



## Effect of the Pt/Ru intermetallic boundary on the carbon monoxide electrooxidation: Excess electrocatalytic activity

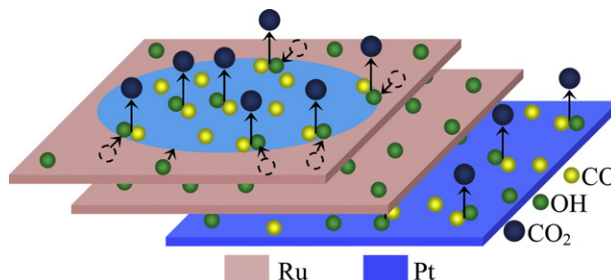
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### HIGHLIGHTS

- ▶ Study of the carbon monoxide oxidation reaction on Pt, Ru and Pt/Ru electrodes.
- ▶ Evaluation of the contribution to the reaction of the intermetallic region on Pt/Ru.
- ▶ Quantification of such contribution through the excess electrocatalytic activity.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The carbon monoxide oxidation reaction was studied on smooth Pt, Ru and Pt/Ru (Ru partially covered by Pt islands) rotating disc electrodes on acid solution saturated with CO gas ( $P_{\text{CO}} = 1$  atm) through steady state measurements. The current density vs. overpotential plot of the Pt/Ru electrode shows a profile qualitatively similar to the sum of both curves corresponding to pure Pt and Ru. On this basis, the excess electrocatalytic activity was defined as the difference between the current densities of the bimetallic electrode and those corresponding to the pure metals, which allowed evaluating the contribution of the intermetallic region to the reaction. It was verified that this property depends on overpotential, defining two ranges of positive excess values,  $0.6 \leq \eta/V < 0.82$  and  $0.88 < \eta/V \leq 1.0$ , separated by the range  $0.82 \leq \eta/V \leq 0.88$ , where the contribution of the boundary region is negligible. A simple model was developed, which explains the experimental results on the basis of the spillover of the adsorbed reaction intermediates, while the reaction between adsorbed species on both sides of the intermetallic edge is not feasible.

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### 1. Introduction

The oxidation of adsorbed carbon monoxide ( $\text{CO}_{\text{ad}}$ ) on Pt and bimetallic Pt–M electrodes has been widely studied, because of its role played in polymer electrolyte membrane fuel cells (PEMFC) [1–15]. It is well known that platinum has a large affinity towards the adsorption of CO, inhibiting the CO electrooxidation reaction,

and therefore higher overpotentials are needed for the occurrence of this reaction. In order to weaken CO–Pt bonding or provide the adsorbed hydroxyl species ( $\text{OH}_{\text{ad}}$ ) from oxyphilic surface atoms, binary electrocatalysts Pt–M were developed, being Ru the most widely employed as M metal [5–7,11–15]. The role of the second metal, particularly Ru, was studied on alloys [12,13], as well as on Pt (or Ru) surfaces partially covered, or decorated, by Ru (or Pt) islands [14,15]. In this context it can be mentioned the works of Gasteiger et al., who used polycrystalline Pt/Ru alloys of different compositions, prepared by arc melting of the pure metals under an argon atmosphere [12,13]. Other authors employed Ru-decorated Pt

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single crystal surfaces as model electrocatalysts, obtained by electrodeposition as well as spontaneous deposition [6]. Another way to obtain model Pt/Ru electrocatalyst, developed by Brankovic et al., consists in the spontaneous deposition of Pt submonolayers on the Ru(0001) surface [15,16]. They obtained columnar shaped Pt clusters covering from submonolayer to multilayer depending on the concentration of Pt ions and on the time of immersion. This method was also applied to deposit Pt submonolayers on Ru nanoparticles supported on Vulcan XC-72 carbon [16,17]. In all cases it was found a larger CO tolerance with respect to Pt. The effect of the intermetallic boundary region was analyzed on the basis of the current–potential curve obtained by the application of the voltammetric stripping of CO adsorbed at low potentials [18–23]. The stripping voltammogram shows two peaks, one at  $0.4 \leq E(\text{vs. RHE})/V \leq 0.6$  called preignition peak and the other, located at more anodic potentials, called ignition peak. Koper et al. considered that the first peak corresponds to the CO oxidation on Ru while the second one to the reaction taking place on Pt [18,19]. On the other hand, Lu et al. proposed that the reaction takes place on both sides of the edge of the Ru island [21,22]. Finally, Roth et al. indicated that the preignition peak corresponds to the CO oxidation on the intermetallic region and the second peak was assigned to the oxidation of the CO that diffused towards such region [23]. It should be noticed that these peaks show the  $\text{CO}_{\text{ad}}$  oxidation in absence of a readsorption process from solution. Thus, despite the numerous works published on this subject, the contribution of the intermetallic boundary region has not been clearly determined yet and still remains an incompletely resolved issue.

