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A novel electrocatalytic polyaniline electrode for methanol oxidation

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Abstract

Pt clusters were electrodispersed on polymeric films to obtain catalytic electrodes for methanol oxidation. The electrodeposit was built up by applying either a constant potential or a repetitive square wave potential routine. The performance of the electrodes was followed by measuring the stripping peak potential of adsorbed CO, each assembly metal/Pani/Pt being characterized by SEM and EDAX. Polymeric electrodes, modified with Pt electrodeposited by the programmed potential variation had a better electrocatalytic activity for CO and methanol oxidation. The novel tailored electrode is the result of a balance between a particular morphology and the number of particles of the catalytic material on the conductive polyaniline matrix.

1. Introduction

Conductive polymers are important materials because of their specific properties, simple preparation and possible application to electrochemical energy conversion. Electrodeposited polyaniline (Pani) films grown under potentiodynamic conditions are easy to form in aqueous solutions. The polymer is a conductor in its partially oxidized state, which occurs in the potential range where most organic fuels oxidize. The possibility of dispersing metallic particles inside the polymer to obtain an electrocatalytically active Pani electrode is very attractive. In this respect, it has been reported that modified Pani electrodes have catalytic properties for organic fuel oxidation [1–4]. It has also been claimed that the use of a rigid matrix of conductive polymers allows a better dispersion of electrocatalytic particles to be obtained because agglomeration is prevented. Thus, a larger portion of the surface is able to participate in the selected reaction [5].

Among noble metals, platinum has the highest catalytic activity for methanol oxidation. Studies of methanol adsorption and oxidation on single-crystal surfaces of platinum have demonstrated that methanol is sensitive to the Miller indices of these surfaces [6, 7]. The adsorption of methanol to form linearly bonded CO is most extensive on Pt (1 0 0) and Pt surfaces having (1 0 0) terraces [8]. The major limiting factor in the catalytic reaction is the formation of adsorbed CO, which acts as a surface poison [9, 10]. It is known that adsorbed CO on Pt is distributed in islands where the oxidation of CO only takes place on the edge of the island [11]. If the islands were assumed to be located on terraces of the structure, Pt surfaces with different morphology would be expected to behave differently in the electrooxidation of methanol. Platinum as an electrocatalyst for methanol oxidation is not sufficiently active but there is an enhancement in its catalytic activity when it is combined with other materials that act as promoters, providing oxygen to facilitate the oxidation of chemisorbed CO [12]. Platinum and platinum-based alloys have been dispersed by constant potential deposition on Pani to activate various electrochemical reactions [2–4]. The electrocatalytic activity for such modified electrodes is similar to, or greater than, that of smooth Pt or bulk Pt/Ru alloy, even with low platinum loading.

It has been claimed that dispersed noble metal microparticles supported on high-area materials are of great significance to obtain effective catalysts. Thus, Kinoshita explained how carbon-supported small Pt particles, with size range of 3.5 to 6.0 nm and a defined crystallographic structure, exhibit the best performance for oxygen reduction [13]. However, there is considerable controversy about whether a size effect exists in methanol oxidation. The existence of an optimum size would be expected from the structure-demanding nature of the adsorption process. Watanabe, however, did not find any evidence for size effects [14].

The use of pulsating electrolysis at high frequency in a chloroplatinic acid solution induces the formation and growth of Pt crystallites with preferential crystallographic orientation on carbon-supported electrocatalysts [15]. Therefore, the electrodeposition mode influences the resultant cluster morphology.

The aim of this work is to present a novel polymeric electrode, which has been modified with Pt by using a periodical potential perturbation, scrutinize its morphology and compare its electrocatalytic activity to that of a polymeric electrode modified with Pt electrodeposited at constant potential.

2. Experimental details

Platinum and gold wires of 0.08 cm^2 geometric area were used as substrates for polymer film deposition, a gold foil was employed as counterelectrode and a saturated calomel electrode as reference. The working electrodes were prepared by modifying the metallic substrates (Pt or Au wires) with a Pani film, deposited by cyclic voltammetry at 0.1 V s^{-1} between −0.2 and 0.68 V, from a 0.1 M aniline 0.5 M H_2SO_4 solution [16]. The film thickness was determined from the anodic charge which was involved between −0.2 and 0.9 V, in a cyclic voltammogram run at 0.1 V s^{-1} in 0.5 M H_2SO_4 solution [17].

