



Short communication

Methanol electrooxidation at aged PtRu electrodeposits as an approach to understand the effects of time

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ABSTRACT

In this work we investigate the catalytic activity of PtRu electrodeposits of distinct atomic composition towards methanol oxidation as a function of the “aging” of the electrodes. Electrochemical results show that those compositions containing more Ru present a peak of activity during the aging, whilst Pt-rich deposits present a continuous deactivation. Results are interpreted in terms of a progressive deactivation of Ru sites, which emulates a continuous change in the atomic composition. The maxima observed for the electrodeposits correspond to the time needed to attain compositions located in the range of good activity for methanol oxidation.

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1. Introduction

Pt-based electrocatalysts have been exhaustively investigated during the past few decades, especially in studies involving the electrooxidation of small organic molecules [1–10]. Among the metals investigated, Ru presents the greatest number of studies, being used as co-catalyst or in alloys with Pt for the electrooxidation of methanol and other molecules, as ethanol [11] and formaldehyde [12].

PtRu catalysts can be obtained by spontaneous deposition [13], chemical reduction [14] and electrodeposition [12]. The catalytic activity of PtRu electrodes is partially ascribed to the capability of Ru to produce superficial oxides that act as oxygen-sources during the steps of oxidation [15]. Another effect is related to the unfulfilled electronic structure of Ru, which lowers the density of the electronic states of Pt and weakens the adsorption of organic molecules (or their fragments, as CO) [16].

Due to these features, several papers report the catalytic activity of PtRu supported nanoparticles towards methanol oxidation, but factors as low coordination number, interaction with carbon support, among others, make the behavior observed for nanoparticles different from that found for extended surfaces.

Restricting our attention to electrodeposits, the literature describes the manufacture of PtRu catalysts by the electroreduction of its ions [12–17], driven by the imposition of potentials lower than 0.24 V (SHE) [17]. For these materials parameters as atomic

composition, relative distribution of Pt and Ru atoms, and degree of oxidation strongly influence the catalytic effect and must be considered in electrochemical studies.

Although PtRu electrodeposits show good catalytic activity towards methanol electrooxidation, they experience a loss of activity after polarization [17]. According to Gavrillov et al., this deactivation is provoked by the formation of stable Ru oxides over the metallic surface [17]. These authors simulate the aging of the electrodeposits by successive voltammetric cycles or by keeping the electrodes in air atmosphere by several months [17]. However, the experimental approach used by the authors does not allow concluding whether the potential cycling is the main cause for the deactivation of the electrodeposits or if the electrodes lose their activities even in non-polarized conditions. In order to separate these effects, we follow the deactivation of PtRu surfaces for methanol as a function of the time elapsed between the preparation of the catalysts and the performing of the electrochemical experiments. The deactivation of PtRu is rationalized in terms of changes in the superficial compositions of the electrodeposits provoked by oxidation of the atoms at the surface.

2. Experimental

Solutions were prepared with Milli-Q® water, CH₃OH (Merck, p.a.) and HClO₄ (Suprapur, Merck). The electrodeposits were prepared by electroreduction of Ru³⁺ and Pt⁴⁺ (obtained from RuCl₃ and H₂PtCl₆ aqueous solutions) in 0.1 M HClO₄ on a gold sheet of 0.5 cm². The solutions for electrodeposition contained variable concentrations of Pt⁴⁺ and Ru³⁺ in order to obtain deposits of PtRu atomic compositions of (60:40), (70:30) and (85:15). These com-

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positions were chosen because they are in the range of maximum catalytic activity towards methanol oxidation [13,18,19].

The metals were electrodeposited at 0.05 V vs. RHE during 60 s. Afterwards the electrodes were thoroughly washed with Milli-Q water, prior to their transference to an electrochemical cell containing 0.1 M HClO₄. The electrode surfaces were checked by cyclic voltammetry in the potential range comprised between 0.05 and 0.9 V with a scan rate of 100 mV s⁻¹ in the supporting electrolyte. Next, the potential was kept at 0.05 V and 0.1 M methanol (J.T. Baker) was admitted into the cell and a new voltammetric cycle was obtained in the presence of the alcohol. All the experiments were performed at room temperature (25.0 ± 1.0 °C). The solutions were purged with N₂ (4.5) before and during the experiments. All potentials were measured against a reversible hydrogen electrode in the same electrolyte.