In order to analyze the contribution of the intermetallic region a model electrode should be used, where the edge between Pt and Ru is clearly defined. In the present case, a Ru electrode partially covered by Pt islands is employed. An aprioristic analysis of the expected response for the CO electrooxidation on this electrode indicates that it should exhibit contributions of Pt and Ru themselves in the surface regions far from the intermetallic boundary as well as a specific contribution corresponding to this boundary region.

On this basis, the aim of the present work is the evaluation of the contribution of the intermetallic region to the CO oxidation reaction, starting from the measurement of the polarization curves on steady state on Pt/Ru electrodes, as well as on pure Pt and Ru electrodes. Thus, the difference between the current densities of the bimetallic electrode and those corresponding to the pure metals will define a property that can be called an “excess electrocatalytic activity”, which allows the quantification of the contribution of the intermetallic boundary region to the electrocatalytic activity of the Pt/Ru electrode to the CO oxidation. An explanation of this contribution is also proposed, on the basis of the spillover of the adsorbed reaction intermediates.

## 2. Experimental

### 2.1. Electrodes preparation and characterization

The working electrodes were rotating discs of polycrystalline platinum 99.99% (Radiometer analytical) and ruthenium 99.95% (MaTecK GmbH) with a geometric area of  $0.07 \text{ cm}^2$ . They were mechanically polished with emery paper of different grit sizes and then alumina powder up to  $0.05 \mu\text{m}$ , followed by sonication in ultra-pure water for 5 min. In order to obtain the bimetallic electrode, a rotating disc of polycrystalline ruthenium was immersed in a deoxygenated  $0.1 \text{ mM H}_2\text{PtCl}_6 + 0.5 \text{ M H}_2\text{SO}_4$  solution during a period of time ranging between  $5 \leq t/\text{min} \leq 20$ , following the procedure described elsewhere [16], although all the results shown correspond to  $t = 10 \text{ min}$ , unless otherwise stated. The morphology

of the deposit was analyzed by AFM observations in the tapping mode, obtained in a microscope AFM/STM Agilent Technologies model 5400. The electrochemical characterization was carried out by cyclic voltammetry at  $0.05 \text{ V s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  solution saturated with nitrogen gas and at  $25^\circ\text{C}$ .

### 2.2. Evaluation of the CO oxidation

The experimental determination of the dependence  $j(\eta)$  for the carbon monoxide oxidation reaction was carried out in a three electrodes cell specially built for the use of a rotating electrode and with a particular design of the gas saturator. The working electrodes were the polycrystalline Pt and Ru discs and the bimetallic Pt/Ru prepared as it is described in the previous item. They were rotated through the use of a rotating disk Radiometer EDI 10K. The counterelectrode was a platinum helical wire of large area. The electrolytic solution was  $0.5 \text{ M H}_2\text{SO}_4$ , prepared with ultra-pure water (PureLab, Elga LabWater). Measurements were carried out at  $25^\circ\text{C}$  under ultra high purity 99.9% CO gas ( $10 \text{ ppm O}_2$ ,  $30 \text{ ppm CO}_2$ ) bubbling at 1 atm, ensuring a continuous saturation of the electrolyte. The applied overpotentials were controlled with respect to a reversible hydrogen electrode in the same solution (RHE). Taking into account that the CO used contains 30 ppm of  $\text{CO}_2$ , the value of the theoretical equilibrium potential of the CO oxidation reaction with respect to the RHE can be calculated ( $E^\ominus = -0.025 \text{ V}$ ) [24].

The first type of experimental determinations to study the CO oxidation was a slow potentiodynamic sweep run at  $0.01 \text{ V s}^{-1}$ , which was applied to the three types of electrodes studied, Pt, Ru and Pt/Ru. The determination of the experimental current–overpotential dependences for the reaction on steady state was carried out on these electrodes, through the application of a potential program consisting in holding the potential at  $0.2 \text{ V}$  during 3 min, followed by successive steps, each with duration of 3 min. On the basis of the behaviour observed on the slow potentiodynamic sweep, the ranges of overpotentials employed in the steady state measurements were adopted:  $0.5 \leq \eta/V \leq 1.2$  for Pt and  $0.4 \leq \eta/V \leq 1.0$  for Ru and Pt/Ru. During the potentiostatization at a given overpotential, the current value was measured each 0.1 s and the mean value of the last 10 s was assigned to this overpotential to ensure that the steady state current was reached. The current densities are referred to the geometric area ( $0.07 \text{ cm}^2$ ), unless otherwise stated. Immediately after these measurements, the Ru and Pt/Ru electrodes were subjected to the electrochemical characterization by cyclic voltammetry described above in order to verify that the electrode surface was not modified.

