are observed at low growth currents. This is most probably due to an extensive formation of soluble olygomers which, at a given concentration
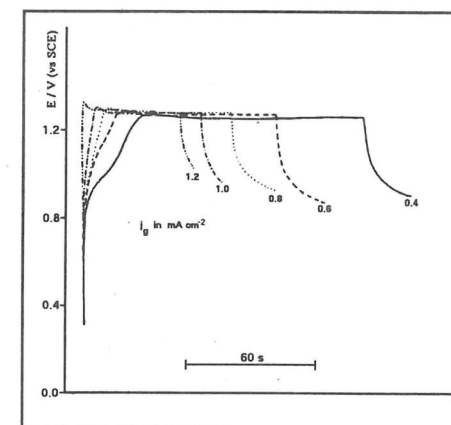

Fig. 4 - Electrode potential profiles for the galvanostatic growth of P-3-Meth at different current densities.

may precipitate on the electrode.

Table 3 - Time needed to reach the maximum potential value (t_{max}), growing time (t_g) and plateau potential (E_{pl}) reached for the galvanostatic growth of P-3-Meth.

i_g / mA cm^{-2}	t_{max} / s	t_g / s	E_{pl} / mV
0.4	30	150	1247
0.6	19	100	1254
0.8	12	75	1257
1.0	8	60	1265
1.2	2	50	1269

Although olygomers formation has been considered the path for conducting film formation [7], low oxidation rates must be avoided in order of obtaining a reasonable growth efficiency and electroactivity.
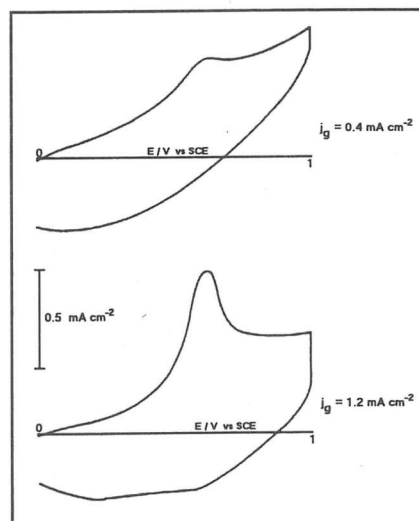

Fig. 5 - Redox behaviour of P-3-Meth films obtained galvanostatically.

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An electrochemical study of the behaviour of chalcopyrite in acid and alkaline solutions

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The refractory behaviour to hydro/electrometallurgical processing of metallic sulphides and the mineralogical complexity of the related ores have justified the study of surface chemical/electrochemical processes of the individual mineral entities [1-3]. Being the most important source for the extraction of copper, chalcopyrite ($CuFeS_2$) has received particular attention [3-5].

Unfortunately the use of both natural specimens from diverse origins and leaching solutions with different chemical composition makes difficult a correlation of published data in order of understanding the dissolution mechanism. Nevertheless, remarkable progress has been made in the knowledge of semiconductor properties of complex sulphides [6].

In the present work electrodes prepared from massive natural chalcopyrites were used to study their electrochemical behaviour under acidic and basic media (H_2SO_4 0.5 M and NaOH 0.5 M).

Cyclic voltammetry is able to show the chalcopyrite capacity to undergo reduction/oxidation reactions. The current response in sulphuric acid solution to a potential sweep starting anodically from the open circuit potential is shown in figure 1a. The mineral dissolution can be expressed by the reactions :