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Galvanostatic and pulse potential synthesis of poly-3-methylthiophene. Polymer as catalytic support

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Abstract

Poly-3-methylthiophene (P3MT) films were electropolymerised on graphite and indium tin oxide electrodes and characterised by cyclic voltammetry and scanning electron microscopy. The polymerisation was carried out by two different techniques, pulse potential program and constant current density, yielding conducting coated polymeric electrodes. The polymeric films display structural differences depending on the polymerisation method. The conducting properties of the polymers also depend on the electropolymerisation method. Polymeric resistance and stability were studied.

P3MT was used as a support for the anchoring of Pt and Pb metal particles. The catalytic oxidation of formic acid was studied with these electrodes and compared with that obtained with graphite/Pt massive electrodes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conducting polymers; Thiophene; Catalysis

1. Introduction

One of the most attractive fields in chemistry is the development of new organic materials such as plastics and polymers [1]. Among all of them, electrochemists are particularly interested in the development of new organic conducting materials such as polyacetylene [2], polypyrrol [3], polythiophene [4], polyaniline [3] and related polymers. This special interest is due to the possibility of electrochemical synthesis of these materials by simple anodic oxidation of the monomers, except in the case of polyacetylene.

Polymers synthesised in this way are formed directly on the electrode surface, so it is possible to study the electrogeneration mechanism, their conducting properties and their thermal stability; furthermore, electrochemically synthesised polymers show higher conducting properties than the same polymers synthesised in any other way.

These properties give these materials some application as rechargeable batteries [5,6], electrochromic devices [7], energy storage [8] and, recently, their use in the biomimicking process [9]. Although these systems do not show electrocatalytic activity themselves, they could be used as supporting materials for many different metal particles, thus rendering catalysts with good metal dispersion, improving in this way their activity and selectivity [10–12]. The nature of the catalyst could be very broad, from metal particles to ions or enzymes.

It is important to note that polymer properties strongly depend on the nature of the polymeric precursor, so a great effort has to be made in order to find optimum electrogeneration conditions such as solvent [13,14], counter-ions [15], electrochemical method of polymerisation [13–16] and the nature of the working electrode [17,18], in order to obtain polymers with the adequate morphology, stability and conductivity to be of use in a wide range of reactions and experimental conditions.

At this point it is necessary to note that polymers are not stable materials. They undergo a wide range of side reactions, including several degradation processes, which may occur because of different reasons such as heat, light and the presence of nucleophilic agents, subjecting the polymer to high anodic potential during the electrogeneration reaction, or simply by cycling the polymer many times [19–21]. These processes will result in the loss of the polymer conducting properties. Submitting the polymeric film to further oxidation processes will cause a rupture of the polymeric structure (backbone).

Polythiophene and derivatives [22–23] are suitable redox polymers because of their range of electrochemical activity [24]. It is possible to control polymer morphology by simple control of the electrosynthesis conditions [25]. It is also

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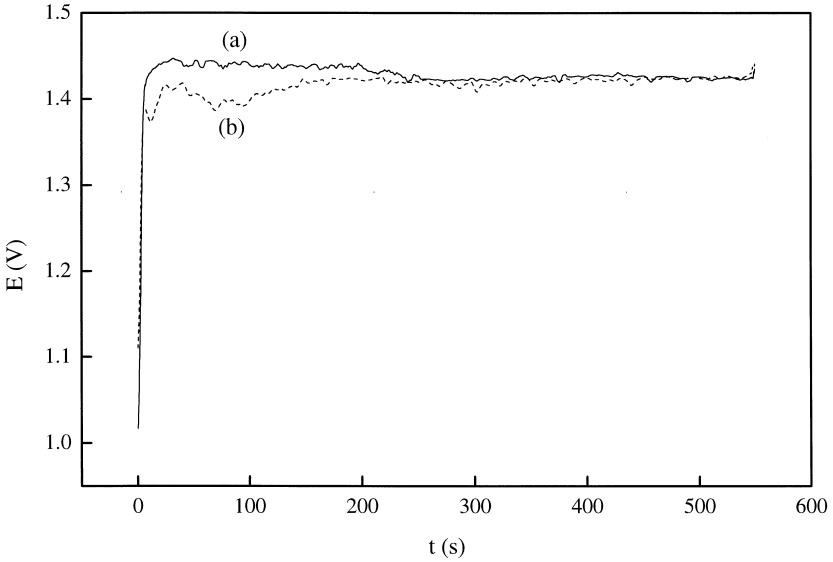

Fig. 1. Chronopotentiometric response monitored for a P3MT generation: (a) $i = 2.23$ mA/cm^2 and (b) $i = 1.28$ mA/cm^2.

possible to improve the polythiophene stability and its conducting properties by some structural modifications such as including some substituents like the methyl groups or by electropolymerisation of precursors combining alkylthiophenes with some azo molecules [26,27]. The polymeric systems do not have any intrinsic electrocatalytic activity. They have been used as host matrices where different chemical species have been incorporated [28–29].