## 3. Results

### 3.1. Electrode surface morphology

The surface morphology of the working electrodes were analyzed by atomic force microscopy operating in the tapping mode. Fig. 1 shows the AFM image corresponding to the Ru surface before the Pt deposition. It can be observed that the surface is fairly smooth, which is verified by the corresponding profile plot depicted in the inset of Fig. 1.

A similar image was obtained for the Pt electrode, subjected to the same surface treatment. The Pt/Ru electrode obtained by spontaneous deposition of Pt on Ru shows a surface morphology (Fig. 2) characterized by the presence of smooth hemispherical particles, which height can be estimated by the corresponding profile (Fig. 2, inset), varying between 15 and 70 nm. It can be appreciated from Fig. 2 that the ruthenium area exposed to the electrolyte solution is significantly lower than the original. From

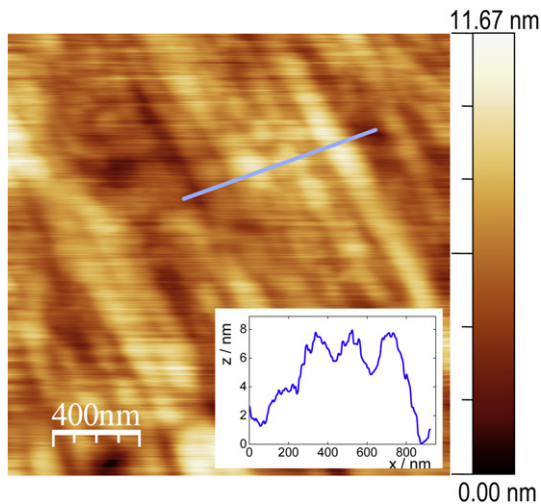


Fig. 1. AFM image of the Ru surface before the spontaneous deposition of Pt. Inset: height profile.

the analysis of the AFM image on different regions of the electrode, a Pt surface coverage of approximately 0.40 can be estimated (projected area of Pt that covers the Ru substrate). The mean value of the radius of the hemispheres was obtained from the analysis of the height profiles evaluated from numerous AFM images. The size (diameter) distribution histogram is shown in Fig. 3, being the average diameter approximately 80 nm. Moreover, the area corresponding to platinum was evaluated as that corresponding to hemispheres of 80 nm diameter, which cover 40% of the Ru surface. The resulting areas were approximately  $0.056 \text{ cm}^2$  for Pt and  $0.042 \text{ cm}^2$  for Ru. It should be important to note that these areas on the Pt/Ru electrode are less than those corresponding to the pure Pt and Ru electrodes ( $0.07 \text{ cm}^2$ ). The perimeter of the intermetallic edge was estimated in  $1.4 \times 10^4 \text{ cm}$ .

### 3.2. Electrochemical studies

Fig. 4 shows the stabilized voltammetric profile  $I/E$  (vs. RHE) of the Pt/Ru electrode obtained by spontaneous deposition of Pt on polycrystalline Ru, subjected to potentiodynamic sweeps run at

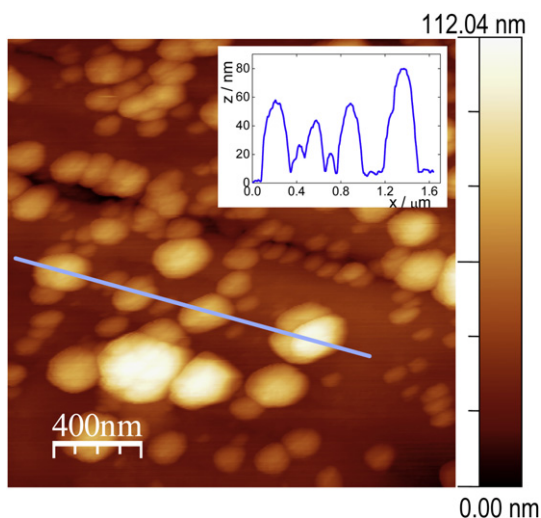


Fig. 2. AFM image of the Pt/Ru surface obtained by spontaneous deposition of Pt. Inset: height profile.