Platinum was electrodispersed on Au/Pani electrodes either by deposition from 0.01 M H_2PtCl_6 in 0.5 M H_2SO_4, at constant potential, or by applying a repetitive square-wave potential routine (RSWP) between –0.4 and 0.7 V, at 2.5 kHz for different times. Pt/Pani, Au/Pani and Pt electrodispersed Au/Pani electrodes were characterized by SEM and analysed by EDAX.

The electrocatalytic behaviour of the electrodes was followed through the stripping peak of adsorbed CO or by measuring the 0.5 M CH_3OH oxidation quasi-steady currents at several potentials. The CO stripping was run at 0.01 V s^{-1}, after the adsorption of CO at −0.2 V from CO-saturated 0.5 M H_2SO_4 for 10 min, and subsequent bubbling of nitrogen for another 10 min. All experiments were performed at room temperature.

3. Results and discussion

3.1. *Influence of the base metal on the electrocatalytic behaviour of Pani electrodes*

A cyclic voltammogram for adsorbed CO electrooxidation recorded at 0.01 V s^{-1} on a 0.1 μm thick Pani film,

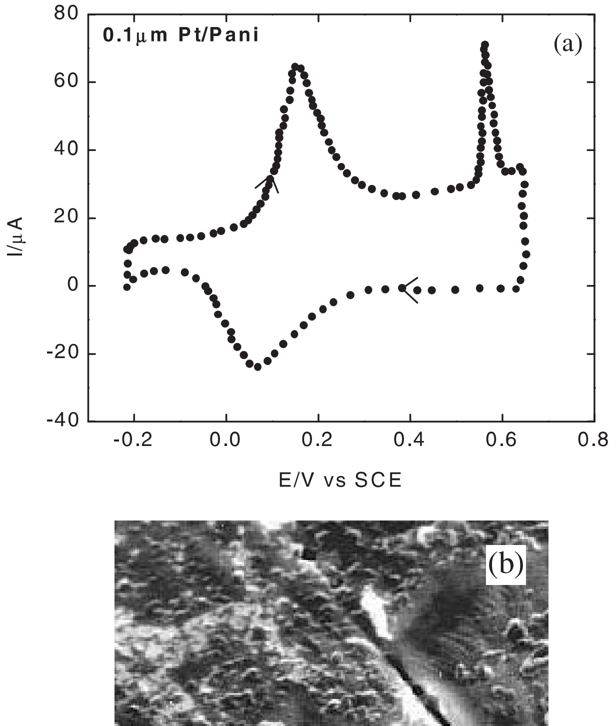

Fig. 1. (a) Stripping voltammogram for adsorbed CO on 0.1 μm thick Pt/Pani run at 0.01 V s^{-1} in 0.5 M H_2SO_4. Adsorption was performed at −0.2 V for 10 min; (b) SEM micrograph of the Pani covered Pt surface.

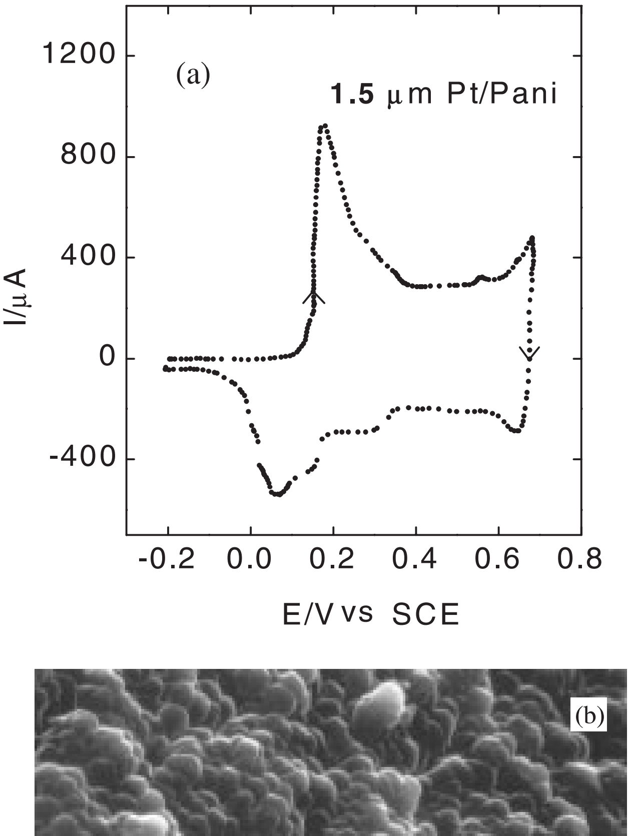

Fig. 2. (a) Stripping voltammogram for adsorbed CO on 1.5 μm thick Pt/Pani run at 0.01 V s^{-1} in 0.5 M H_2SO_4. Adsorption was performed at −0.2 V for 10 min; (b) SEM micrograph of the Pani covered surface.