We have undertaken the synthesis of poly-3-methylthiophene (P3MT) in an organic medium PC by two different electrochemical methods, the galvanostatic and the pulse potential program methods. The P3MT conducting properties were found to be sensitive to the electropolymerisation method. Thermal and continuous cycling polymer stability was studied for P3MT films generated on graphite electrodes. Finally, we have employed the polymeric film on graphite electrodes as catalyst support. Both Pt and Pt–Pb metal particles were incorporated applying a constant potential technique into the P3MT/graphite electrodes, and were used as catalyst for the formic acid oxidation reaction. A great promotion effect was found when metal particles were incorporated into the polymeric coated electrodes.

2. Experimental

P3MT films were electrogenerated and tested in an electrochemical cell equipped with an EG and GPARC potentiostat/galvanostat VersaStat™.

An Ag wire was used as the pseudoreference electrode [30]. All potentials are reported versus this electrode unless otherwise indicated. A Pt foil was used as the counter electrode.

3-Methylthiophene (3MT) (Merck), was distilled prior to use. All other reactants were AR grade. Propylene carbonate (PC) (Merck) was used as solvent.

Polymer morphologies were observed on ITO-sputtered samples using a Philips XI-30 microscope fitted with a EDAX/PV 9900 analyser.

P3MT films were generated in graphite and indium tin oxide (ITO) electrodes by two different methods: (i) potential step E anodic (E_a) between 2.8 and 0.8 V, E cathodic (E_c) between -0.8 and 0.8 V; and (ii) galvanostatic methods ($i = 9.5$ and 0.32 mA/cm^2) in a 3MT 0.1 M/LiClO$_4$ 0.5 M/PC solution. The polymers were tested by means of cyclic voltammetry techniques between -0.1 and 1.5 V at a scan rate of 100 mV/s in free monomer solutions.

Polymer stability was studied by cyclic voltammetry techniques. Different series of P3MT films were generated on a graphite electrode by a pulse potential program. E_a was kept constant at 1.4 V during 5 s, while E_c varied between -0.2 and 0.8 V ($\Delta E = 0.2$ V for each series) in a 3MT 0.1 M/LiClO$_4$ 0.5 M/PC solution. The P3MT films were submitted to continuous cycling between -0.2 and 1.6 V at a scan rate of 100 mV/s, in a LiClO$_4$ 0.5 M/PC solution. The total anodic charge variations (Q_a) were quantified during the process.

Thermal stability was studied by submitting P3MT films, generated by the pulse potential program on ITO electrodes, at different working temperatures and monitoring the anodic charge evolution in time. Q_a was measured from the voltammograms obtained by cycling the film in a LiClO$_4$ 0.5 M/PC solution at 100 mV/s.

For the resistance measurements, a P3MT film was generated by both pulse potential program and galvanostatic ($E_a = 1.6$ V, 15 s; $E_c = -0.1$ V, 5 s; and $i = 1.9$ mA/cm^2 in a 3MT 0.1 M/LiClO$_4$ 0.5 M/PC solution) methods between two gold wires; in this way the polymer can interconnect both electrodes. Resistance measurements were obtained by applying a constant potential between the electrodes and monitoring the total current at a given potential.

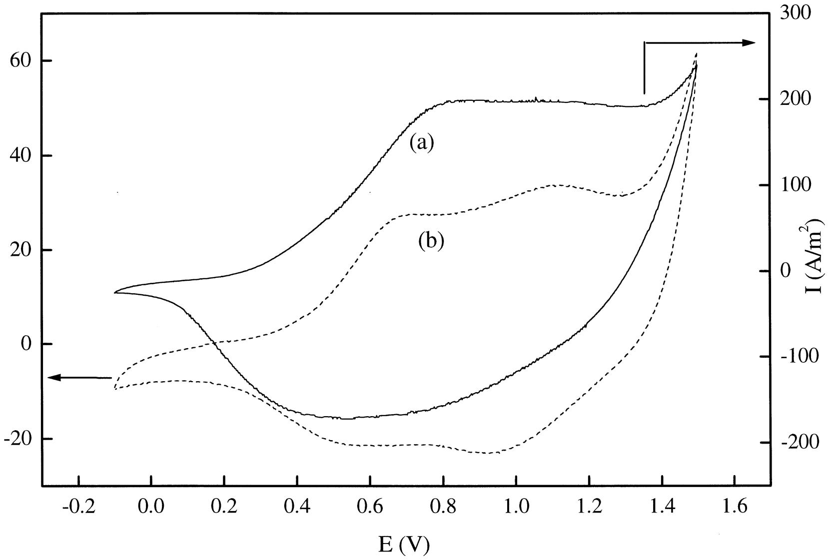

Fig. 2. Cyclic voltammogram profiles for P3MT films generated at: (a) $i = 2.23$ mA/cm^2 and (b) $i = 1.28$ mA/cm^2.

Graphite/P3MT electrodes were generated by potential step (Ea = 1.4 V, time 15 s; Ec = −0.1 V, time 5 s; total time 600 s) in a 3MT 0.1 M/$LiClO_4$ 0.5 M/PC solution, and were tested by cyclic voltammetry between −0.1 and 1.5 V at a scan rate of 100 mV/s in a free monomer solution.

Graphite/P3MT/Pt electrodes (electrode type 1) were generated by immersing a graphite/P3MT electrode in a $HPtCl_6$ 3×10^{-3} M/HCl 1 M solution, and then applying a reduction potential $E = -0.8$ V during 500 and 300 s, respectively.