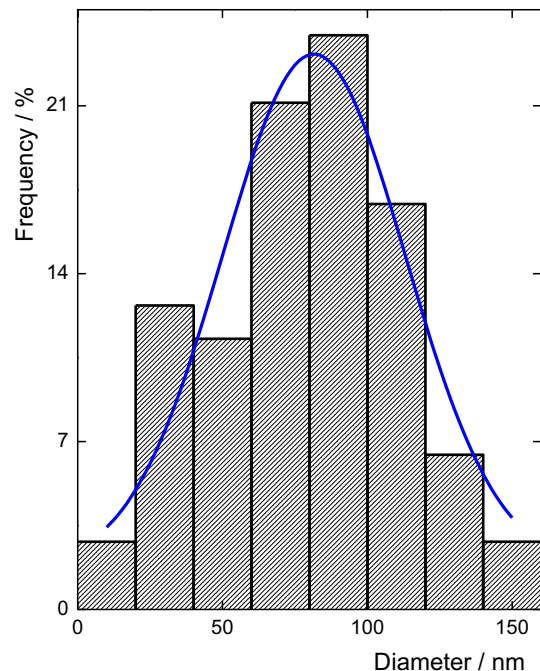


Fig. 3. Size distribution histogram obtained from AFM image of the Pt/Ru surface.

$0.05 \text{ V s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  solution. It can be observed the current peaks corresponding to the hydrogen electroadsorption in the potential range  $0.05 \leq E/V \leq 0.3$ . From the voltammetric charge corresponding to the hydrogen electroadsorption, which can be estimated as  $12 \mu\text{C}$ , the resulting value for the Pt area was  $0.057 \text{ cm}^2$ . This value is in agreement with that evaluated from the AFM image.

Fig. 5 shows the experimental current density–overpotential dependences for the CO oxidation on the three electrodes studied, rotated at 4900 rpm in a  $0.5 \text{ M H}_2\text{SO}_4$  solution saturated with carbon monoxide (30 ppm  $\text{CO}_2$ ) at  $P_{\text{CO}} = 1 \text{ bar}$ , obtained through the application of a potentiodynamic sweep run at  $0.01 \text{ V s}^{-1}$ . The response corresponding to Pt (Fig. 5(a)) exhibits the influence of pseudocapacitive effect as well as a pronounced hysteresis, with the presence of a sharp anodic peak at  $0.92 \text{ V}$  in the anodic sweep and another anodic peak at  $0.88 \text{ V}$  in the cathodic

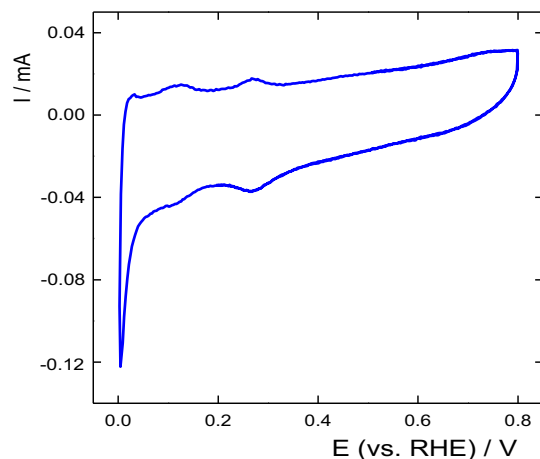
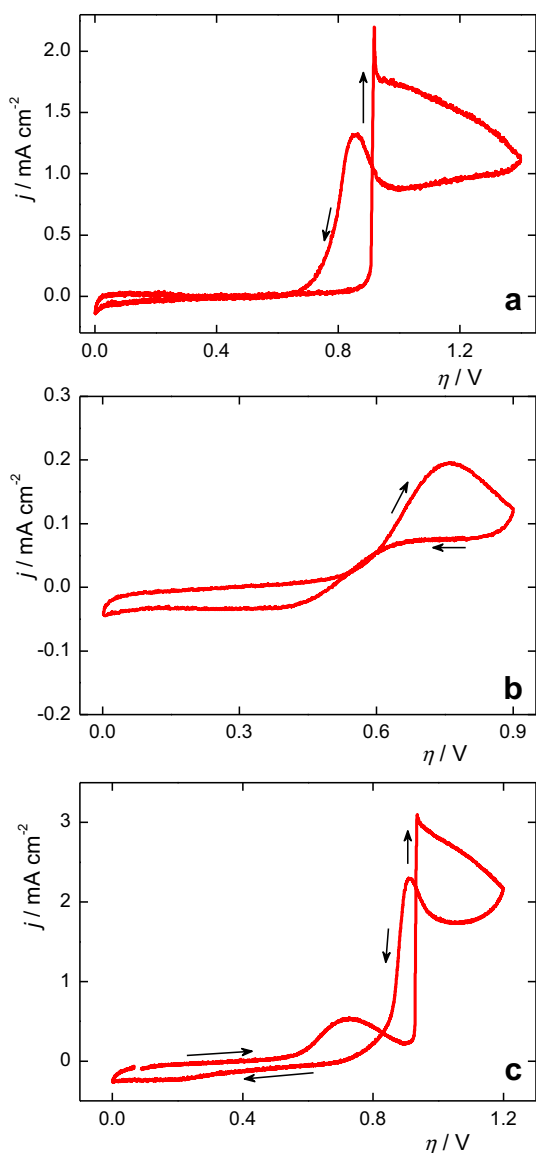


