Electrocatalytic oxidation of methanol on (Pb) lead modified by Pt, Pt–Ru and Pt–Sn microparticles dispersed into poly(o-phenylenediamine) film

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Abstract

The electrocatalytic oxidation of methanol at a (Pb) lead electrode modified by Pt, Pt–Ru and Pt–Sn microparticles dispersed into poly(o-phenylenediamine) (PoPD) film has been investigated using cyclic voltammetry as analytical technique and 0.5 M sulfuric acid as supporting electrolyte. It has been shown that the presence of PoPD film increases considerably the efficiency of deposited Pt and Pt alloys microparticles toward the electrocatalytic oxidation of methanol. The catalytic activity of Pt particles is further enhanced when Ru and especially Sn, is co-deposited in the polymer film. The effects of various parameters such as concentration of methanol, medium temperature as well as the long term stability of modified electrodes have also been investigated.
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Keywords: Electrooxidation; Methanol; Fuel cell; Poly(o-phenylenediamine); Pt alloys; Cyclic voltammetry

1. Introduction

Fuel cells are devices in which an electrochemical reaction is used to generate electricity. A variety of materials may be suitable for use as a fuel, depending on the materials chosen for the components of the cell. Organic materials, such as methanol, are attractive choices for fuels due to their high specific energies. The direct anodic oxidation of methanol requires uneconomically large loadings of noble metals in the anode, even when the direct methanol fuel cell (DMFC) is operated at a high temperature, namely 130 °C [1–4]. The platinum and platinum alloy particles can be used as an effective electrocatalyst for oxidation of methanol in DMFC. Platinum alloy catalysts such as Pt–Ru [5–7], Pt–Sn [8–13], Pt–Pd [14], Pt–W–O [15], Pt–Ru–Sn–W [16] and Pt–Re [17]

in acidic solutions have been used for electrooxidation of methanol.

In the recent years, a large number of papers dedicated to the electrocatalytic properties of platinum group metals and their alloys incorporated into polymeric matrices have been published [18–22]. It has been shown that such modified electrodes exhibit better catalytic effects than smooth platinum for oxidation of organic fuels. Among these, polypyrrole, polythiophene and polyaniline have certain advantages rather than other conducting polymers, such as simplicity and rapidity of preparation of the polymer by chemical and electrochemical methods, chemical durability against aerial oxidation, possibility of being formed in aqueous electrolytic solutions and stability in such media [23].

However, it is of interest to extend such studies to other polymers, which might be suitable as host material of the catalyst microparticles. In this work, we first prepared Pb/Pt by electrodeposition of Pt microparticles

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at the Pb surface, because our various experiments show that *o*-phenylenediamine cannot be electropolymerized at the surface of a bare Pb surface. Then Pb/Pt electrodes were modified by electropolymerization of a thin layer of poly(*o*-phenylenediamine) containing dispersed Pt, Pt–Ru and Pt–Sn particles. In continuation, we investigated the electrooxidation of methanol in aqueous acidic solutions using these modified electrodes.

2. Experimental

2.1. Reagents

1,2-Phenylenediamine with pure grade product (98%) and hexachloroplatinic acid (10% solution), $SnCl_4 \cdot 5H_2O$, $K_2RuCl_5 \cdot 2H_2O$, methanol and sulfuric acid were pro-analysis grade and purchased from Merck. They were used without any further purification. All solutions were prepared in twice distilled water.

2.2. Apparatus

Potentiostat–galvanostat model DEA-332 in connection with an IMT-102 electrochemical interface from Radiometer was used as the voltammetric experiment apparatus. A three-electrode system constituted of a Pb (lead disc) (3 mm diameter) as working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode was used in this work. Data storage and processing were accomplished by means of a Pentium III computer connected to DEA-332 potentiostat.

2.3. Modified electrodes preparation

Prior to each experiment, the Pb electrode surface was mechanically polished first with 600 grit sand paper and then with 0.05 μm alumina powder to a mirror finish. The electrode was then washed thoroughly with acetone and distilled water. The modification of Pb electrode was performed in the following steps:

(a) Electrodeposition of a Pt monolayer at the surface of Pb disc performed by electroreduction of chloroplatinic acid (0.01 M) in 0.5 M sulfuric acid. Electroreduction was performed by a potentiostatic method. The electrode potential was fixed at −0.20 V (versus SCE).
(b) Electropolymerization of *o*-phenylenediamine at the Pb/Pt electrode was achieved by a potentiodynamic method. The electrode potential was swept between −0.2 and 1.2 V (versus SCE) (at a scan rate of 50 mV s^{-1}). An aqueous solution containing 0.50 M H_2SO_4 + 0.04 M $C_6H_4(NH_2)_2$ was used as electrolyte. The thickness of the deposited film was calculated from the charge consumed during the electrodeposition of P*o*PD film. The overall charge, *Q*, was integrated by DEA 332 digital analyzer and monitored automatically. This charge corresponds to

that passed during the anodic sweep of potential. For a given *Q*, the mass of deposited P*o*PD was estimated using the Faraday law, considering a value of 2 for *n* and 108 for 1,2-phenylenediamine molecular weight. Assuming a value of about 1.14 g cm^{-3} for P*o*PD density at 20 °C, and 0.0707 cm^2 for the geometric area of the electrode, the P*o*PD film thickness can easily be calculated. A mean value of 0.6 mm was obtained for polymer film thickness when *Q* was 130 mC cm^{-2} [24,25].