Graphite/P3MT/Pt–Pb electrodes (electrode type 2) were generated by immersing type 1 electrodes in a $Pb(NO_3)_2$ 3×10^{-3} M solution during 5 or 60 min. Then they were transferred into an electrochemical cell in a $LiClO_4$ solution and a reduction potential of $E = -0.2$ V was applied during 6 s.

The amount of Pt and Pb incorporated in the different electrodes was evaluated by integration of the i vs. t response of the modified polymers when a constant potential was applied. The polymeric contribution was previously eliminated in all systems.

Electrocatalytic properties of electrodes 1 and 2 were tested in the formic acid oxidation process by cyclic voltammetry and constant potential techniques in H_2SO_4 0.5 M/HCOOH 0.5 M solutions.

3. Results and discussion

3.1. Growth and stability

The P3MT films were electrogenerated by means of two different techniques. The first one was a galvanostatic method and the second one by square waves of potential (pulse potential method).

3.1.1. Galvanostatic method

Polymerisation was carried out by the application of different constant current densities (i). Values of i between 3.0 and 1.0 mA/cm^2 were employed. The E–t response is shown in Fig. 1 corresponding to the P3MT films generated at 2.23 mA/cm^2 and 1.28 mA/cm^2 (a) and (b), respectively. The potential increases up to values of 1.43 V, where it remains constant.

P3MT behaviour in a free monomer solution was monitored by cyclic voltammetry techniques. Typical profiles are shown in Fig. 2. The voltammograms display two peaks at 0.8 and 1.1 V in the anodic sweep, and at 0.9 and 0.5 V in the cathodic one, corresponding to the redox pairs of the polymer.

The amount of polymer deposited on the electrode surface strongly depends on the current density applied. The amount of polymer deposited into the electrode surface increases with the increasing current density although, when very high current density was applied, oligomeric species fell down from the polymer to the solution.

With such a method, the electrogenerated films display, at best, good adherence into the electrode surface. The electrode coating is not homogeneous. The optimal current density for the galvanostatic generation is ca. 2.0 mA/cm^2 for graphite electrodes and 2.5 mA/cm^2 for an ITO electrode.

3.1.2. Pulse potential program

Polymerisation was carried out by application of consecutive square waves of potential in which monomer oxidation–polymerisation and polymer oxidation occurs within the anodic wave, and polymer reduction within the cathodic one. The influence of the anodic and cathodic applied potential values in the polymerisation process was studied by the generation of different series of polymers in which the

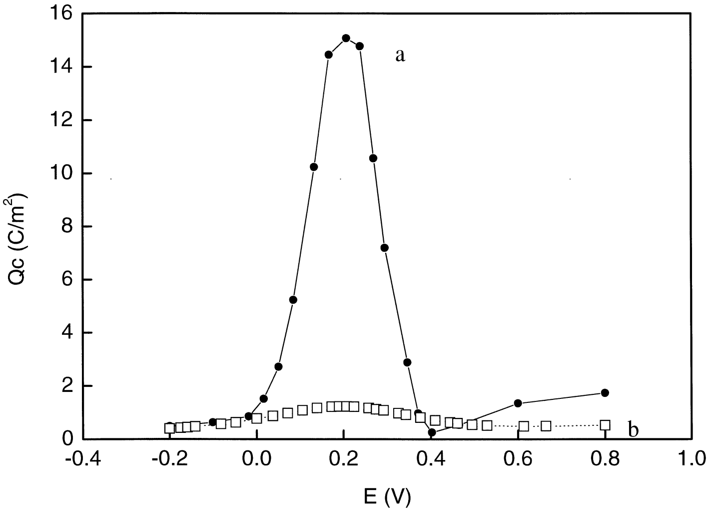

Fig. 3. Total amount of cathodic charge (Q_{red}) as a function of the cathodic potential (E_c) at which polymers were generated: (a) $E_a = 1.4$ V and (b) $E_a = 1.2$ V.

anodic potential was kept constant while the cathodic one varies in each series. The polymers synthesised in this way were subsequently studied by following the variation of the total cathodic charge (Q_{red}) of the polymeric films generated in each series, by cycling the polymer-coated electrode in a monomer free solution. Q_{red} served as an indirect measure of the quantity of electropolymerised material.

The experimental values for Q_{red} thus obtained are shown in Fig. 3. The variation of the total amount of Q_{red} is represented as a function of the cathodic potential applied in each series. The anodic potential was kept constant at values of 1.4 and 1.2 V.

As can be seen in Fig. 3, for the series of polymers generated at $E_a = 1.2$ V the amount of Q_{red} shows no significant modifications. The maximum value is reached at $E_c = 0.2$ V. For the series of polymers generated at $E_c = 1.4$ V, the total amount of Q_{red}, strongly depends on the E_r reaching a maximum value at $E_c = 0.2$ V. There is a large increase in the reduction charge, and thus in the quantity of polymerised material when the pulse procedure is utilised. A possible reason for the increase of the Q_{red} in this range could be the periodic relaxation of the concentration gradient of 3MT in the immediate vicinity of the electrode surface. The activation effect is observed when the cathodic pulse is situated in a potential region where the growing polymer film attained a particular stage; the polymerised material is almost fully reduced, but still partially conducting. This continuous reduction process of the polymer material could be connected with a special state of the growing polymer film. The periodic pulsing could favour the access of monomer molecules to the electrode surface, thus promoting the overall polymerisation process in an early stage.