Fig. 4. Voltammogram of the Pt/Ru electrode, obtained by spontaneous deposition of Pt on Ru.  $0.05 \text{ V s}^{-1}$ ;  $0.5 \text{ M H}_2\text{SO}_4$ ,  $25 \text{ }^\circ\text{C}$ .



**Fig. 5.** Experimental  $j(\eta)$  curves for the CO oxidation obtained by potentiodynamic sweep at  $0.01 \text{ V s}^{-1}$  and 4900 rpm and  $P_{\text{CO}}=1 \text{ atm}$ . (a) Pt; (b) Ru; (c) Pt/Ru.  $0.5 \text{ M H}_2\text{SO}_4$ ,  $25^\circ \text{C}$ .

sweep. It was also found a current increase with rotation rate, in agreement with previous results [25].

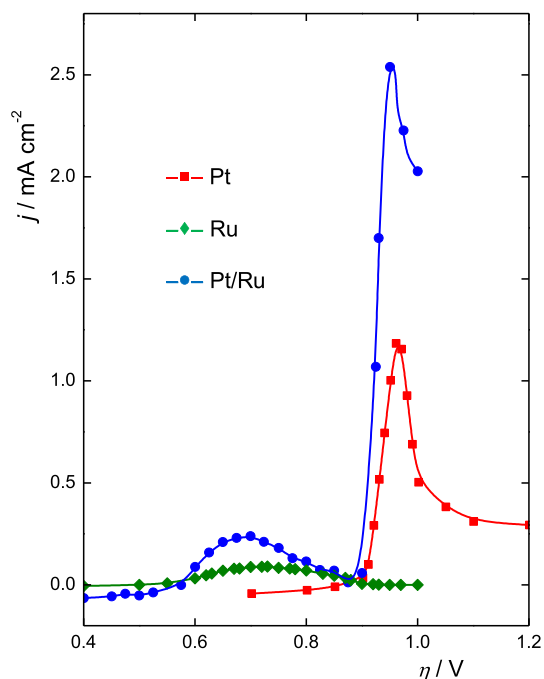
The corresponding potentiodynamic response obtained for the CO oxidation on the polycrystalline Ru electrode at 4900 rpm is shown in Fig. 5(b). The profile, which presents also pseudocapacitive effects and a current peak at 0.75 V in the anodic sweep, is similar to that obtained by Gasteiger et al. [13]. Finally, the voltammogram corresponding to the Pt/Ru electrode (Fig. 5(c)) shows a more complex profile than those of Pt and Ru. There are two anodic peaks in the anodic sweep at approximately 0.74 V and 0.94 V, respectively, and another anodic peak at 0.90 V in the cathodic sweep. It should be noticed that the current values of all these peaks are greater than those corresponding to the Pt and Ru electrodes at similar overpotential values, although the surface area occupied by each metal in the bimetallic electrode is smaller than that of the pure electrodes, showing the synergistic effect of the intermetallic region. The behaviour of Pt–Ru surfaces obtained at different times of immersion of the Ru electrode on the Pt ion

containing solution are quite similar, with a variation of the relative values of the two current peaks of the anodic scan.

The results of the slow potentiodynamic sweeps, although interesting, have only an indicative importance. It is not possible to infer how the surface coverage of the reaction intermediates, as well as the surface concentration of CO gas, vary on overpotential as they also change on time and produce pseudocapacitive current contributions. Thus, the interpretation of such dependences is quite difficult. The situation changes completely when experiments are carried out on steady state [24].