grown on Pt, is depicted in Figure 1(a). The anodic peak at 0.59 V is associated with CO oxidation. The corresponding micrograph in Figure 1(b) reveals that the structure of the thin polymer coating is formed by nodular elements that partially cover the metallic substrate.

In Figure 2(a), the voltammetric stripping of adsorbed CO on a 1.5 μm thick Pani film is hard to see at 0.6V. The micrograph of the surface is shown in Figure 2(b). The electrocatalytic nature of the base metal is evident for Pani films thinner than 1.5 μm. This fact describes the noncompact nature of the polymeric film [18, 19].

3.2. *Electrodispersion of Pt on Au/Pani*

Au/Pani electrodes are inactive for methanol or CO oxidation. To obtain catalytic polymer electrodes, Pt is deposited on Au/Pani from a suitable chloroplatinic solution either at constant potential, E_d, or by applying the RSWP routine.

3.2.1. *Electrodispersion at constant potential*

The cyclic voltammograms for CO electrooxidation employing two different 0.9 μm thick Au/Pani electrodes, modified by Pt deposition at (a) $E_d = -0.22$ V for 60 s and (b) at $E_d = -0.14$ V for 100 s are shown in Figure 3 together with the micrograph of each surface. In the voltammograms, the small oxidation peak at about. 0.6 V indicates the presence of electrocatalytic Pt in the polymeric matrix, whereas in the micrographs it is possible to distinguish Pt particles, deposited in the film, of a size varying between 100 and 300 nm. If we take into account the coulombic charge recorded during the metal deposition, determine the real area throughout the CO stripping peak, and follow the same procedure described by Lamy et al. [4], the size of the particles are

