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# A catalytic platinum–ruthenium–polyaniline electrode for methanol oxidation

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## Abstract

Polyaniline films prepared on Au wires were employed as substrates to deposit Pt and/or Ru using a potential-programmed perturbation. Different compositions of Pt and Ru ions in acid electrolyte were employed to decorate the electrodes. The atomic percentages of Pt and Ru on Pani were determined by EDAX and particle size and distribution by SEM. The catalytic activity was tested for adsorbed CO and $CH_3OH$ electrooxidation. Nanoparticles of Pt–Ru with different Pt–Ru contents were obtained and characterized for each reaction.

## 1. Introduction

The search for suitable anode materials for methanol fuel cell faces two important obstacles related to the catalytic material and its distribution on a suitable matrix. For most of the electrode materials, the electrochemical reaction is limited to the catalytic surface. One way of getting a better distribution of the catalytic particles is to disperse the material within a convenient electron conducting matrix affording a three-dimensional array of the catalyst, thus, achieving efficient transport of charge from the underlying support electrode to the reaction site.

Polyaniline is a particularly attractive material as catalyst support because the polymer adheres strongly to the electrode surface and also has high conductivity and durability under conditions applicable to the operation of fuel cells employing aqueous acidic electrolytes [1]. The incorporation of metallic particles into polymer matrices has gained wide interest for electrocatalytic purposes [2].

Moreover, as adsorbed carbonyl species derived from methanol oxidation poison Pt catalysts, several composite systems have been investigated to improve the methanol oxidation rate, concluding that Ru is one of the most effective co-catalysts for Pt. The role of Ru is to provide oxygenated species to convert adsorbed methanol fragments on neighbouring Pt atoms into carbon dioxide. In this respect, Rolison et al. showed that in commercially available Pt–Ru blacks most of the Ru is present as hydrated Ru oxides, $RuO_xH_y$, which are considered the active species [3]. Moreover, it has been claimed that addition of Ru to Pt causes an increase in Pt d-band vacancies and contractions in the lattice parameters. The reduced CO adsorption energy on Pt–Ru is due to electronic modifications of the Pt atoms interacting with neighbouring Ru atoms [4]. The bifunctional mechanism for the electrocatalysis of methanol oxidation needs to be modified to take into account Ru electronic effects on Pt [5]. Different binary Pt–Ru materials have been prepared, namely Ru adatoms or Ru nanoparticles on Pt polycrystal and single crystal electrodes [6–10], Pt–Ru nanoparticles [11, 12], Pt–Ru bulk alloys [13, 14], carbon-supported Pt–Ru alloys [15, 16] and Pt–Ru electrochemically codeposited on Au electrodes [17].

The application of a repetitive square wave potential signal (RSWPS) is a suitable method for obtaining a better electrodispersion of Pt on Pani films, thus improving the electrocatalytic properties of the modified electrodes for methanol oxidation [18]. Only one or two different alloy compositions have been employed in most of the works on Pt–Ru codeposition on Pani, but the full composition range has not been investigated systematically. In this work, a wide range of Pt and Ru compositions in solution were employed to obtain Pt–Ru Pani electrodes applying the RSWPS technique. The goal is to ascertain the composition, which yields the best Pt–Ru ratio on the polymeric matrix to improve the oxidation of adsorbed CO and methanol.

## 2. Experimental details

Conventional three-electrode electrochemical cells were used. The working electrodes were Au wires of about

$0.08\ cm^2$ geometric area covered with a polyaniline film; the counter electrode was a $2\ cm^2$ Au foil and the reference electrode was a reversible hydrogen electrode. All the potentials are referred to this electrode.

Pani films were built up on Au wires by electropolymerization of the monomer from 0.1 M aniline + 0.5 M $H_2SO_4$ cycling the potential between 0.0 V and 0.90 V at 0.1 V $s^{-1}$. The film thickness was calculated through the anodic charge involved between 0.0 V and 1.20 V in the voltammogram recorded at 0.10 V $s^{-1}$ in 0.5 M $H_2SO_4$ [19]. The average thickness of the films was about 0.5 $\mu$m.

Pani electrodes were decorated with Pt–Ru particles using a repetitive square wave potential signal (RSWPS) between a lower potential $E_l = -0.20$ V and an upper potential $E_u = 0.60$ V with a frequency of 2.5 kHz for a time $t = 10$ min. Aqueous acid solutions of $H_2PtCl_6$ and $RuCl_3$ with concentrations varying in the range $0.002\ M \leqslant C_{H2PtCl6} \leqslant 0.05\ M$ and $0.013\ M \leqslant C_{RuCl3} \leqslant 0.1\ M$, respectively, both in 0.1 M $HClO_4$ were employed.