(c) Platinum, platinum–ruthenium and platinum–tin particles were incorporated in the polymer film by electrochemical deposition from an aqueous sulfuric acid solution containing 5×10^{-3} M H_2PtCl_6 (for Pb/Pt/P*o*PD/Pt), 2×10^{-3} M H_2PtCl_6 + 3×10^{-3} M $K_2RuCl_5 \cdot 2H_2O$ (for Pb/Pt/P*o*PD/Pt–Ru) and 3×10^{-3} M H_2PtCl_6 + 2×10^{-3} M $SnCl_4 \cdot 5H_2O$ (for Pb/Pt/P*o*PD/Pt–Sn) at a constant potential of −0.2 V (versus SCE).

3. Results and discussion

3.1. Electrooxidation of methanol

The oxidation of methanol was investigated at the Pb/Pt electrodes covered by a thin layer of poly(*o*-phenylenediamine) containing Pt and Pt alloys microparticles. Thus, a brief discussion about preparation of Pb/Pt/P*o*PD modified electrode seems to be proper initially. Our various experiments showed that *o*-phenylenediamine could not be electropolymerized at the surface of bare Pb electrode by potential cycling between −0.2 and 1.2 V versus SCE. It may be due to the fact that by application of potentials higher than −0.3 V, the Pb^{2+} species produced at the electrode surface can be combined with *o*PD to form Pb(*o*PD)$_2$$^+$ complexes. The insoluble Pb(*o*PD)$_2$$^+$ species acts as a nonconductive layer and prevents passing of current through the electrode surface. In fact at this condition the *o*PD$^+$ cation radicals (that act as initiator for electropolymerization) cannot be produced and consequently the electropolymerization does not occur. In addition, it is well known that the electropolymerization of *o*PD can be performed easily at the Pt surface [34]. Thus, initially we loaded Pt particles on the Pb surface by electrochemical deposition. The minimum amount of Pt loading at the Pb electrode surface for formation of a monolayer of Pt was calculated according to the following equation:

$$A = n \times 3.14 \times r^2$$

where *A* is the geometric surface area of the lead electrode, *r* the atomic radius of Pt atoms and *n* the number of Pt atoms.

In this case the diameter of Pb disc is 3 mm (*A* = 0.0707 cm^2), the atomic radius of Pt is 1.3 Å and the atomic mass of Pt is 195.078 g. With respect to this data we calculated that 0.043 μg for 0.0707 cm^2 Pb surface area (or 0.61 μg cm^{-2}) is necessary for formation of Pt monolayer. We investigated the effect of Pt loading amounts at
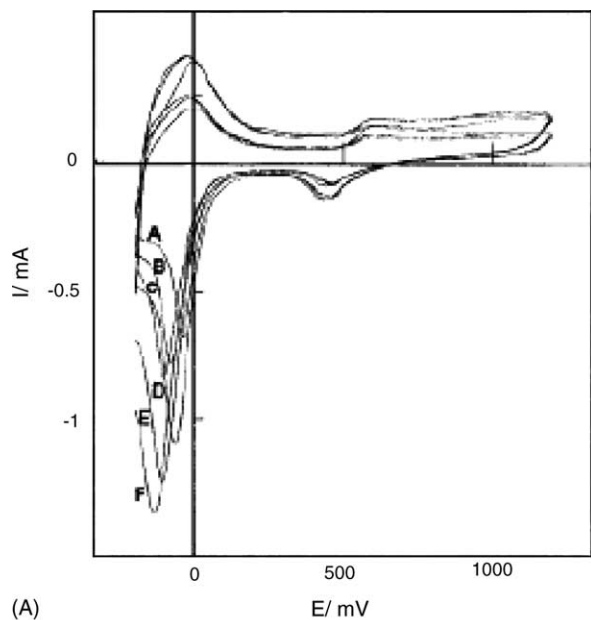
(A)
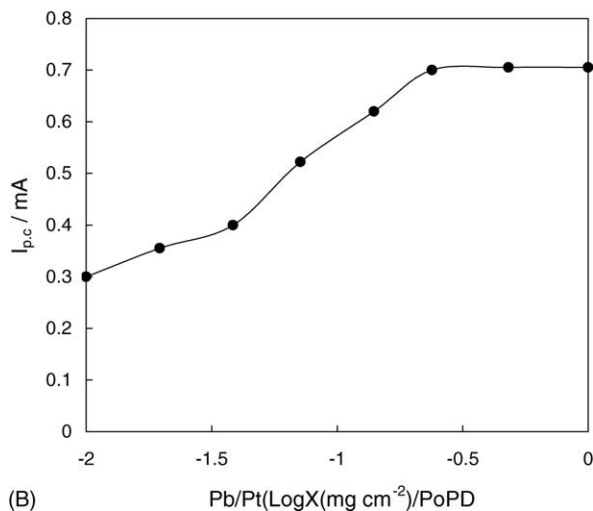
(B)

Fig. 1. (A) Cyclic voltammograms of Pb/Pt/P*o*PD electrodes with various Pt loadings on Pb surface, in 0.5 M H$_2$SO$_4$ (scan rate: 50 mV s^{-1}). (B) Plot of cathodic current ($I_{p,c}$) of mentioned voltammograms versus Pt loading at bare Pb electrode.