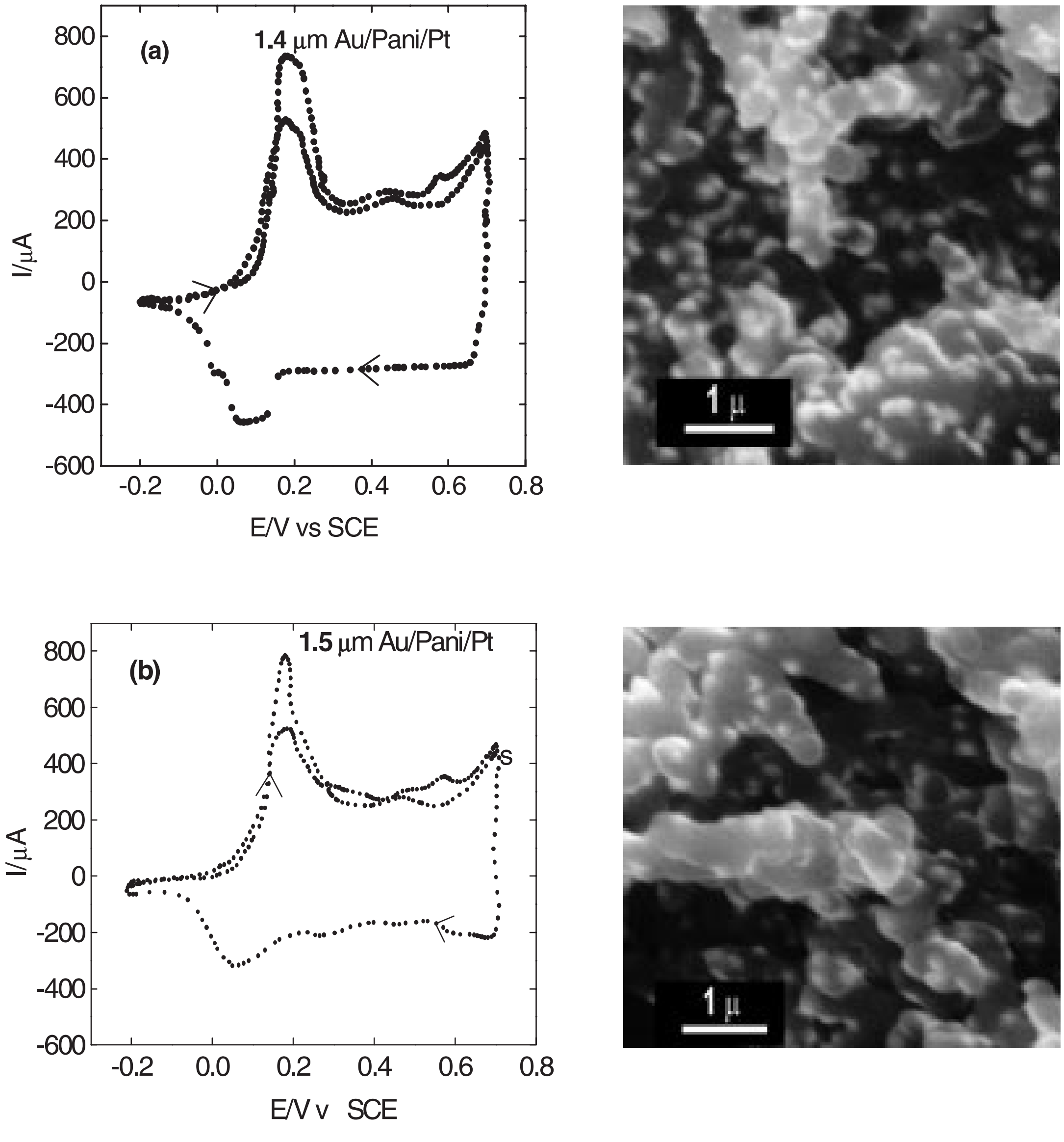

Fig. 3. Micrographs and stripping voltammograms for adsorbed CO run at 0.01 V s^{-1} in 0.5 M H_2SO_4 on of Pt/Pani a 1.5 μm thick Au/Pani electrode modified with Pt deposited at (a) $E_d = -0.22$ V for 60 s. (b) at $E_d = -0.14$ V for 100 s. CO adsorption was performed at -0.2 V for 10 min.

found to vary between 200 and 400 nm, in accordance with those measured in SEM micrographs.

When more cathodic Pt deposition potentials are applied, the calculated size of the particles increases to almost 1 μm. The stripping of CO adsorbed on Pani with Pt electrodeposited at −0.34 V, is shown in Figure 4(a). A micrograph is shown in Figure 4(b). The Pt particles are spread in a nonhomogeneous arrangement, the average size of the particles being of the order of 250 nm. It should be noted that the mismatch between the size measured in the micrograph and that calculated according to [4] is because of the charge consumed in H_2 evolution.

3.2.2. *Electrodispersion with a repetitive square wave potential routine, RSWP*

The peak potential values for CO oxidation obtained after applying the RSWP routine for different times on Au/Pani electrodes of 0.6 and 1.5 μm film thickness, respectively, are plotted as a function of the application time of the RSWP routine, in Figure 5. The lower the CO stripping peak value, the better the electrocatalytic properties of the modified electrodes. There seems to be an optimal application time region for the RSWP routine, which is located at ca 90 s for the thinner film and between 180 and 210 s for the 1.5 μm thick film. There is a 0.1 V cathodic shift in the CO stripping peak potential value for 1.5 μm thick Au/Pani/Pt modified by varying the application time of the RSWP routine from 30 to 180 s.