The catalytic performance of the Pt–Ru Pani electrodes was evaluated for the oxidation of 0.5 M $CH_3OH$ + 0.1 M $HClO_4$ and adsorbed CO, applying electrochemical techniques such as stripping voltammetry and chronopotentiometry. Real areas were determined considering the anodic charge involved under the CO stripping peak ($1\ cm^2 \equiv 420\ \mu C$).

The electrode surfaces were examined by SEM and their compositions determined by EDAX. All experiments were performed at room temperature.

## 3. Results and discussion

Chemical and/or physical attraction between the ions and the substrate is needed to give stable and reproducible electrodeposits of Pt–Ru on Pani electrodes.

To obtain Pt–Ru Pani electrodes, the $E_u$ value found for RSWPS Pt deposits on Pani [18] was modified, since at potentials above 0.7 V, corrosion and loss of Ru has been reported [13]. In this sense, the initial attempts to get Pt–Ru deposits were accomplished after applying RSWPS to a Pani electrode, immersed first in 0.05 M $H_2PtCl_6$ and then in 0.1 M $RuCl_3$. In Figure 1, the stripping voltammogram of adsorbed CO on a Pt–Ru Pani electrode shows a remarkable displacement of the CO stripping peak potential, $E_{peakCO}$, when Ru is present on the surface. CO is adsorbed on Ru and Pt sites coexisting in a wide potential region between 0.4 and 0.8 V. It has been demonstrated that Ru sites nucleate oxygenated species at low potentials producing a reduced overpotential for CO oxidation [13]. EDAX analysis of the sample resulted in a composition of 56.4 at.% Pt and 43.6 at.% Ru.

When RSWPS was applied to a Pani electrode immersed first in $RuCl_3$ and then in $H_2PtCl_6$, Pt deposits were obtained according to the stripping CO signal but Ru–Pt was not deposited. All attempts to get Ru deposits on Pani applying RSWPS in 0.1 M $RuCl_3$ solution failed since no Ru signal was detected by EDAX, SEM micrographs did not show deposited particles and no CO stripping signal was measured. Pt deposits on Pani are achieved because the reduction of Pt(IV) to Pt(0) occurs at potentials above that corresponding to the first oxidation potential peak of the polymer that acts as a mediator in the metal deposition process. An explanation for this behaviour is to consider that the film is conductive in the oxidized state and nonconductive in the reduced state [20]. In solutions of commercial $RuCl_3$ + 0.1 M $HClO_4$, species such as $[RuO(H_2O)_4]^{2+}$ and Ru(IV) have been reported [21]. In the case of Ru deposition potentials below 0.47 V have to be applied to obtain Ru(0) [22].

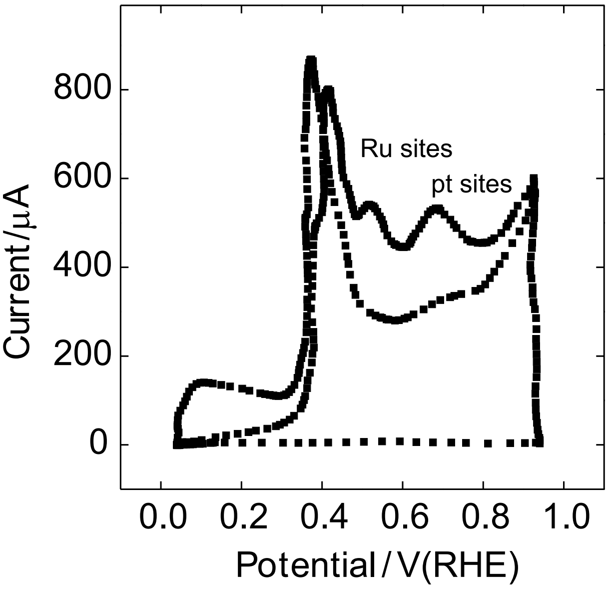

*Fig. 1.* Stripping voltammograms of adsorbed CO on Pt–Ru Pani film, 0.5 $\mu$m thickness, obtained applying RSWPS for 15 min in $H_2PtCl_6$ solution plus 8 min in $RuCl_3$ solution.