When polymer generation is undertaken at anodic potentials higher than 1.4 V, the amount of material polymerised is high but some parallel process may occur at the same time such as oligomerisation, further nucleation and degradation.

The films obtained in the best conditions are adherents, homogeneous and thin layers in general.

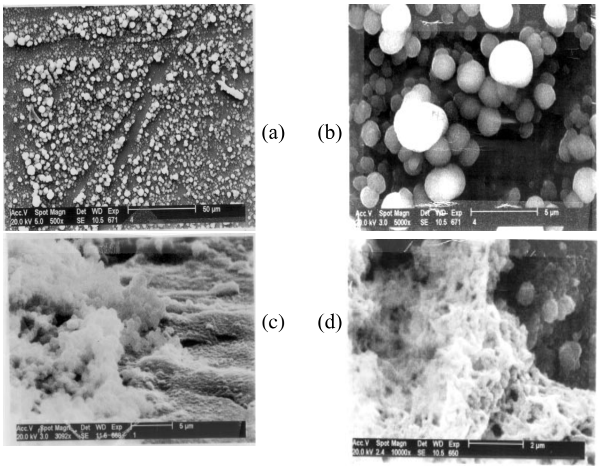

Fig. 4. Some representative SEM micrographs of P3MT films generated on ITO electrodes: (a) $i = 3.0$ mA/cm^2, (b) $i = 2.7$ mA/cm^2, (c) $E_a = 2.8$ V and $E_c = 0.4$ V, and (d) $E_a = 2.8$ V and $E_c = -0.2$ V.

3.2. Scanning electron microscopy (SEM)

The structure and morphology of the P3MT films generated on ITO electrodes were studied by SEM techniques. Some representative micrographs of these polymers are shown in Fig. 4. As it can be seen, the morphology of the polymeric films depends on the generation method. Polymers generated by pulse potential programs are deposited on the electrode surface in a more homogeneous way than the galvanostatic ones, coating almost all the electrode surface. Films generated by galvanostatic methods and grown in very compact spherical grains are shown in Fig. 4(a)–(b). The polymers generated by pulse program potential are presented in an open morphology in which channels may be observed (Fig. 4(c)–(d)).

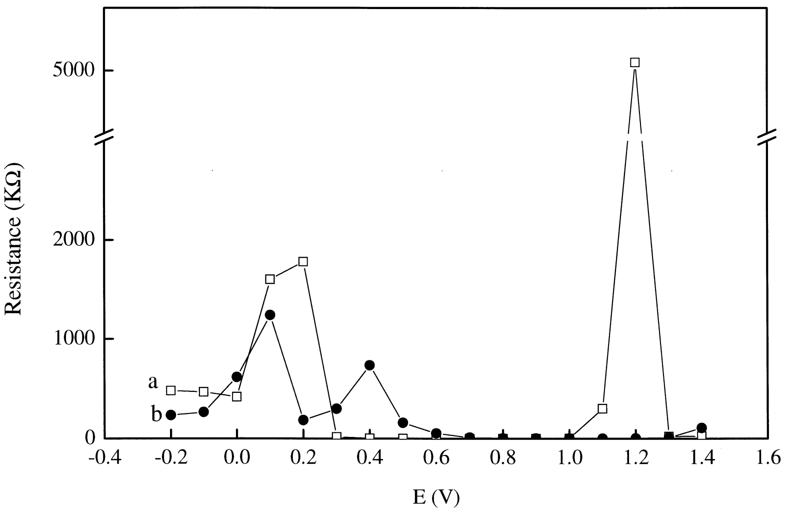

Fig. 5. Resistance value as a function of the potential applied between two Au wires interconnected by P3MT films grown by different methods: (a) galvanostatic method, and (b) pulse program potential method.

3.3. Resistance

Resistance measurements were carried out at 25°C in a PC/LiClO$_4$ solution following a previously described method [31].

Fig. 5 shows the dependence of the P3MT film resistance as a function of the potential applied and the electrogeneration method. As it can be seen, polymers can be insulating or conductors depending on the potential. The conducting window depends on the electrogeneration method. The film generated by the pulse potential program is conducting between ca. 0.5 and 1.4 V, while the galvanostatic one is