Chronoamperometric experiments were performed by monitoring the current–time response after application of a potential step from 0.05 to 0.5 V. In order to obtain *i*–*t* curves, the electrodes were kept at 0.05 V in 0.1 M HClO₄ and 0.1 M CH₃OH was added to the cell. Next, a potential step from 0.05 to 0.5 V was applied and the electrocatalytic activity was evaluated by measuring the current after 30 min. At 0.05 V a CO layer is already being formed on Pt surface. It can influence the coverage degrees and consequently the methanol oxidation currents. As a way to control this initial condition all *i*–*t* curves were obtained after a polarization time of 60 s.

Once the experiments were performed with fresh electrodeposits, the electrodes were kept in a clean recipient in the presence of ordinary air (at 25 °C) and the same routine of experiments was repeated after 05, 10, 15, 20 and 30 days.

3. Results and discussion

3.1. Voltammetric profile of PtRu fresh electrodeposits

Fig. 1 presents the voltammetric profiles for fresh deposits in 0.1 M HClO₄ for the compositions investigated. The current response in the hydrogen region shows a clear relation with the Pt content [17,18,20]. The H adsorption peaks are better defined for the electrode with a higher content of Pt, i.e., PtRu (85:15). This is the only composition where two quasi-reversible peaks of

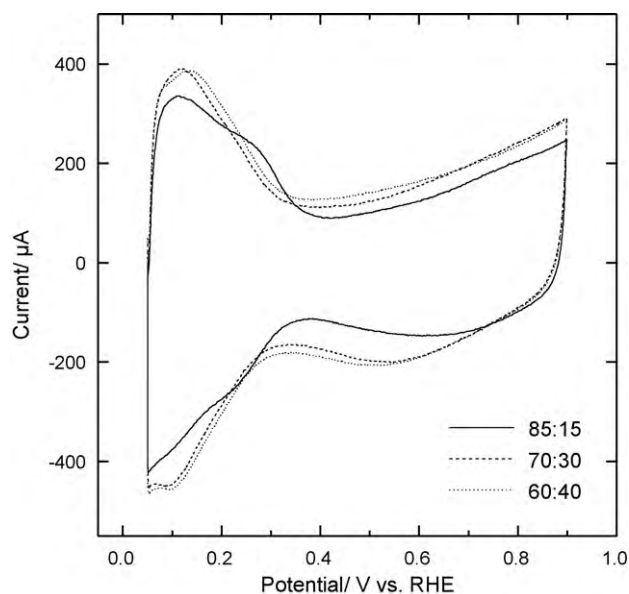


Fig. 1. Cyclic voltammograms of PtRu electrodeposits in 0.1 M HClO₄ at 25 °C. $\nu = 100 \text{ mV s}^{-1}$. Nominal compositions of 85:15 (solid line); 70:30 (dashed line); 60:40 (dotted line).

hydrogen adsorption can be discriminated, whilst PtRu (70:30) and (60:40) show a sole asymmetric peak in the same region. Currents in the double layer region are also dependent on the Ru content. The currents for PtRu (85:15) resemble those ones observed for pure Pt in the range comprised among 0.36 and 0.49 V, whilst PtRu (70:30) and (60:40) present higher currents at this potential range. This feature is associated with the production of Ru oxides which coincides with the occurrence of capacitive currents at Pt [20].

3.2. Electrochemical behavior of PtRu deposits as a function of time

Our electrodes were aged in air without polarization between successive experiments, similarly to the procedure adopted by Gavrilov et al. [17]. However, we decide to perform electrochemical experiments at intervals of 5 days to follow eventual changes of the surfaces at short times after the deposition. Fig. 2a–c illustrates the voltammetric responses for PtRu deposits of nominal compositions (60:40), (70:30) and (85:15), respectively. For ends of visualization, we present four representative results for each figure.

From figures it can be noted that the currents decrease systematically when the deposits are aged, particularly in the region comprised among 0.3–0.6 V. Furthermore, this reduction is more accentuated for PtRu 85:15 than for other compositions. At a first glance, the results seem to indicate a decrease in the superficial area. However, as discussed by Gavrilov et al., the aging process seems to provoke mainly the formation of oxygen-containing Ru species – as demonstrated by the qualitative modification of Cu-UPD stripping voltammograms – whilst the decrease of surface area is a minor consequence of it [17]. In the present case, con-