The results corresponding to chronoamperometric measurements are shown in Fig. 6 for the three electrodes. It should be noticed that the values of the current density are in all cases much lower than those delivered under the slow potentiodynamic sweeps. Another aspect that should be mentioned is that long term chronoamperometric measurements (60 min) were also carried out in order to ensure the absence of oscillation in the current response, which had been observed in the presence of inhibiting anions [26,27]. It has not been observed in these experiments carried out at different overpotential values any oscillatory behaviour.

The polarization curve corresponding to Pt (square dots) shows a well defined peak located at approximately 0.97 V followed by a current plateau. In the corresponding curve obtained on Ru (rhomboid dots), the peak is located at approximately 0.7 V and the current values are much lower than that of Pt. Finally, the steady state polarization curve corresponding to the Pt/Ru electrode (circle dots), obtained in the overpotential range  $0.4 \leq \eta/\text{V} \leq 1.0$  for Pt/Ru, can be divided into two regions. The range comprised between 0.4 and 0.55 V initially presents negative current values already observed in the potentiodynamic sweeps and known in the literature [13], although this overpotential range is not directly involved in the present study and its interpretation is beyond the scope of this work. In the other region ( $\eta > 0.55 \text{ V}$ ), the current is anodic and there are two peaks. The peak at 0.70 V is characterized by a current density almost three times greater than that of Ru. Then, there is an abrupt increase in the current density, passing through a peak at



**Fig. 6.** Experimental  $j(\eta)$  curves for the CO oxidation obtained by potentiostatic pulses at 4900 rpm and  $P_{\text{CO}} = 1 \text{ atm}$ .  $0.5 \text{ M H}_2\text{SO}_4$ ,  $25^\circ \text{C}$ .

near 0.96 V, being the corresponding current density higher than that of Pt. It was also found that this behaviour is independent of the time of immersion in the  $\text{H}_2\text{PtCl}_6$  solution. Another important point is related to the electrochemical characterization by cyclic voltammetry carried out immediately after the steady state measurements on Ru and Pt/Ru. In both cases it was verified that the voltammetric response was the same before and after the experiments.

#### 4. Discussion

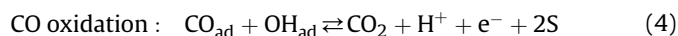
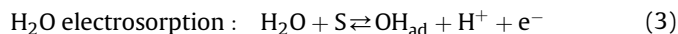
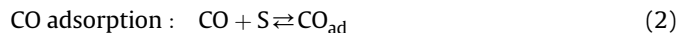
The study of the carbon monoxide oxidation reaction in acid solution saturated with CO was carried out on Pt, Ru and Pt/Ru electrodes through potentiodynamic sweeps and chronoamperometric measurements, under well defined mass transport conditions. The steady state curves show the same response independently if the measurements were run in the anodic or cathodic direction, with smaller current values and well defined peaks.

The main characteristics of the CO oxidation reaction in steady state on the electrodes studied can be summarized as follows: (i) The reaction takes place on platinum only at  $\eta > 0.88$  V and on ruthenium in the range  $0.6 \leq \eta/V \leq 0.8$ . (ii) For bimetallic electrode Pt/Ru, two regions were observed, one in the range  $0.6 \leq \eta/V \leq 0.82$ , coincident with that of the CO electrooxidation on Ru and the other in the overpotential region  $0.88 \leq \eta/V \leq 1.0$ , which is the same range as that on Pt. (iii) Pt/Ru electrode shows better electroactive behaviour than both Pt and Ru, which is in agreement with results obtained from potentiodynamic or stripping CO oxidation [6].

In order to interpret these results, it should be taken into account that the carbon monoxide electrooxidation reaction in acid solution can be written as:



The kinetic mechanism originally proposed by Watanabe and Motoo [7] is now generally accepted [28]. This mechanism assumes a Langmuir–Hinshelwood type reaction between the carbon monoxide and a surface oxygen-containing species, adsorbed on adjacent sites, to form  $\text{CO}_2$ . The oxygen-containing species results from the oxidation of water at the electrode surface and is usually supposed to be  $\text{OH}_{\text{ad}}$ . Thus, the following steps can be considered for the kinetic mechanism of the CO electrooxidation on a metallic surface:



where S represents a free active site where the reaction intermediates,  $\text{CO}_{\text{ad}}$  and  $\text{OH}_{\text{ad}}$ , can be adsorbed, which can be provided by different metals in the intermetallic boundary region. Moreover, a previous study of the CO electrooxidation on pure Pt and Ru electrodes allowed establishing the dependences of the surface coverage of  $\text{CO}_{\text{ad}}$  and  $\text{OH}_{\text{ad}}$  on overpotential [24], which should correspond in this case to regions far from the intermetallic edges.