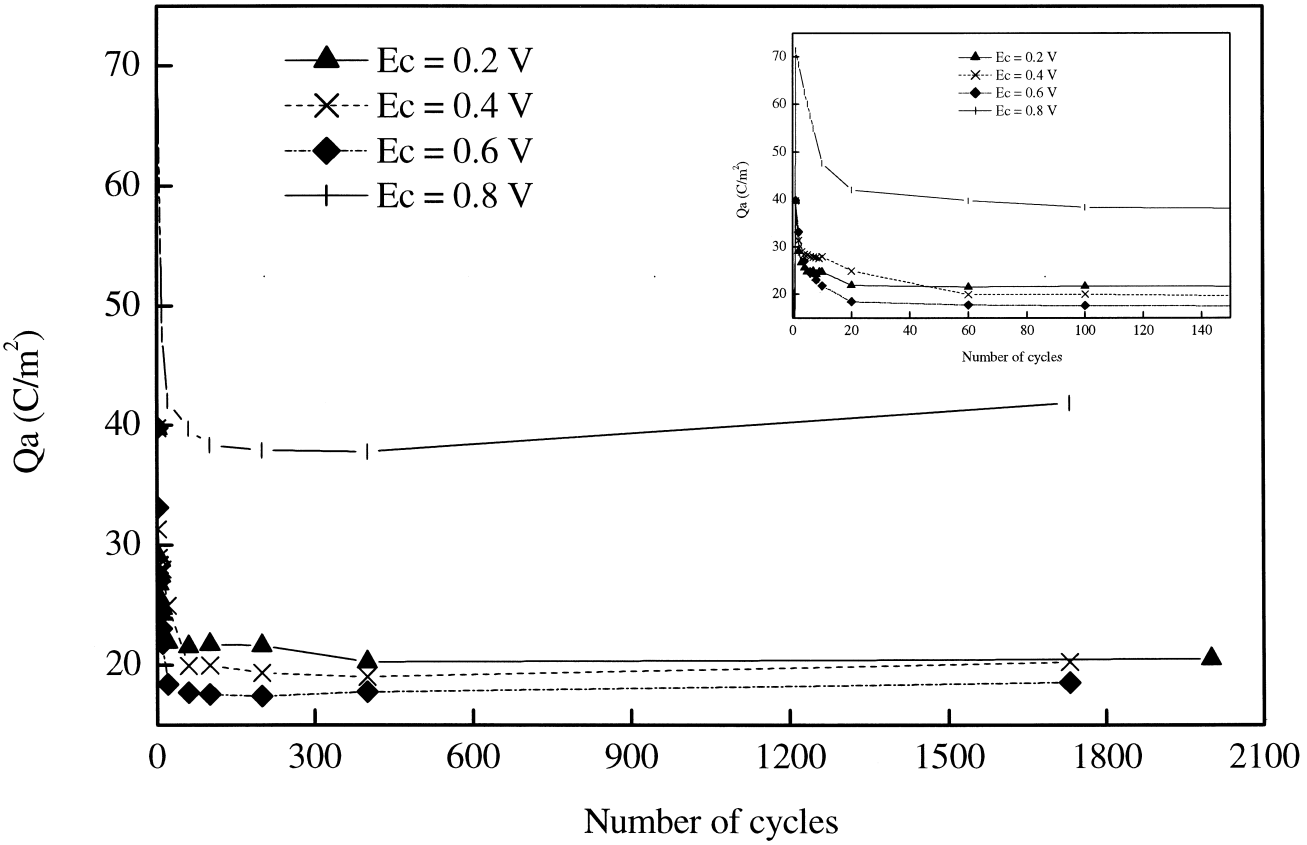

Fig. 6. Total amount of anodic charge (Q_a) as a function of the number of oxidation–reduction cycles for a P3MT film generated by a pulse potential program between $E_a = 1.4$ V and: $E_a = 0.2$ V, $E_a = 0.4$ V, $E_a = 0.6$ V, $E_a = 0.8$ V.

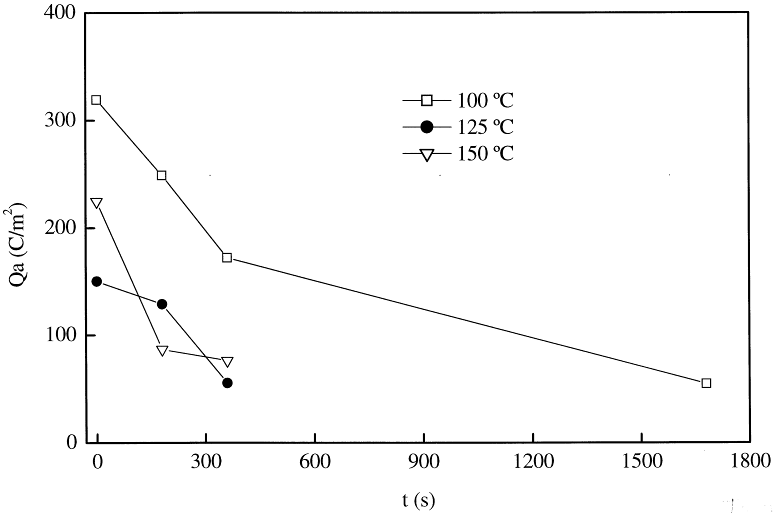

Fig. 7. Variation of the anodic charge (Q_a) as function of time when a P3MT film is submitted at different temperatures: (–□–)100°C, (–●–) 125°C, and (–▽–) 150°C.

conducting between 0.3 and 1.1 V. The polymer will be able to drive redox reactions whose equilibrium potential lies in its conducting range. Thus, by a simple choice of the polymerisation method it is possible to achieve or avoid some redox reactions at the electrode surface.

3.4. Degradation

The process of deterioration of the chemical and conducting polymer properties involving chemical reactions is defined as degradation. There are many reasons for degradation such as heat, light and continuous cycling.

The stability during consecutive potential cycles and the thermal stability of the P3MT films have both been studied.