It is well known that the position of the standard potentials according to the electrochemical series is by no means conclusive for the possibility of discharge of two different metal ions. In the electrolysis of solutions of a certain composition the behaviour expected on the basis of the electrochemical series is often reversed. It is possible to vary the deposition potential of a metal within wide limits by changing, not only the concentration of the salt of a given metal, but also the total concentration of all the charged species in the solution [23]. Working solutions containing variable concentrations of Pt and Ru ions were prepared to obtain particles with a different Pt–Ru ratio deposited on Pani electrodes. The ratios employed between $H_2PtCl_6$ and $RuCl_3$ concentrations, $R$, are collected in Table 1.

The atomic percentages of Pt and Ru on the films for different $R$ values obtained from EDAX analysis, are shown in Table 2. EDAX data correspond to bulk particles and may differ from the surface values due to surface segregation. When the $RuCl_3$ concentration (0.05 M) is fixed and the $H_2PtCl_6$ concentration is

*Table 1.* Ratio of $H_2PtCl_6$ and $RuCl_3$ concentration in aqueous acid solutions

| $[H_2PtCl_6]$/M | $[RuCl_3]$/M | $R$ |
|---|---|---|
| 0.02 | 0.013 | 1.5 |
| 0.02 | 0.02 | 1.0 |
| 0.02 | 0.025 | 0.8 |
| 0.02 | 0.033 | 0.6 |
| 0.02 | 0.05 | 0.4 |
| 0.02 | 0.08 | 0.25 |
| 0.004 | 0.05 | 0.08 |
| 0.002 | 0.05 | 0.04 |

*Table 2.* Catalyst composition derived from EDAX
Catalyst prepared by RSWPS, $t = 10$ min; $[H_2PtCl_6] = 0.02$ M.

| $R$ | Pt/at.% | Ru/at.% |
|---|---|---|
| 0.04 | 17 | 83 |
| 0.08 | 15 | 85 |
| 0.4 | 65 | 35 |
| 0.6 | 68 | 32 |
| 0.8 | 64 | 36 |
| 1.0 | 56 | 44 |
| 1.5 | 59 | 41 |

lowered, the amount of Pt on the film decreases. The Ru percentage on the film increases for $1.5 < R < 0.4$, obtained by fixing the $H_2PtCl_6$ concentration (0.02 M) and decreasing the $RuCl_3$ concentration steadily.

Stripping voltammogram of adsorbed CO on a Pt–Pani electrode (Figure 2(a)) and on a Pt–Ru–Pani electrode (Figure 2(b)), both obtained after 10 min RSWPS are shown. The effect of Ru addition on Pt is measured throughout the shift of the onset of CO oxidation towards lower potentials on Pt–Ru Pani compared to Pt Pani electrodes [18].

Pt–Ru deposits on Pani are obtained taking into account that Pt is easily reduced on the film and that the potential of zero charge is about 0.2 V for Pt and about −0.25 V for Ru [20]. Thus, at $E_1 = -0.2$ V, the Pt would be negatively charged and the deposition of Ru on Pt should be more rapid than on Ru [24]. It is important to point out that the formation of alloys is accompanied by a change in the free energy of the components and, hence, the equilibrium potential of each metal should shift positively.

The dependence of the cathodic charge corresponding to the deposition process on the Ru atom percentage is shown in Figure 3(a). An increase in the cathodic charge occurs when the Ru content increases from 0 to 36 at.%. A subsequent increment in the surface Ru concentration leads to a decrease in the cathodic charge. This behaviour is related to the different amount of charge required to deposit Pt or Ru. The same qualitative behaviour is noticed when the dependence of the real electrode area on Ru atom percent (Figure 3(b)) is considered. It is known that, just like Pt, Ru adsorbs CO resulting in a higher real surface area measured for Pt–Ru Pani in comparison to Pt alone. A Ru content of about 30 at.% yielded the largest area. For higher Ru percentages, Ru atoms covered the deposited Pt and a coalescence of the deposited particles resulted in larger particles; consequently real area values diminished.