the Pb surface on the polymerization of P*o*PD at the electrode surface. For this purpose, similar Pb electrodes with different Pt loadings were prepared. Then the polymerization of P*o*PD was accomplished on these electrodes. The experiments showed that the electropolymerization does not occur at Pt loadings less than 0.01 mg cm^{-2}. At higher Pt loadings, the thickness of the polymer increases proportional to the Pt loading at the Pb surface. Then, a compact layer of polymer is produced. The results are shown in Fig. 1. Indeed, it can be said that to start electropolymerization of *o*PD, it is necessary to have deposition of more than a monolayer of Pt at the Pb surface. Our purpose was the use of Pb as a basic electrode with minimum Pt particles on that. Therefore we chose 0.05 mg cm^{-2} Pt loading at the Pb surface to prepare
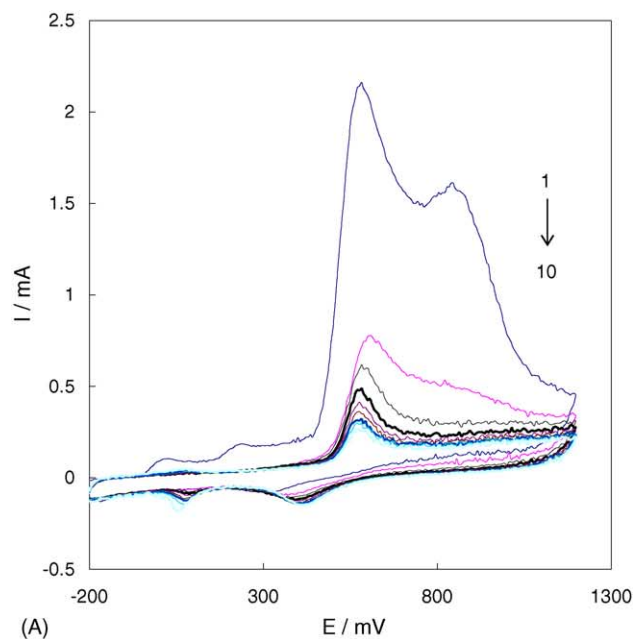
(A)
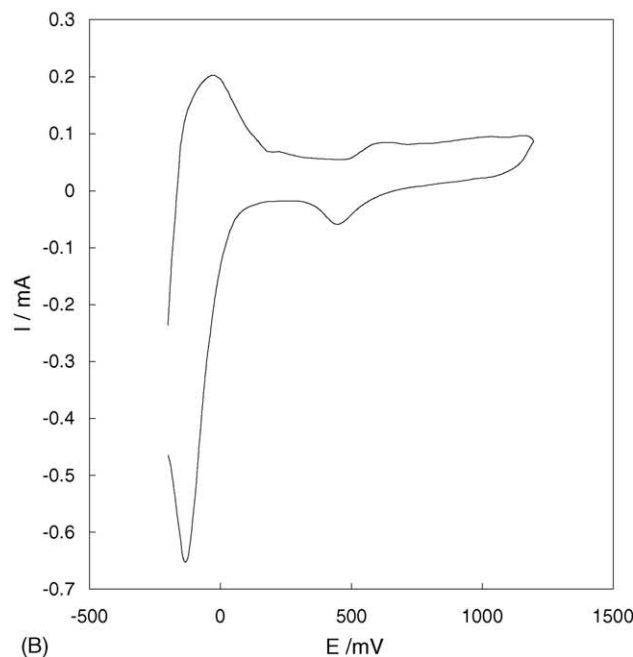
(B)

Fig. 2. (A) Electropolymerization of *o*-phenylenediamine (*o*PD) at the Pb/Pt (0.05 mg cm^{-2}) in 0.5 M H$_2$SO$_4$ solution containing of 0.04 M *o*PD. (B) Cyclic voltammogram of the Pb/Pt (0.05 mg cm^{-2})/P*o*PD in 0.5 M H$_2$SO$_4$. Scan rate: 50 mV s^{-1}.

modified electrodes. Fig. 2A indicates the polymerization of *o*PD at Pb/Pt (0.05 mg cm^{-2}) and Fig. 2B shows the cyclic voltammogram of the Pb/Pt (0.05 mg cm^{-2})/P*o*PD prepared electrode in 0.50 M H$_2$SO$_4$ at a scan rate of 50 mV s^{-1}.