For the consecutive potentials cycling test stability, some P3MT films were generated by a pulse potential program, in which E_c changed between -0.2 and 0.8 V (with a 0.2 V increment); E_a was kept at a constant value of 1.4 V. The films were generated using a graphite electrode as substrate. The films generated were checked in PC/$LiClO_4$ 0.5 M at 25°C by consecutive triangular waves of potential between -0.2 and 1.6 V at a scan rate of 100 mV/s. As the number of cycles increased, the anodic and cathodic current densities diminished. This loss in the redox capacity is the variable studied here. The variation of the total amount of charge involved in the anodic process is proportional to the number of polarisation cycles as can be seen in Fig. 6. For the first 50–60 cycles, the anodic and cathodic peaks strongly diminish their intensities, and the degradation process is very important. From that point, a stabilisation of the total amount of anodic and cathodic charge is observed. This behaviour is the same for all the samples studied, irrespective of their initial charge. As long as a polymeric degradation process occurs, an oxidation/reduction parallel process is taking place in the polymer films by the continuous potential cycling. This means that the film oxidation may occur at the same time as the anodic discharge process, thus promoting the degradation of the film and the loss if its redox properties. This loss in the charge storage efficacy could arise from any alteration of the conjugated structure of the polymeric chains, making the polymer more and more non-oxidisable in each cycle. The degradation process takes place with simultaneous loss of oligomers in solution, these oligomers, may be polymerised again in the oxidation cycle; this polymerisation process is in competition with the degradation one. These phenomena can be a possible reason for the apparent end of the degradation process beyond the 60th cycle.

The degradation process proceeds with the number of cycles being very fast in the early stages of the cycling. However, under the studied conditions, none of the P3MT films loses half of its initial amount of charge.

3.5. Thermal stability

We have undertaken the study of the thermal stability of P3MT films heated at different work temperatures between 100 and 300°C in air atmosphere, but those were grown at 25°C. The change of the anodic charge was monitored in a free monomer solution (PC/$LiClO_4$). Fig. 7 shows the variation of the anodic charge in time at the given temperatures. The rate of deterioration of the polymeric films is very high, the loss of the conductivity is obvious, and the time when the charge storage is half the initial value has been taken as a measure of their stability. At temperatures higher than 150°C, the polymer films become no conductors and the degradation is very fast. Several processes can contribute to the instability and degradation of these conducting materials. The reaction of the main chain with nucleophiles such as oxygen or some counter-ions will result in an irreversible loss of the conjugation of the polymeric chain, thus yielding a non-conducting material. Further, at higher temperatures

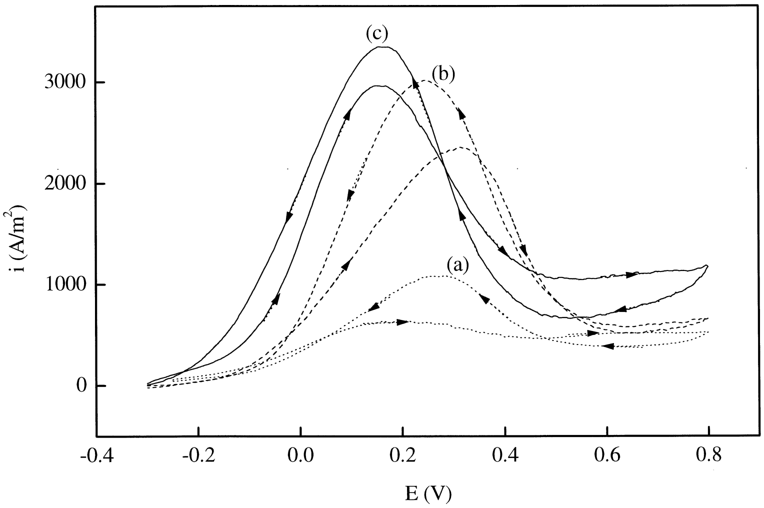

Fig. 8. Voltammograms registered from a HCOOH 0.5 M/H_2SO_4 0.5 M with different working electrodes: (a) graphite/P3MT/Pt electrode (type 1), (b) graphite/P3MT/Pt/Pb (30 μg/cm^2) electrode (type 2), and (c) graphite/P3MT/Pt/Pb (133.3 μg/cm^2) electrode (type 2).

and oxidising conditions, the organic materials 'sublimate', and even disappear from the electrode surface, yielding some inorganic agglomerates arising from the counterions present within the polymeric chains.

4. Electrocatalitic applications

The polymeric system acquires a catalytic functionality. Polymer electrodes modified by electrodeposition of Pt or Pb particles have been proposed for the oxidation of small molecules such as hydrogen, formic acid and methanol [11,32–34]. The anchoring of metal microparticles in polymers is a promising route for obtaining electrode systems, which present a very high electrocatalytic activity.

These properties depend mainly on the film conductivity, the possibility of including some chemical precursors for the emplacement of the catalytic metal and the diffusion of the substrate into the film towards the electrocatalytic active centres.

The use of intrinsically conductive polymer with a suitable morphology (open morphology) and adequate conductivity allows both the incorporation of metal particles and an easy accessibility of the substrate to the catalytic sites.

The stable potentiodynamic response of the graphite/P3MT films, obtained by means of pulse of potential in the conditions ($E_c = -0.2$ V, $t_c = 5$ s; $E_a = 1.4$ V, $t_a = 15$ s) with total polymerisation time = 600 s in 0.1 M 3MT/0.5 M $LiClO_4$ in PC solutions, was utilised for the preparation of the Pt electrodeposited material electrode. These polymer films display an open structure available for the emplacement of the catalytic metal.