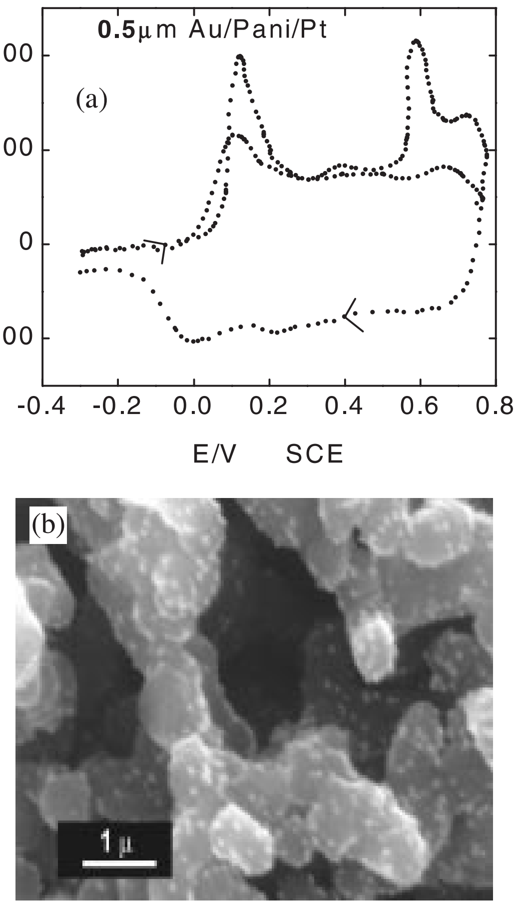

Fig. 4. Stripping voltammogram for adsorbed CO, run at 0.01 V s^{-1}, in 0.5 M H_2SO_4, on a 0.5 μm thick Au/Pani electrode modified with Pt deposited at $E_d = -0.340$ V for 140 s.

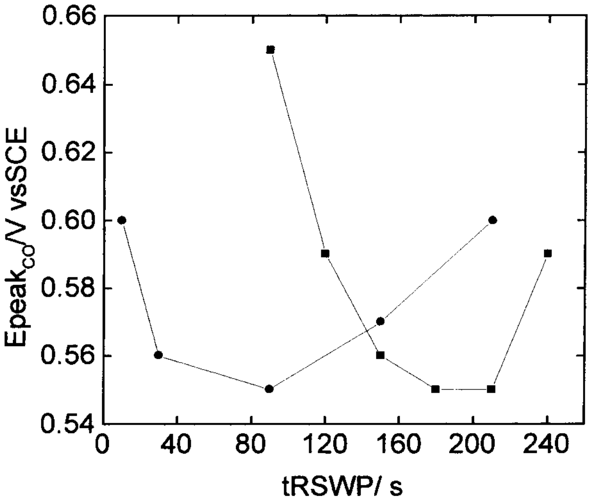

Fig. 5. CO stripping peak potential as a function of the application RSWP time for 0.6 μm (●) and 1.5 μm (■) thick Au/Pani electrodes. Adsorption was performed at −0.2 V for 10 min.

The cyclic voltammogram for CO electrooxidation applying a 180 s RSWP routine to the 1.5 μm Au/Pani/Pt electrode is shown in Figure 6(a), and the micrograph and the EDAX plot of the same surface are shown in Figure 6(b) and 6(c), respectively. The peak potential value of CO oxidation is located at ca 0.55 V. The peak involves a charge larger than that obtained with a Pt polymer modified using a constant deposition potential, (see Figure 3(a), (b)), which means that higher real areas are produced by RSWP. The micrograph in Figure 6(b), shows how the platinum particles tend to completely cover the globular polymer clusters.

We were unable to calculate the size of the particles in the same way as for the potentiostatic Pt deposition experiment because the RSWP signal is extended up to cathodic potentials at which not only Pt deposition, but also hydrogen evolution, take place at the same time. According to SEM micrographs, the particles are dispersed in the bulk of the Pani agglomerates and have a size in the region of 130 nm. The EDAX plot, Figure 6(c) shows the existence of Pt and Au in the modified electrode, atoms and also of other elements such as S and Cl, which are due to the composition of the working solutions.

Micrographs corresponding to different application times of the RWSP routine on 0.9 μm thick Au/Pani electrodes, modified with electrodispersed Pt, are shown in Figure 7 for increased application times, namely (a) 90 s, (b) 120 s, (c) 150 s and (d) 180 s. The micrographs of the modified surfaces show Pt particles of average size varying from 60 nm, for $t = 90$ s, to 130 nm for $t = 150$ s. The most noticeable variation is the number of Pt particles, which increases from 90 to 150 s.