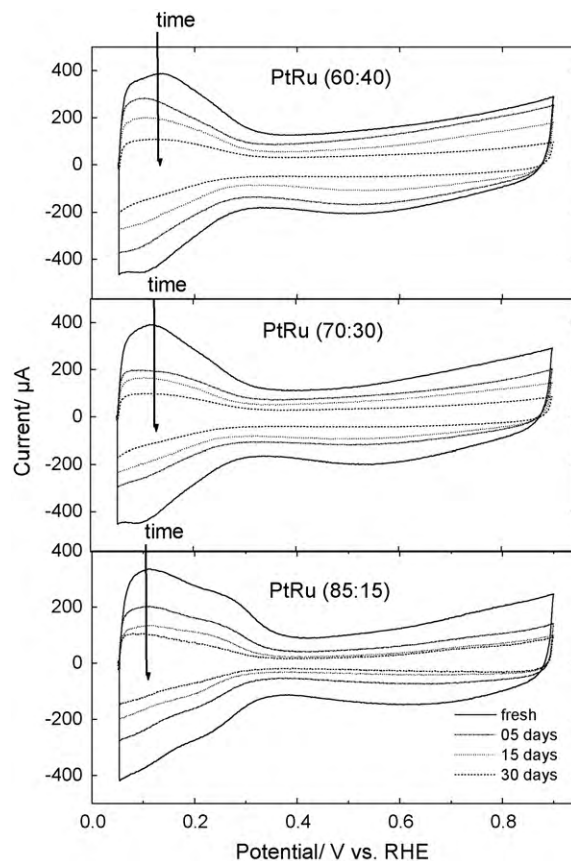


Fig. 2. Cyclic voltammograms in 0.1 M HClO₄ for PtRu fresh deposits (solid lines) and at different times after prepared. Compositions indicated in the figure. $\nu = 100 \text{ mV s}^{-1}$, $T = 25 \text{ °C}$.

versely to the behavior observed for these authors, the currents in the hydrogen region are also affected by the aging of the electrodes (Fig. 2a–c). The reason for the discrepancies between these results remains unclear at the present stage, but the existence of both behaviors brings a new question to this matter: the aging of PtRu surfaces causes mainly the deactivation of Ru sites or the reduction of PtRu surfaces has been underestimated? In order to throw some light to this issue we follow the catalytic activity of the deposits in the presence of methanol. The results are presented and discussed in the next section.

3.3. The catalytic activity of PtRu deposits towards methanol oxidation: cyclic voltammetry and *i*–*t* curves.

Fig. 3 illustrates the voltammetric profile of a PtRu (85:15) fresh deposit in the presence of 0.1 M HClO₄ (solid line) and 0.1 M HClO₄ + 0.1 M methanol (dashed line). The currents in the hydrogen region are barely affected by the presence of methanol, showing a negligible adsorption of the alcohol for potentials lower than 0.23 V, where a small anodic current can be discerned. After the beginning of methanol oxidation, the current increases at a constant slope and reaches a maximum at ~0.8 V. In this potential range the currents in the presence of methanol easily overwhelm those observed in HClO₄. During the negative going-scan there is a region (0.9–0.4 V) which shows a small hysteresis, followed by the increasing of cathodic currents which resemble the profile observed in the presence of HClO₄ alone.

With the aim of monitoring the effect of aging the deposits on their catalytic activity current–time curves were obtained after the application of a single potential step from 0.05 to 0.5 V for 30 min in the presence of methanol. Fig. 4a–c shows the currents for methanol oxidation measured after different aging times for all the compositions. The results represent the currents values averaged from three experiments.

It is important to note that, as we do not estimate the surface area, there makes no sense to compare the activities among different electrodes. Nevertheless, *i*–*E* curves shown in Fig. 1 suggest that the surface areas are very similar, which could lead us to conclude that PtRu (85:15) is the more active composition. Anyway, the important comparison here is that made for several aging periods for the same catalyst. Fig. 4 shows that the activity of the electrodeposits is dependent on aging time for all the compositions.

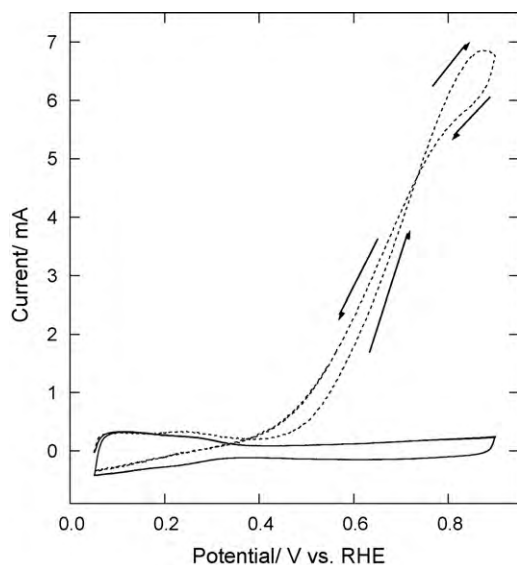


Fig. 3. Cyclic voltammograms of PtRu (85:15) fresh deposit in 0.1 M HClO₄ (solid line) and 0.1 M HClO₄ + 0.1 M methanol (dashed line). $v = 100 \text{ mV s}^{-1}$.