In the graphite/P3MT/Pt electrode, the ClO_4^- and $PtCl_6^{2-}$ anions were both incorporated into the polymeric matrix during the slow positive potential sweep applied to graphite/P3MT electrodes. According to the results, $PtCl_6^{2-}$ was mainly incorporated by means of an absorption process. The immediate application of a negative potential step allows the reduction of Pt (IV) simultaneously with the dedoping process, in which ClO_4^- anions leave the polymeric matrix. In this way, it is possible to control the size and distribution of Pt particles in the polymer matrix by varying the time of application of the cathodic potential step. When a constant potential is applied in order to deposit platinum microparticles, the structure changes, platinum is deposited on the polymer surface and it seems that the platinum does not get into the polymer bulk [11,33]. When formic acid is present, graphite/P3MT/Pt electrodes (type 1) show a potentiodynamic profile in both the positive and the negative sweep as can be seen in Fig. 8. According to Ref. [35]:

$$\mathrm{Pt} + \mathrm{HCOOH} \rightarrow \mathrm{Pt(COOH)_{ads}} + \mathrm{H^+} + 1\mathrm{e^-} \tag{1}$$

$$\mathrm{Pt(COOH)_{ads}} \rightarrow \mathrm{Pt} + \mathrm{CO_2} + \mathrm{H^+} + 1\mathrm{e^-} \tag{2}$$

$$\mathrm{Pt(COOH)_{ads}} \rightarrow \text{Poisoning species.} \tag{3}$$

The processes (Eqs. (1) and (2)) are responsible for the anodic current peak at ca. 0.2 V. The oxidation of strongly adsorbed intermediate (poisoning) species, i.e. $Pt_n(COH)$ [36–38], $Pt_n(CO)$ with $n = 1, 3$ [39] and $Pt(COOH)_{ads}$ requires the presence of oxygen species on the platinum sites such as $Pt(OH)_{ads}$ which are formed at potentials beyond 0.4 V (Eq. 3).

The direct oxidation of formic acid appears to be strongly favoured by the use of the graphite/P3MT/Pt electrode, compared with the bulk platinum electrode under the same conditions. In view of the higher dispersion of Pt crystallites into the polymer film and the high effective area, it can be assumed that the poisoning of the catalytic sites due to chemical species produced by side reactions

Table 1
Electrooxidation of formic acid as a function of the amount of Pt and Pb incorporated

Pt[a] (mg/cm^2)	Pb[b] (μg/cm^2)	R[c]	i_+[d] (mA/cm^2	i_-[e] (mA/cm^2)	i_+/i_-	i_l[f] (mA/cm^2)
69.8	23.1	3.0	299	234	1.28	11
201.4	133.3	1.5	297	335	0.88	48
209.5	105.7	1.9	245	184	1.30	12
332.5	30.5	10.9	148	143	1.03	21

[a] Total amount of Pt incorporated in the electrode.
[b] Total amount of Pb incorporated.
[c] Weight ratio ($R \times 10^{-3}$) between Pt and Pb incorporated into the electrode.
[d] Maximum anodic current density.
[e] Maximum cathodic current density.
[f] Limit current density for type C electrodes.

during the electrooxidation of formic acid is lower than on bulk platinum electrodes.

Graphite/P3MT/Pt/Pb electrodes (type 2) were used in order to obtain the electrooxidation of formic acid. Some typical i–E profiles are depicted in Fig. 8. The catalytic effect of the incorporation of a second metal, namely Pb, into electrodes type 1 is clearly seen when its response in the electrooxidation of formic acid is compared with the one