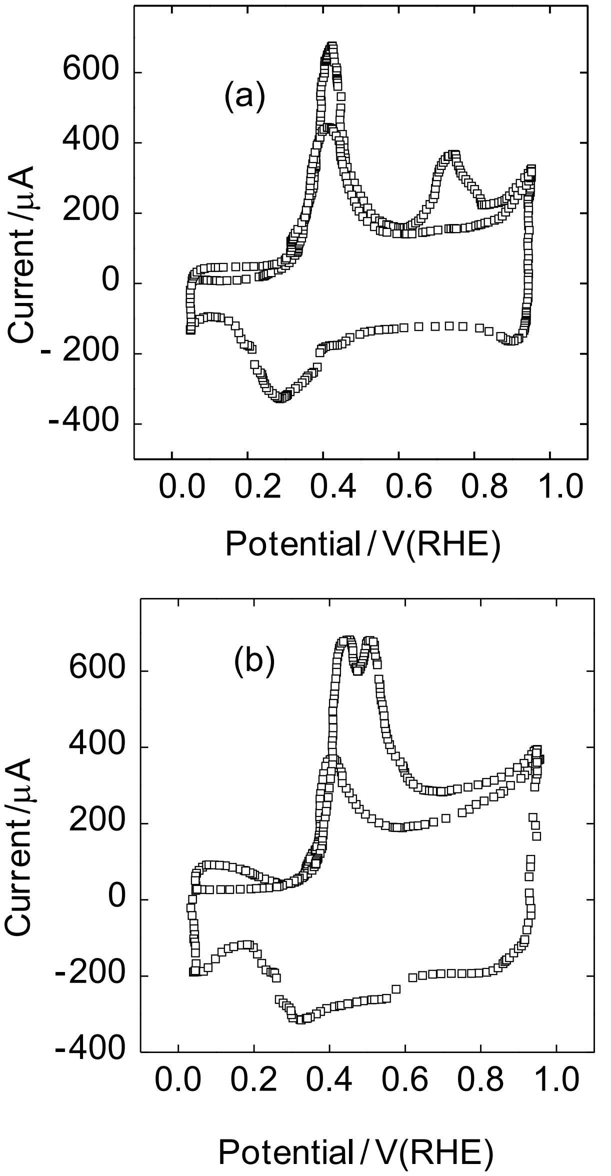

*Fig. 2.* Stripping voltammograms of adsorbed CO on catalytic Pani films, 0.5 μm thickness, covered with 10 min RSWPS deposit of (a) Pt and (b) Pt–Ru, $R = 1$.

The CO stripping peak potential value, $E_{\mathrm{peakCO}}$, on different catalysts as a function of Ru atom percent is shown in Figure 4. Ru atoms seem to be deposited on Pt clusters making CO oxidation possible on or around Ru particles acting as sinks for mobile CO adsorbed on Pt, leading in all cases to CO peak values more negative than that obtained with a Pt–Pani electrode ($E_{\mathrm{peakCO}} =$ 0.73 V) [18]. For a Ru content around 45 at.%, a value close to that reported as the best Pt–Ru ratio on a surface to electrooxidize CO [13], a minimum at about 0.47 V is attained.

Atomic percentages of Pt and Ru on Pani films for $R = 0.6$, obtained by applying RSWPS for different