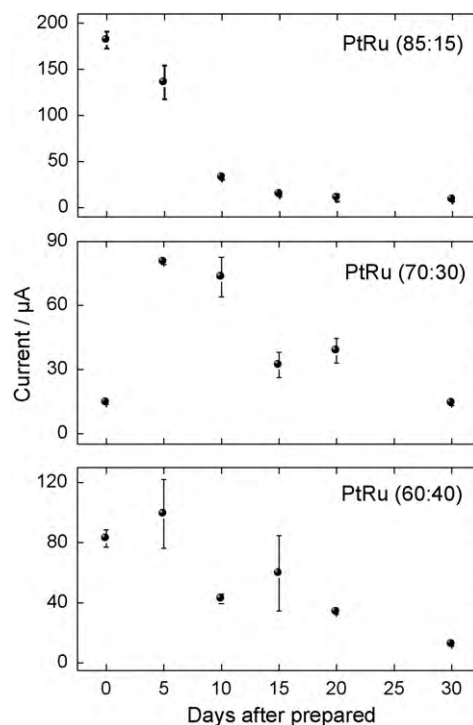


Fig. 4. Currents for methanol electrooxidation taken from current–time curves, after 30 min of polarization at 0.5 V, plotted as a function of the time of ageing of the electrodeposits. $T = 25^\circ \text{C}$. PtRu compositions indicated in the figure.

Furthermore, the changes in the activity with time are qualitative different for PtRu (85:15) when compared with PtRu (70:30) and PtRu (60:40).

For PtRu (85:15) the maximum activity is attained for the fresh deposit, and a non-linear decay is observed when the electrode is aged (Fig. 4a). On the other hand, PtRu (70:30) and (60:40) present a maximum catalytic activity after a few days of aging. Afterwards the electrodes show a continuous deactivation for longer periods.

From the comparison of Figs. 2 and 4 a contradictory behavior seems to emerge: the currents in acidic media show a progressive lowering with time, which suggests a reduction of the surface area, whilst the activity towards methanol oxidation grows for the respective times! As the currents presented in Fig. 4a–c refer to the same electrodes, the results cannot be rationalized in terms of a simple reduction of area. As an attempt to conciliate both the observations we interpret the behavior as follows:

In the presence of HClO₄: the aging of the electrodeposits provokes a slow (although constant) deactivation of Ru sites, with the formation of stable oxides (we assume that an oxide is stable if it cannot be reduced in the range of potentials investigated). After being formed, these species do not exchange charge with the solution, resulting in a reduction of the currents in the voltammogram.

In the presence of methanol: it is well known that methanol electrooxidation is sensitive to the composition of PtRu surfaces [13,19], being the best activity found for PtRu compositions around 80:20 [13]. If this is true, PtRu (70:30) and (60:40) correspond to compositions containing an “excess” of Ru in the surface, whilst PtRu (85:15) is situated in the optimum range of activity. As Ru sites are deactivated the initial compositions of 70:30 and 60:40 tend to move closer to this value, justifying the increasing activity. After the activation, Ru sites continue to oxidize until that the “real” PtRu composition eventually falls to values lower than those need to promote methanol oxidation at high rates, provoking a reduction of the catalytic activity. For PtRu (85:15) the reasoning is basically the same, the only difference is that the initial PtRu

composition already corresponds to the maximum activity. This assumption means that any Ru oxidation will generate surfaces that contain less Ru than the optimum composition. The consequence is the continuous deactivation of the PtRu (85:15) electrodeposit.

We are aware that this interpretation is speculative. Complementary studies are necessary to clarify this matter and determine the specific role of the PtRu aging towards methanol oxidation. However, the results presented here clearly show new trends for the discussion of this topic.

4. Conclusions

- The catalytic activity of PtRu electrodeposits towards methanol electrooxidation is dependent on aging time for all the compositions.
- PtRu (85:15) shows a continuous deactivation of the surface as a function of time, whilst PtRu (70:30) and (60:40) present better activity after aged for a few days. After this maximum the activity follows the behavior observed for PtRu (85:15).
- Results are interpreted in terms of a progressive deactivation of Ru sites, which emulates a continuous change in the atomic composition. The maxima observed for the electrodeposits correspond to the time needed to attain compositions located in the range of good activity for methanol (typically 10–30% of Ru atoms on the surface).

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