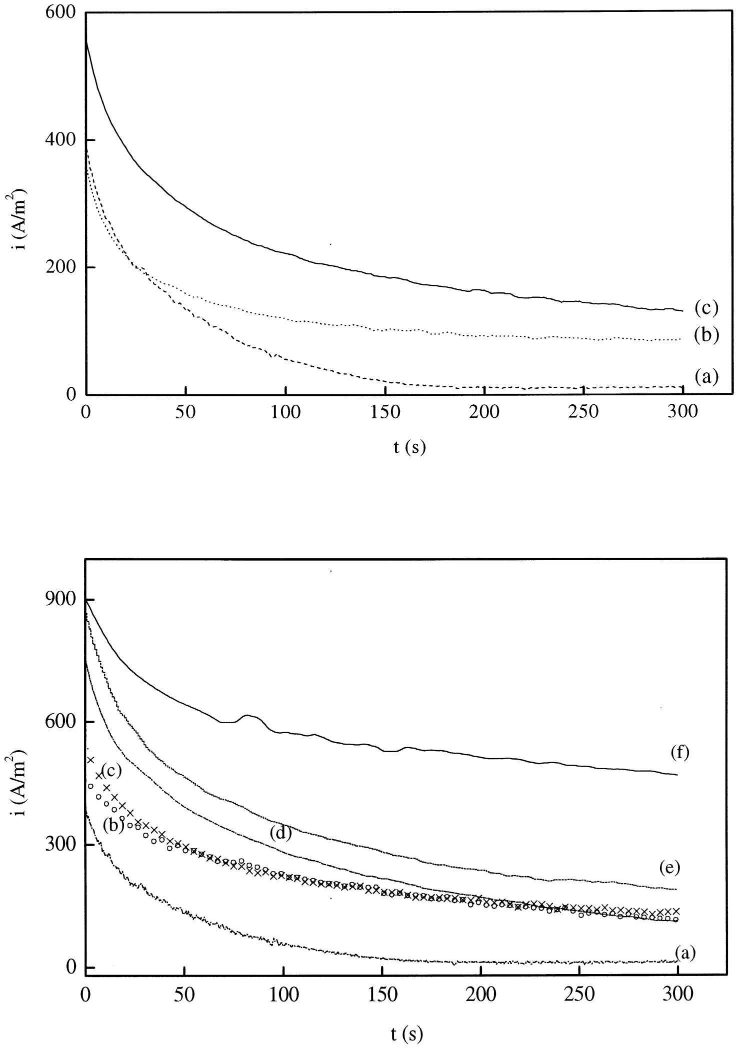

Fig. 9. (A) i (A/m^2) vs. t response monitored from HCOOH oxidation at 0.8 V/(SCE saturated calomel electrode) with the following electrodes: (a) graphite/Pt, (b) graphite/P3MT/Pt (300 s), and (c) graphite/P3MT/Pt (500 s). (B) i (A/m^2) vs. t response monitored from HCOOH oxidation at 0.8 V/(CSE) with the following electrodes: (a) graphite/Pt, (b) graphite/P3MT/Pt, (c) graphite/P3MT/Pt/Pb (23.1 μg/cm^2.), (d) graphite/P3MT/Pt/Pb (30 μg/cm^2.), (e) graphite/P3MT/Pt/Pb (105.7 μg/cm^2.), and (f) graphite/P3MT/Pt/Pb (133.3 μg/cm^2).

obtained with graphite/P3MT/Pt electrodes under the same conditions. A large increase in the current peaks associated with the direct oxidation of the substrate is observed, together with a clear decrease in the charge associated to the oxidation of strongly adsorbed intermediates in the anodic region.

As shown in Table 1, the magnitude of the i_+ and i_- current density peaks for the formic acid oxidation observed with electrodes type 2, depends on the amount of Pb incorporated into the film, which depends on the time for which the electrode type 1 was in contact with the $Pb(NO_3)_2$ solution. The current peaks i_+ and i_- display a very large increment as the amount of Pb incorporated into the polymer matrix increased. The maximum catalytic activity was achieved when the amount of Pb incorporated in the Pt cluster was the highest (133.3 μg/cm^2). Under optimal conditions, the current density peaks were increased by ca. 300%. This means that the strongly chemisorbed poisoning species were formed less easily on the Pt–Pb modified polymer electrodes.

The behaviour of the different electrodes in the formic acid electrooxidation process was studied at constant oxidation potential ($E = 0.8$ V/CSE) and was compared for each electrode under the same conditions. Fig. 9(A) shows the i vs. time response obtained for graphite/Pt massive and type 1 electrodes. The activity of the electrodes decreases with time, reaching a quasi-stationary value after about 100 s. Graphite/Pt massive electrodes display lower activity than type 1 electrodes, independently of the amount of Pt incorporated into electrodes type 1. The electrocatalytic oxidation of formic acid increased when different amounts of Pb were incorporated into electrodes type 1 as can be seen in Fig. 9(B) As the amount of Pb incorporated into the electrodes increases, the oxidation response increases. The oxidation profiles obtained with electrodes type 2, resembles that obtained with electrodes type 1. The activity decreases with time reaching a constant value after ca. 24 h.

The structure of the bimetallic electrodes permits the retention of Pb^{2+} ions within these electrode systems. In a reduced state, the Pb atoms are disposed on the Pt cluster surface as well as in the polymer matrix itself. The electroadsorption of formic acid could occur on the active Pt sites, and the polymer, during the dedoping process, ejects the ClO_4^- anions.

In the oxidised state, the direct oxidation of formic acid, partial oxidation of the polymer with its consequent anion doping and total oxidation of the Pb atoms, which were not rejected from the modified electrode because Pb^{2+} ions could remain co-ordinated into the polymeric chains, all occur together.

Therefore, additional anion doping is required in order to maintain the electroneutrality of the electrodic system. This electrode, with a stable bimetallic system incorporated in the polymer matrix, shows important electrocatalytic activity, for the formic acid oxidation process. We must emphasize that the aim of this work was to contribute towards additional knowledge on the electrode P3MT/Pt/Pb as a bimetallic system which shows important electrocatalitic activity for the oxidation of formic acid.

5. Conclusions

Films of P3MT grown by the galvanostatic method show good adherence on ITO and graphite, but the electrode coating is not homogeneous. When polymerisation was carried out by consecutive square waves of potential, the polymers generated for $E_a = 1.4$ V and different E_r, the total Q_{red} was strongly dependent on the E_r, reaching a maximum value at $E_r = 0.2$ V. The films obtained are adherents, homogeneous and with an open structure. The degradation process proceeds with the number of cycles but none of the P3MT films loses half of its initial amount of charge. The rate of deterioration is very fast when the films are heated at temperatures between 100 and 300 K. The catalytic properties of Pt and Pb microparticles have been evaluated with good results in formic acid solution in comparison with a bulk platinum electrode. The current density peaks depend on the amount of Pb incorporated into the film. Under optimal conditions the current density peaks are increased by ca. 300%.

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