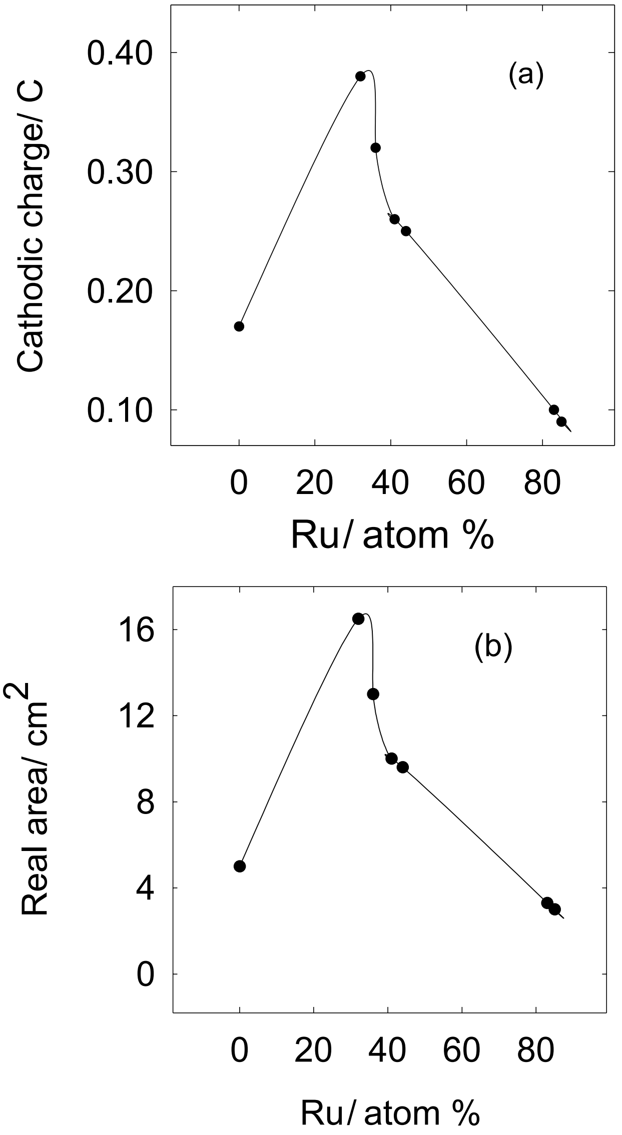

*Fig. 3.* (a) Dependence of the cathodic charge measured during the application of 10 min RSWPS as a function of Ru content. (b) Dependence of the real area with Ru content.

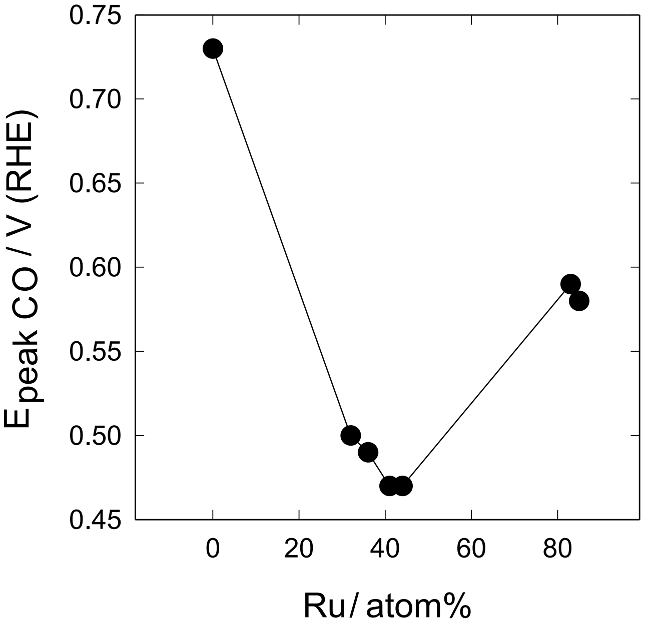

*Fig. 4.* CO stripping peak potential against Ru content, on Pt–Ru Pani films.

*Table 3.* Catalyst composition for different RSWPS application times Catalyst prepared by RSWPS, $R = 0.6$, $[H_2PtCl_6] = 0.02$ M.

| $t$/ min | Pt / at.% | Ru / at.% |
|---|---|---|
| 1 | 76 | 24 |
| 10 | 68 | 32 |

times are assembled in Table 3. As expected, for 1 min the Pt amount on the matrix is higher than that obtained for 10 min.

The deposition process can be interpreted as follows:

(i) Pt ions are reduced to Pt(0) more easily than Ru ions to Ru(0). This fact is experimentally proved in Table 3 where it is shown that the Pt content on the electrode is higher at short times and decreases as the time of RSWPS increases. Indeed, Ru ions needed to have Pt atoms on Pani in order to be reduced to Ru(0).

(ii) Deposits by RSWPS on Pani consist of Pt–Ru clusters. To a first approximation we assumed that each cluster grows independently of the other. As a result, the current consumed for the discharge of each kind of ion at a given potential should be lower in the case of codeposition than in the deposition of only one type of ion. In codeposition process, there is a change in the double layer structure. The concentration of ions within the double layer would be lower compared to the case of separate deposition because of a partial displacement of ions of one type by ions of another. This should cause a decrease in the reduction reaction rate.

(iii) The striking fact is that on Pani, Ru atoms seem to need Pt atoms to be anchored; subsequently, Ru could be piled on initial Ru atoms deposited on Pt, and then on the first row of Ru atoms. Then, a competition between Pt and Ru ions for being deposited takes place. Pt and Ru can be alloyed but they may also coexist as unalloyed metals.

The outermost surface layer composition is an important factor to determine the activity of a catalyst. A strong surface segregation of the metals in an alloy may occur. It has been reported that for bulk compositions of Pt–Ru alloys with a Pt content from 20 to 60 at.%, clean annealed Pt–Ru particles are Pt surface enriched by approximately 87 at.% Pt [25].