The anodic current of CH$_3$OH oxidation depends on the amount of Pt deposited on the P*o*PD layer [26,27]. Fig. 3 shows the effect of Pt loading in P*o*PD on the anodic current of methanol oxidation. At Pt loadings less than 0.05 mg cm^{-2} there is a minor increase in anodic current, but with increase
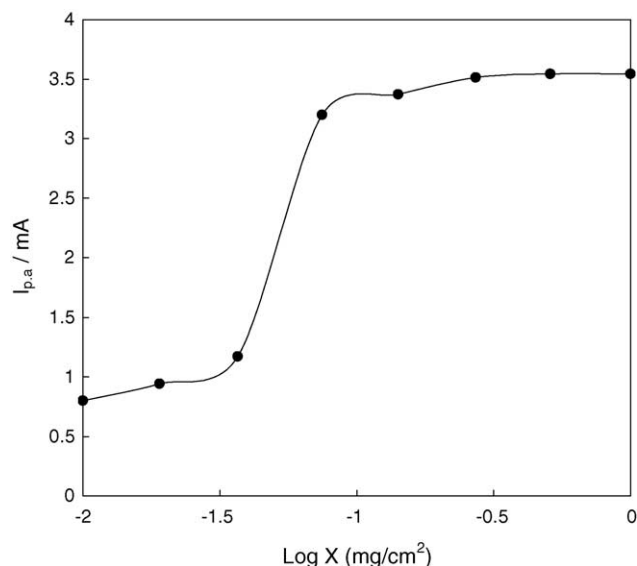
Fig. 3. Plot of anodic peak current ($I_{p,a}$) as a function of Pt loadings at the PoPD film (Pb/Pt (0.05 mg cm^{-2})/PoPD/Pt (x mg cm^{-2})) in solution containing 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH. Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}.

in the loaded Pt to 0.1 mg cm^{-2}, an extensive improvement in the electrocatalytic properties of modified electrode is observed. At higher amounts of Pt, the variation of $I_{p,a}$ is constant up to a value of 0.5 mg cm^{-2} Pt. This observation can be attributed to the saturation of active sites of the electrode surface at higher loadings. Whereas, at the lower loadings of Pt, the area of Pt particles is increased in proportion to increasing Pt loading, and the electrocatalytic activity of the modified electrodes is enhanced.

The conditions of dispersion of bimetallic electrocatalyst (Pt–Ru and Pt–Sn), in order to obtain an optimized electrode are very critical. These optimum conditions were found by systematically changing the relative concentration of the ruthenium and tin salts to platinum salt. These salts were chosen as the best compromise for electrodeposition carried out at a fixed potential, i.e., −0.20 V (versus SCE). Fig. 4A reports the values of the maximum current for electrooxidation of methanol (0.5 M sulfuric acid) obtained from voltammograms (recorded at 50 mV s^{-1}) versus Pt/Ru ratio in loading solution. The current increases abruptly and then a slight decrease is observed for very high Pt/Ru concentrations. This increase is due to a progressive formation of Pt–Ru microparticles with larger surface area inside the PoPD film, whereas, the decrease in peak current probably corresponds to the agglomeration of microparticles to form clusters with a smaller surface area. During this work, we intended to obtain the best catalytic activity at the lowest potential, and as a compromise, a relative concentration of (Pt 40%–Ru 60%) was chosen. Similarly, optimization of the electrode made by electrodeposition of platinum and tin was carried out by the same procedure as for Pt–Ru (Fig. 4B). The best results were obtained by (Pt 60%–Sn 40%).
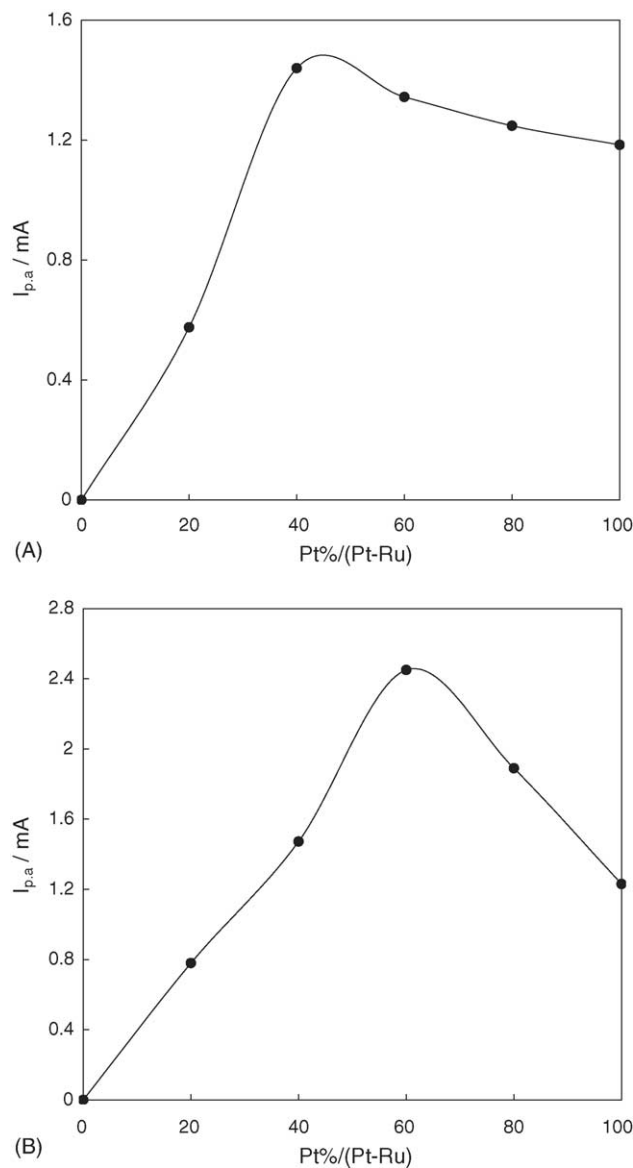

Fig. 4. Plot of anodic peak current ($I_{p,a}$) as a function of (A) Pt/Ru and (B) Pt/Sn ratio loading at PoPD film. Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}. Pt or Pt alloy loading: 0.05 mg cm^{-2}.