As the maximum current densities in the polarization curve of the Pt/Ru electrode are located at the same overpotentials of those in the Ru and Pt electrodes respectively, it can be inferred in agreement with previous proposals that each region corresponds mainly to the response of one metal surface [18,19]. Consequently, the increase in the electrocatalytic activity in the bimetallic

electrode with respect to that of the pure metals can be attributed to the role played by the intermetallic boundary region, which could be considered proportional to the edge length.

#### 4.1. Excess electrocatalytic activity

In order to enhance the role of the intermetallic boundary region in the CO electrooxidation reaction, the excess electrocatalytic activity was defined as the difference between the current density on the bimetallic electrode and those corresponding to the pure metals. If such difference would be null, then it could be concluded that the intermetallic boundary region does not have any effect on the CO electrooxidation. In this sense, the excess electrocatalytic activity shown in Fig. 6 exhibits clearly two overpotential domains with positive excess activity, at  $0.6 \leq \eta/V < 0.82$  and  $0.88 < \eta/V \leq 1.0$  respectively, separated by a neutral region at  $0.82 \leq \eta/V \leq 0.88$ . In order to carry out a correct comparison of the electrocatalytic activity, it should be mentioned that current densities were evaluated considering the corresponding surface area of Ru ( $0.042 \text{ cm}^2$ ) and Pt ( $0.056 \text{ cm}^2$ ) in contact with the electrolyte solution. It can be concluded from Fig. 7 that the behaviour of the intermetallic region is strongly determined by the applied potential, being negligible the effect in the domain  $0.82 \leq \eta/V \leq 0.88$ , suggesting that in this range step (4) is hampered.

As a result of the present analysis, it can be concluded that the presence of the intermetallic boundary region produces a significant increase of the CO electrooxidation current density. The possible explanation for such contribution could be the direct reaction, through step (4), between  $\text{CO}_{\text{ad}}$  located on the Pt side and the nearest  $\text{OH}_{\text{ad}}$  located on the Ru side. Another possibility could be the spillover of one of the reaction intermediates, followed by the oxidation reaction on one side of the intermetallic edge.

In this context, an interpretation of the results obtained for the CO electrooxidation on the Pt/Ru electrode in the two overpotential

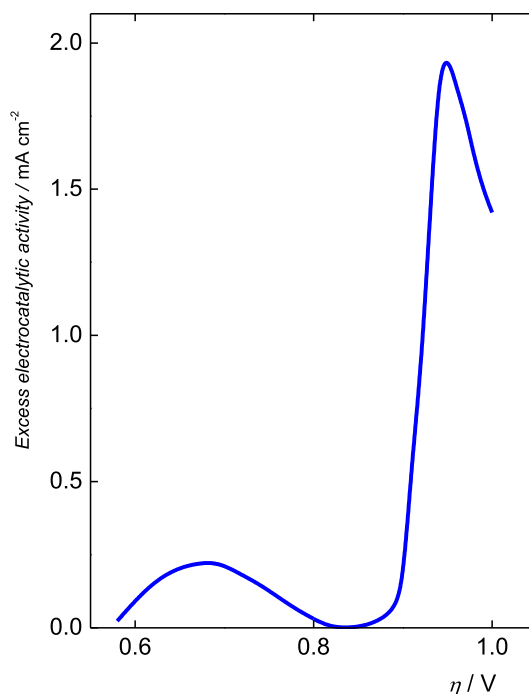
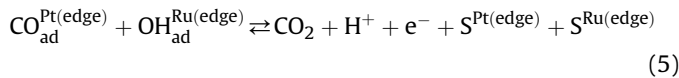


Fig. 7. Dependence of the excess electrocatalytic activity on overpotential for the CO electrooxidation.

regions is given below, as well as the absence of excess electrocatalytic activity in the middle range of overpotentials.