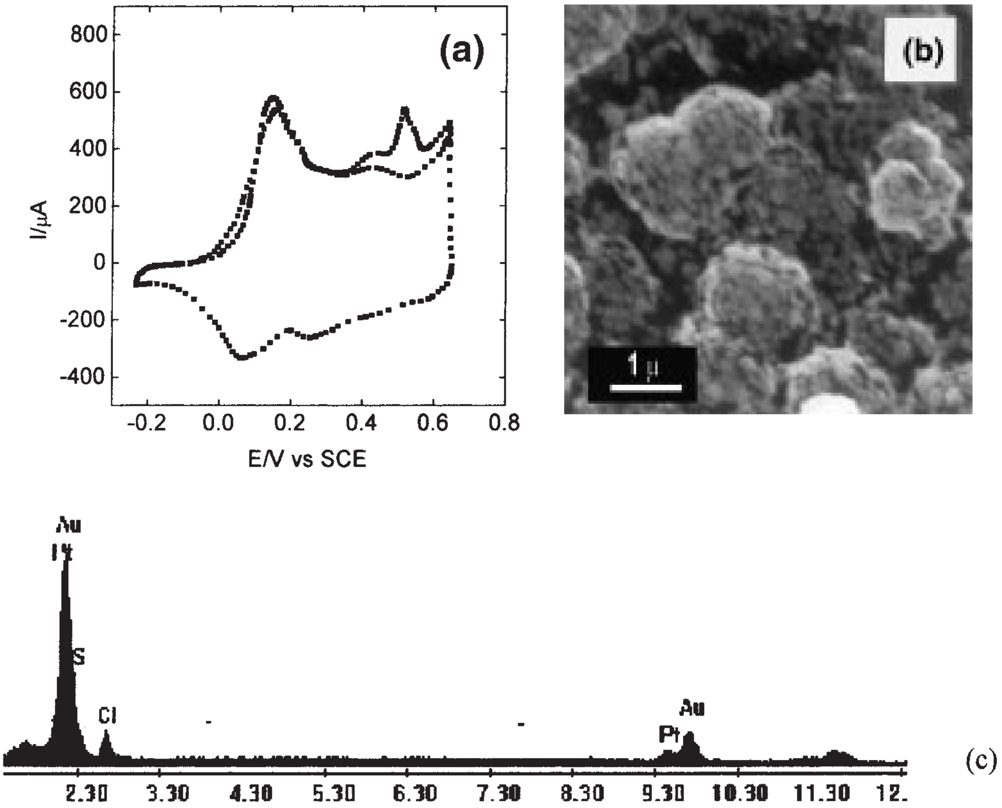

Fig. 6. (a) Stripping voltammogram run at 0.01 V s^{-1}, in 0.5 M H_2SO_4, for adsorbed CO on 1.5 μm thick Au/Pani electrode with Pt deposited after a 180 s application RSWP time. Adsorption was performed at −0.2 V for 10 min; (b) micrograph of the surface; (c) EDAX plot.