The typical cyclic voltammograms showing the electrooxidation of methanol at various modified Pb electrodes are given in Fig. 5. All cyclic voltammograms are recorded by sweeping the potentials from 0.00 to 1.00 V (versus SCE) and vice-versa, without any stay in initial potential. Voltammogram A of this figure corresponds to Pb/Pt (curve 1) and Pb/Pt/PoPD/Pt (curve 2) electrodes, respectively. It is clearly seen that the peak current for the oxidation of methanol increases from 0.46 mA (for Pb/Pt) to 1.2 mA (for Pb/Pt/PoPD/Pt), confirming the crucial effect of PoPD film on enhancement of platinum microparticles' efficiency towards the catalytic oxidation of methanol. Indeed, the PoPD film is a proper bed for deposition of electrocatalyst particles. It increases electrocatalysis active sites and the anodic current for oxidation of methanol is ultimately increased. Similar results

are obtained when platinum is replaced by Pt–Sn or Pt–Ru alloys. Meanwhile the peak currents are increased relative to those of Pt alone. This increase is very clear in the case of Pt–Sn loading. Fig. 5B and C exhibits the cyclic voltammo-
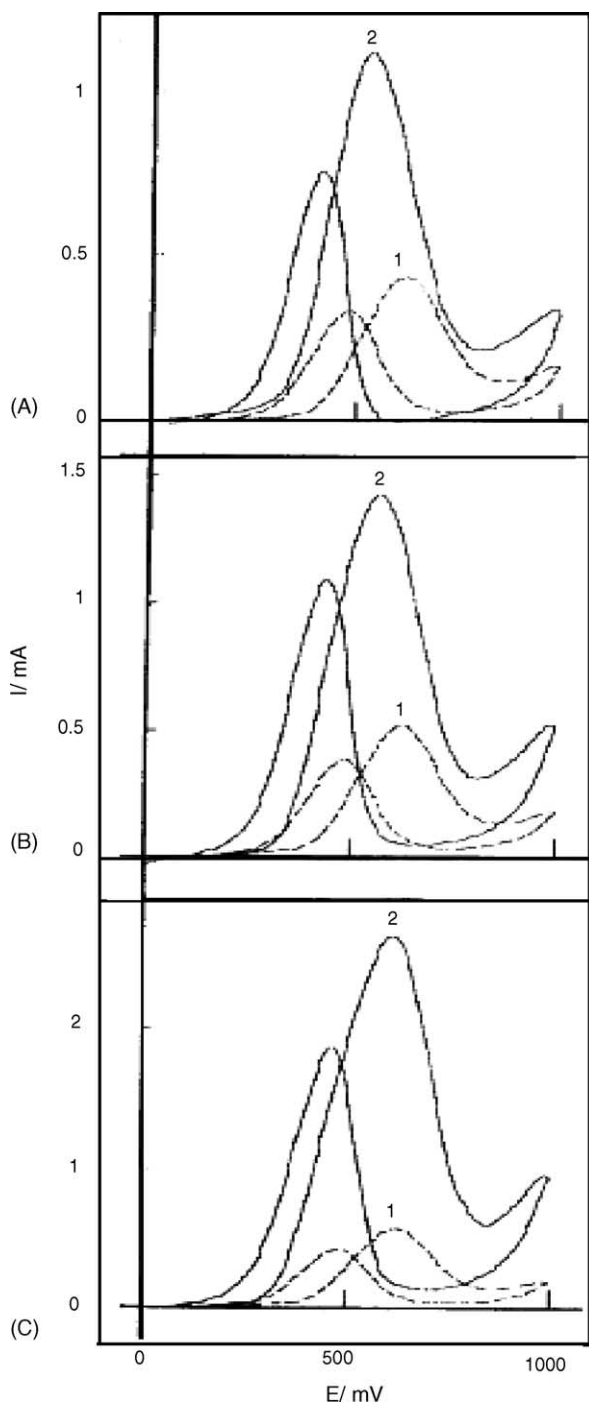

Fig. 5. Cyclic voltammograms of: (A) Pb/Pt (0.1 mg cm^{-2}) (curve 1), Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (0.05 mg cm^{-2}) (curve 2); (B) Pb/Pt (0.05 mg cm^{-2})/Pt (40%)–Ru (60%) (curve 1) and Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (40%)–Ru (60%) (curve 2); (C) Pb/Pt (0.05 mg cm^{-2})/Pt (60%)–Sn (40%) (curve 1) and Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (60%)–Sn (40%) (curve 2) in solution containing 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH. Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}. Pt or Pt alloy loading: 0.05 mg cm^{-2}.

grams obtained for electrooxidation of methanol at Pt–Ru and Pt–Sn loaded electrodes, respectively. These results clearly show that the presence of polymer film considerably enhances the catalytic current of methanol oxidation, especially in the case of Pt–Sn microparticles. This may be attributed to the large surface area of the electrode formed from Pt and Pt alloys particles in the polymer layer. On the other hand, it may also be due to the fact that the catalyst micro- and nanoparticles in polymer media are probably less sensitive to poisoning by adsorbed CO species [28].