As for CO oxidation, for methanol there is a Ru percentage value, that exhibits the highest current density (i.e., 32 at.%). In Figure 5, the quasi-stationary current density at 0.5 V for methanol oxidation is plotted as a function of Ru content. Considering the possible use of RSWPS Pt–Ru Pani electrodes in DMFC

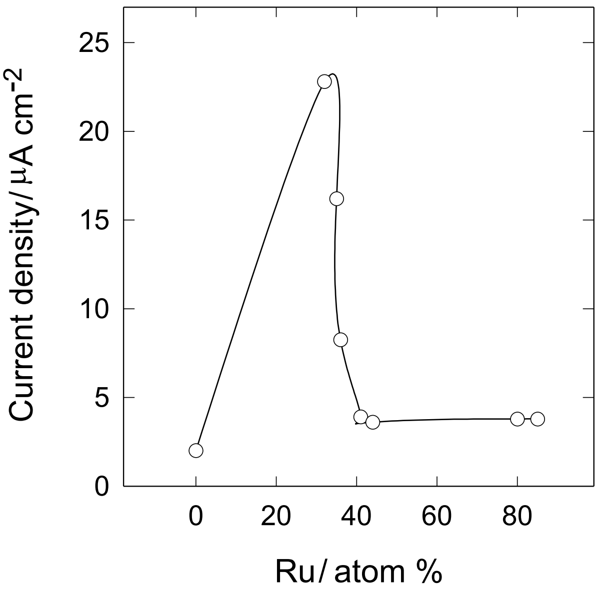

*Fig. 5.* Dependence of the current densities for methanol oxidation as a function of Ru content, after 5 min at $E = 0.5$ V in 0.5 M $CH_3OH$.

(direct methanol fuel cells), it must be pointed out that the operating temperature of these cells is higher than that used in this study. It is worth noting that Hable et al. probed their Pt–Ru Pani assemblies for methanol oxidation, increasing the operating temperature to the methanol boiling point, reporting a steady increase in the catalytic activity. However, these results are variable at higher temperatures due to degradation of the catalysts [1]. Moreover, Lima et al. reported measurements with Pt–Ru–Mo Pani anodes in a single DMFC cell, at 95 °C, confirming the results obtained in a classical three-electrode cell, although the performances were modest compared to those generally obtained in a DMFC [26].

SEM micrographs obtained for a catalyst with 32 at.% Ru show a wide spread of catalytic particles of an average size of about 90 nm distributed over the whole polymeric film (Figure 6). It should be emphasised that the RSWPS technique applied to metal deposition results in smaller particles compared to the potential cycling method which leads to Pt–Ru particles of 300–500 nm size deposited either on glassy carbon [27] or Pani [1].

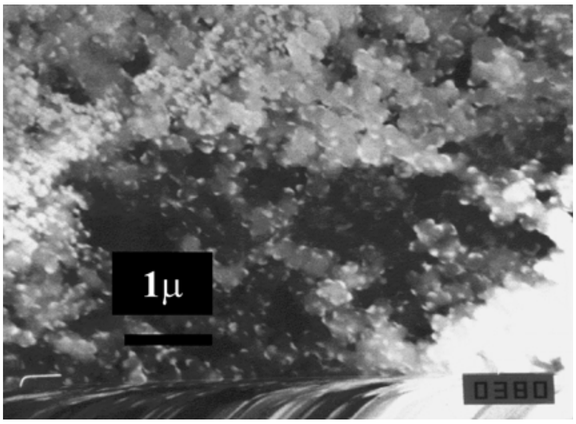

*Fig. 6.* SEM micrograph of a Pt–Ru Pani electrode (32 at.% Ru, obtained applying 10 min RSWPS).

## 4. Conclusions

(i) Co-deposition of Ru and Pt ions from suitable combinations of $H_2Cl_6Pt$ and $RuCl_3$ solutions on Pani, produce Pt–Ru Pani electrodes with catalytic properties for CO and methanol oxidation.
(ii) The RSWPS technique applied to Pani electrodes in a suitable Pt/Ru solution ($R = 0.6$) leads to deposited particles around 90 nm in size.
(iii) Neither a CO stripping signal nor an EDAX signal are measured for Ru RSWPS deposits on Pani.
(iv) The best Ru concentration on Pt–Ru Pani electrodes resulted in 44 at.% for CO oxidation and 32 at.% for methanol oxidation.

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