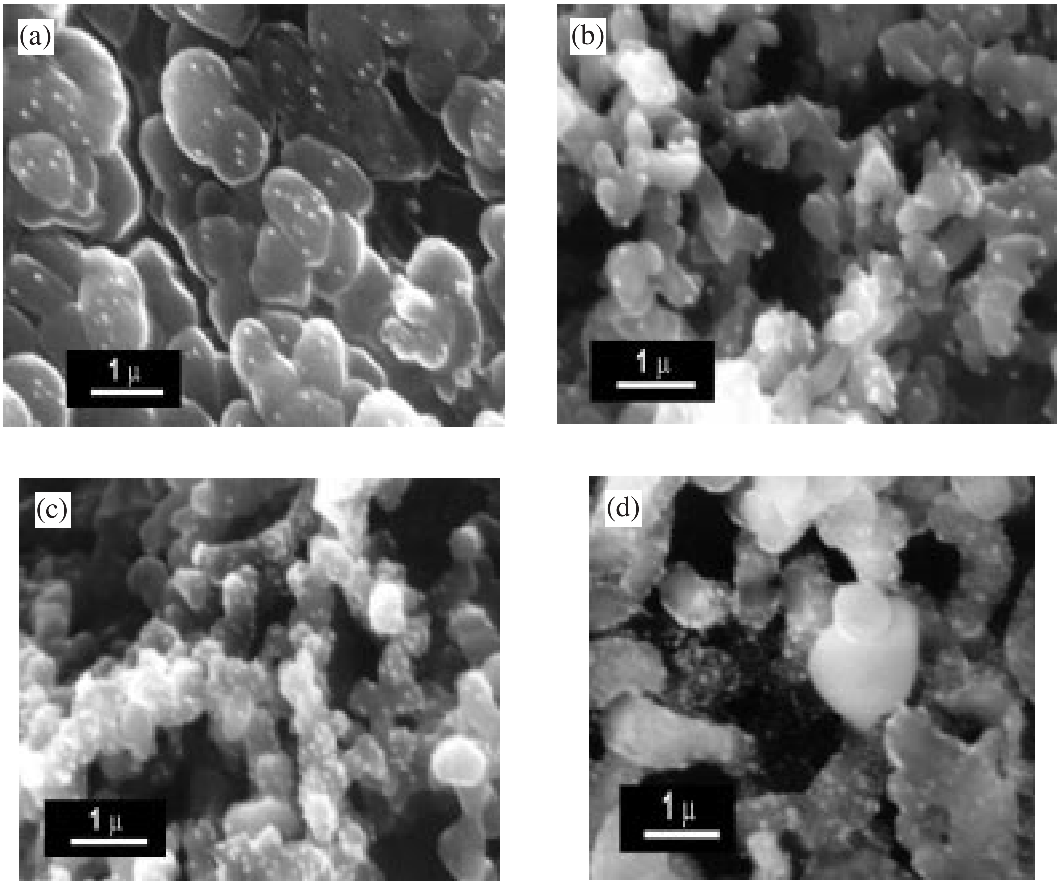

Fig. 7. SEM micrographs of 0.9 μm thick Au/Pani electrodes after Pt deposition for different application RSWP times, *t*: (a) 90, (b) 120, (c) 150 and (d) 180 s.

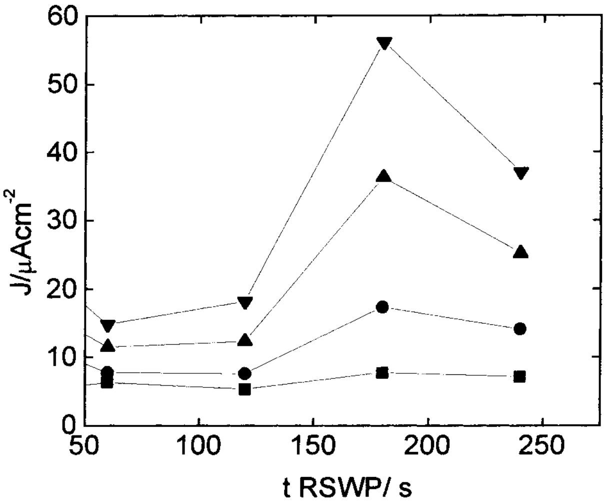

Fig. 8. Quasi-steady current density values for 0.5 M CH_3OH oxidation at different oxidation potentials on 1.3 μm thick Au/Pani modified with Pt as a function of the application RSWP time. Key: (■) 0.36, (●) 0.41, (▲) 0.46 and (▼) 0.51 V.

It is possible to describe different catalytic surfaces depending on the RSWP application time. In this respect, the enhancement of the catalytic properties of Au/Pani/Pt electrodes up to 150 s can be attributed to an increase in the number of small Pt agglomerates on the surface while the particle size remains almost constant. On the other hand, for RSWP application times higher than 150 s, the size of Pt agglomerates increases and its number diminishes, resulting in a low catalytic activity.

3.3. *Methanol electrooxidation on polymer modified electrodes*

The current density associated with 0.5 M CH_3OH oxidation on different 1.5 μm thick Pt electrodispersed polymer films at different oxidation potential values is plotted as a function of the application time of the RSWP routine in Figure 8. Current density values are referred to real areas determined through the CO oxidation charge taking as reference 420 $\mu C \equiv 1\ cm^2$. In this experiment there is an optimal application RSWP time to obtain better electrocatalytic behaviour, which for 1.5 μm thick Au/Pani/Pt corresponds to a surface perturbed for 180 s.

The morphology of the deposit appears to be the relevant factor in explaining the better electrocatalytic performance of the Pt RSWP modified polymer electrodes for methanol and CO oxidation. Further experiments to improve this novel electrode, by codispersing Pt and Ru by means of the RSWP routine, are in progress.

4. Conclusions

(i) Conductive polymer films deposited on a substrate such as Pt show catalytic properties for CO oxidation due to the nature of the metal, even with film thickness of about 1.5 μm.
(ii) Conductive polymers such as polyaniline grown on Au are suitable matrices for the electrodispersal of noble metals.
(iii) The RSWP routine proved to be a suitable method for electrodispersing Pt on Au/Pani films
(iv) The application of the RSWP routine on Au/Pani films improved the electrocatalytic properties of the modified Au/Pani Pt electrodes, shifting the CO stripping peak towards cathodic potential values.
(v) The application of the RSWP routine on Au/Pani films improved the electrocatalytic properties of the modified electrode for 0.5 M CH_3OH oxidation.
(vi) The thickness of the polymer film has a notable influence on the morphology of Pt deposits.

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