When the electrode structure contains a dispersed co-deposit of Pt–Ru and Pt–Sn, the voltammogram corresponding to the oxidation of methanol shows an increase in peak current, especially in the case of Pt–Sn. Such an effect has been previously observed [29–31]. It has been interpreted as a bifunctional effect of the electrocatalyst on dissociative adsorption of methanol on platinum, mainly on CO adsorbed species. CO can be further oxidized to carbon dioxide due to the presence of Ru, allowing a sufficient coverage by OH species at lower potentials [35]. Indeed, it is assumed that the chemical properties of Pt and Ru surface atoms are similar to those of the respective monometallic surfaces, while the CO$_{ad}$ species formed in a methanol dehydrogenation step are mainly facilitated by Pt sites:

$$CH_3OH_{ad} \rightarrow CO_{ad} + 4H^+ + e^-$$

The removal of CO$_{ad}$ proceeds via adsorbed OH on both Pt and Ru sites formed by dissociative water adsorption:

$$M + H_2O \rightarrow OH_{ad} + H^+ + e^-, \quad M = Sn, Ru, Pt,$$

$$CO_{ad} + OH_{ad} \rightarrow CO_2 + H^+ + e^-$$
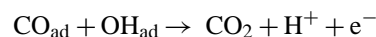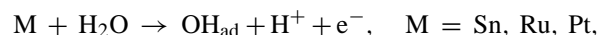
Due to the higher affinity of Ru and Sn towards oxygen-containing species, the amount of OH$_{ad}$ formed to support reasonable CO oxidation rates at lower potentials on Ru and Sn sites is more than that on Pt sites. This effect leads to a higher activity for the overall methanol oxidation process on Pt–Ru and Pt–Sn compared to Pt alone [35].

In addition, the polymeric matrix electropolymerized at the surface of the electrodes seems to provoke a change in the structure of platinum alloys deposits in the form of a decrease of the average particle size and an increase of the specific surface of the electrodes. An almost similar result has been reported for the deposition of some metals on bare and poly(*o*-phenylenediamine) modified glassy carbon electrodes. Probably the polymeric structure prevents the microparticles from agglomerating and coalescing during deposition and also stabilizes them on the electrode. A three-dimensional growth of deposited microparticles in the presence of a polymeric film instead of a two-dimensional growth at a bare electrode is also postulated [32–34].

In the case of a Pb/Pt electrode, the oxidation of methanol starts at around 0.2 V (versus SCE) while for Pb/Pt/P*o*PD/Pt it starts shortly earlier. Unlike the Pb/Pt electrode, Pb/Pt/P*o*PD/Pt current rises rapidly, as shown in Fig. 5A. Methanol oxidation starts at the same potential for

Pb/Pt/Pt–Ru, Pb/Pt/P*o*PD/Pt–Ru and also for Pb/Pt/Pt–Sn, Pb/Pt/P*o*PD/Pt–Sn.

The increase of oxidation current in the presence of a polymer layer indicates that the polymer can improve the adsorption of methanol on the catalytic sites, especially in the case of Pb/Pt/P*o*PD/Pt–Sn electrode. Another noticeable feature is the fact that in the case of the Pb/Pt/P*o*PD/Pt–Ru and Pb/Pt/P*o*PD/Pt–Sn electrodes, in contrast to the case of the corresponding polymer-free electrodes, the curves recorded during the positive and negative sweeps are close to each other, which is an indication of a weak poisoning effect (see Fig. 5B and C). This confirms that the poisoning decreases when the electrocatalysts are Pt alloys and are highly dispersed into a polymer film. A similar result has been reported for methanol oxidation at gold and glassy carbon electrodes modified by polyaniline and poly(*o*-phenylenediamine) films, respectively. These films contain dispersed platinum and platinum alloy microparticles [33,34].

The comparison behavior of different electrodes can also be seen in Fig. 6, where the peak currents for catalytic oxidation of methanol in similar conditions are illustrated. This figure shows, without ambiguity, that dispersed Pt–Sn prepared under precise conditions, is perhaps more active than dispersed Pt and Pt–Ru.

3.2. Parameters affecting the electrooxidation of methanol

3.2.1. Effect of methanol concentration

Fig. 7 shows the effect of methanol concentration on the anodic current of methanol oxidation. It is clearly observed
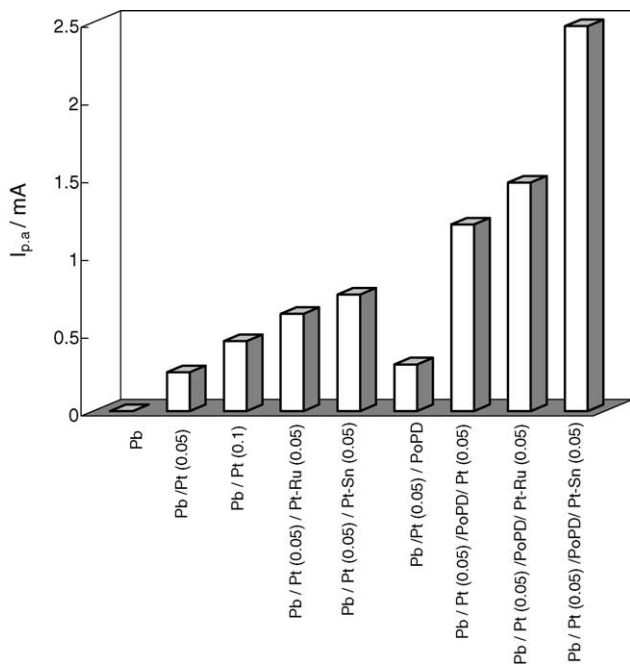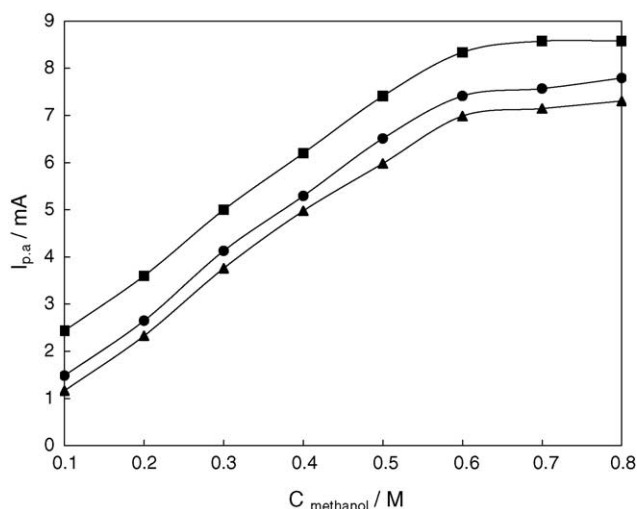

Fig. 7. Plot of anodic peak current ($I_{p,a}$) as a function of methanol concentration for: (■) Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (60%)–Sn (40%), (●) Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (40%)–Ru (60%) and (▲) Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (0.05 mg cm^{-2}) in solution containing 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH. Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}. R or Pt alloy loading: 0.05 mg cm^{-2}.

that the anodic current increases with increasing methanol concentration and levels off at concentrations higher than 0.6 M. It seems this effect is due to the saturation of active sites at the surface of the electrode. In accordance with this result, the optimum concentration of methanol to obtain a higher current density may be considered as about 0.6 M.
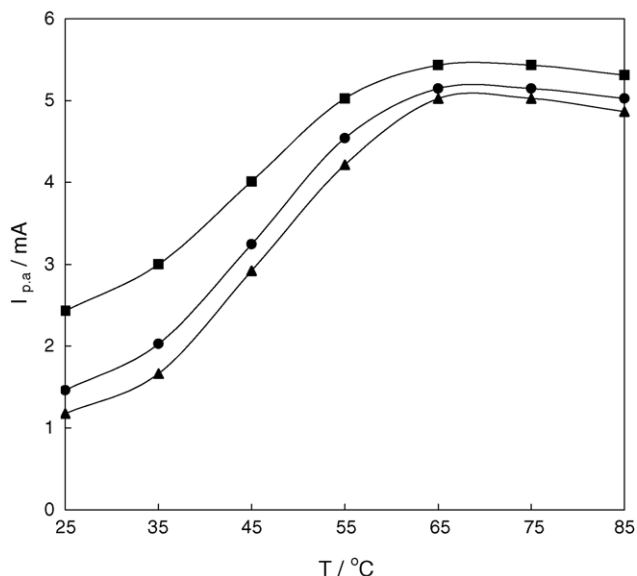

Fig. 6. Comparison of anodic currents for various Pb modified electrodes in solution containing 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH. Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}. Pt or Pt alloy loading: 0.05 mg cm^{-2}.

Fig. 8. Plot of anodic peak current ($I_{p,a}$) as a function of medium temperature for: (■) Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (60%)–Sn (40%), (●) Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (40%)–Ru (60%) and (▲) Pb/Pt (0.05 mg cm^{-2})/P*o*PD/Pt (0.05 mg cm^{-2}) in solution containing 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH. Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}. R or R alloy loading: 0.05 mg cm^{-2}.

3.2.2. Effect of medium temperature

The effect of medium temperature on the anodic current is shown in Fig. 8. A linear increase in the peak current with increasing temperature up to 65 °C is observed for the
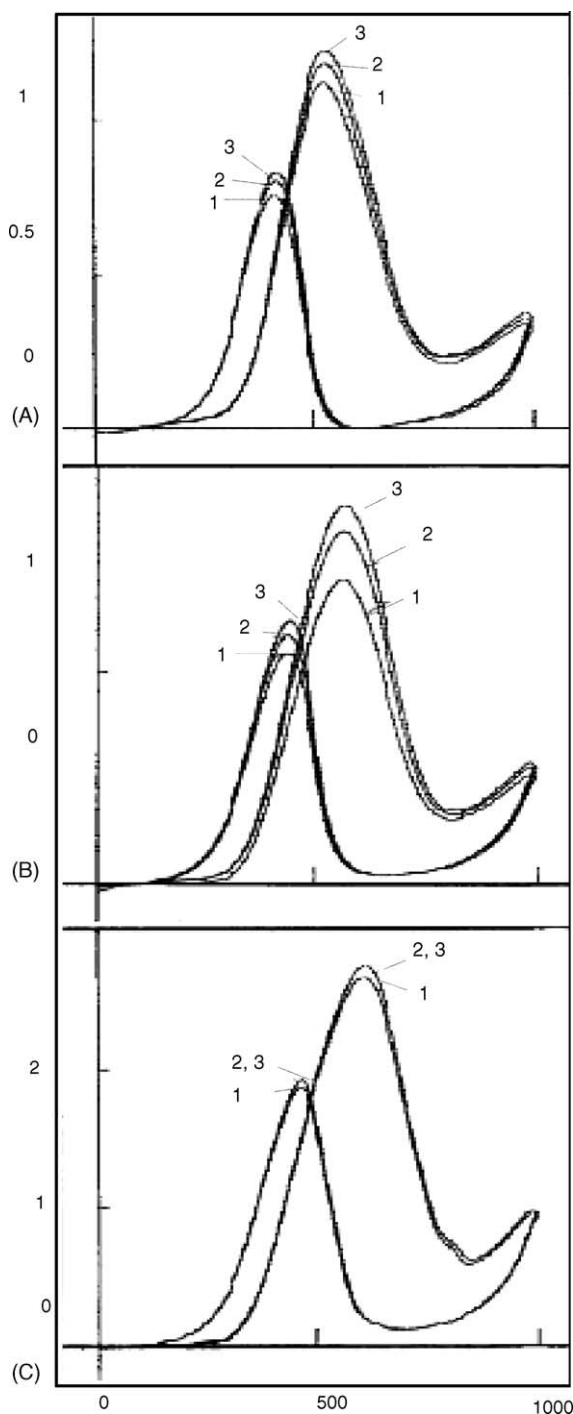
Pb/Pt/PoPD/Pt, Pb/Pt/PoPD/Pt–Ru and Pb/Pt/PoPD/Pt–Sn electrodes. It indicates an enhancement of the methanol oxidation rate with temperature. The next decrease of peak current can be attributed to the progressive evaporation of methanol with temperature increase. Assuming that no azeotrope is formed in the methanol and water mixture, it is expected that a progressive decrease in peak current appears during the temperature elevation, due to a loss in methanol concentration. However, a linear increase of the peak current is observed in practice at temperatures below 65 °C (the boiling point of methanol is 64.5 °C), which can be assigned to proportional acceleration of the electrode reaction kinetics with temperature.

3.2.3. The stability of the electrode responses

The stability of modified electrodes was examined by successive potential cycling and also in the course of time. Results are given in Figs. 9 and 10. As can be seen in Fig. 9, the responses of the electrodes increase in the first three cycles of potential then they become constant in the presence of methanol. It seems that the Pb acts as a co-catalyst for the oxidation of methanol and prevents the surface of electrodes being poisoned and increases the reproducibility of the electrode responses.

Fig. 10 shows the responses of electrodes stored in a laboratory atmosphere and in the course of time. The result indicates that, neglecting the weak decrease in peak current during the first 10 days, the responses are reproducible up 30 days.
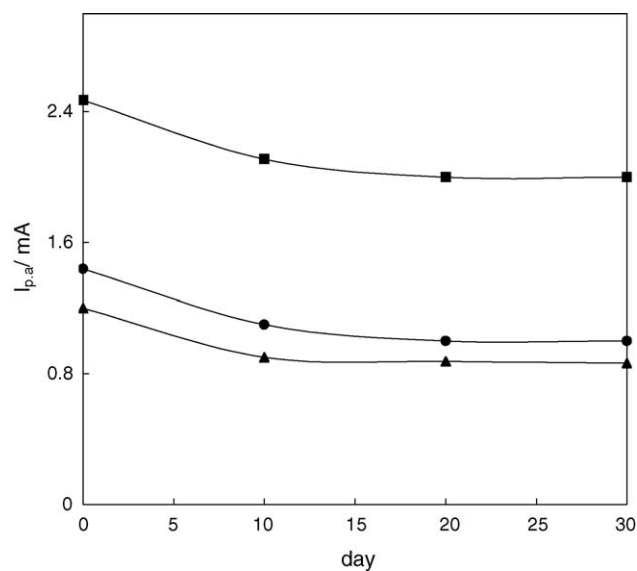

Fig. 9. Multicyclic voltammograms obtained for the oxidation of 0.1 M methanol in 0.5 M H$_2$SO$_4$ at: (A) Pb/Pt (0.05 mg cm^{-2})/PoPD/Pt (0.05 mg cm^{-2}), (B) Pb/Pt (0.05 mg cm^{-2})/PoPD/Pt (40%)–Ru (60%) and (C) Pb/Pt (0.05 mg cm^{-2})/PoPD/Pt (60%)–Sn (40%). Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}. R or R alloy loading: 0.05 mg cm^{-2}.

Fig. 10. Variation of anodic peak current during the time for: (■) Pb/Pt (0.05 mg cm^{-2})/PoPD/Pt (60%)–Sn (40%), (●) Pb/Pt (0.05 mg cm^{-2})/PoPD/Pt (40%)–Ru (60%) and (▲) Pb/Pt (0.05 mg cm^{-2})/PoPD/Pt (0.05 mg cm^{-2}) in solution containing 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH. Polymer film thickness: 0.6 μm. Scan rate: 50 mV s^{-1}. Pt or Pt alloy loading: 0.05 mg cm^{-2}.

4. Conclusions

The Pb/Pt electrodes modified by a thin film of poly(*o*-phenylenediamine) incorporating platinum and platinum alloys act as efficient catalysts for the oxidation of methanol. The reactivity of the electrodes is fully enhanced when an optimized mixture of Pt–Sn and Pt–Ru microparticles is deposited inside the P*o*PD film. The prepared electrodes exhibit satisfactory stability and reproducibility when stored in ambient conditions.

Acknowledgements

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