4.2. Overpotential region:  $0.82 \leq \eta/V \leq 0.88$

It is not observed in this region a synergistic effect due to the presence of the intermetallic edge, although previous results obtained on pure Pt and Ru<sup>24</sup> indicate that in this range Pt is completely covered by a monolayer of CO<sub>ad</sub> while Ru is almost completely covered by a monolayer of OH<sub>ad</sub>. Consequently and beyond electronic effects, it can be considered that the edge contribution:



is not significant. The other explanation, which would imply the spillover of the CO<sub>ad</sub> from the Pt edge to the Ru side, where it would react with the OH<sub>ad</sub> or conversely, the spillover of OH<sub>ad</sub> from Ru to Pt, followed by its reaction with CO<sub>ad</sub> on the Pt surface, is neither feasible because the almost absence of free sites on both sides of the edge turns negligible the spillover of the adsorbed species.

4.3. Overpotential region:  $0.6 \leq \eta/V \leq 0.82$

In this overpotentials range, the current response is attributed mainly to the surface sites on Ru, as the surface sites corresponding to Pt are completely covered by CO<sub>ad</sub> species, consequently the coverage of OH<sub>ad</sub> is null and the CO electrooxidation on Pt is totally inhibited, as it is illustrated in Fig. 8(a). On the other hand, the surface of the Ru electrode would be predominantly covered by OH<sub>ad</sub> species, with a less amount of CO<sub>ad</sub>. Thus, the carbon monoxide oxidation takes place on Ru through step (4) with low values of the current density, as it can be observed in Fig. 8(b). Then, taking into account that reaction (5) does not take place, the excess in the electrocatalytic activity in this range should be due to the spillover of the CO<sub>ad</sub> from the Pt edge to the free sites located in the

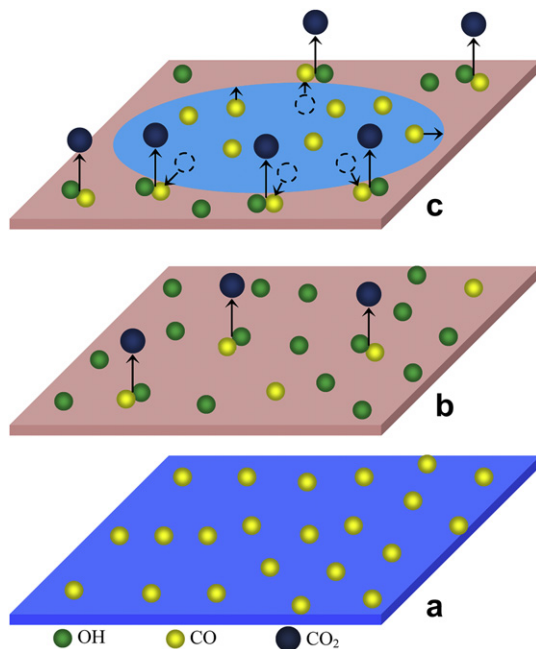
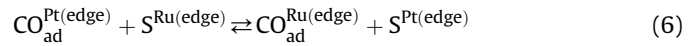


Fig. 8. Schemes of the electrode surface in the overpotentials range  $0.6 \leq \eta/V \leq 0.82$ . (a) Pt; (b) Ru; (c) Pt/Ru.

Ru edge, as this metal has low coverage of both CO<sub>ad</sub> and OH<sub>ad</sub>. This process can be described as:



Step (6) allows the subsequent occurrence of step (4) on the Ru surface. Thus, the intermetallic boundary acts as a source of CO<sub>ad</sub> which is added to the direct CO adsorption on Ru (step 2), as it is illustrated in Fig. 8(c). It should be noticed that the spillover of OH<sub>ad</sub> in the opposite direction should not be verified due to the absence of free sites on the Pt side. In this sense, the free site left on Pt for the spilled over CO<sub>ad</sub> is quickly occupied by another CO adatom (step 2). Meanwhile, the site on Ru left by the OH<sub>ad</sub> is immediately regenerated through step (3), which can be considered a quasi-equilibrium reaction [24,29,30].

Then, the extensive overall net reaction rate for the CO oxidation (V) on the Pt/Ru electrode in the overpotential region  $0.6 \leq \eta/V \leq 0.82$  can be expressed as the sum of the reaction rate on Ru,  $v_{\text{Ru}}$ , and the reaction rate on the boundary region (step 6),  $v_{\text{Pt/Ru}}$ , which is referred to the edge length:

$$V = A_{\text{Ru}}v_{\text{Ru}} + l_{\text{Pt/Ru}}v_{\text{Pt/Ru}} \quad (7)$$

where  $A_{\text{Ru}}$  is the ruthenium surface area and  $l_{\text{Pt/Ru}}$  is the edge length of the intermetallic boundary. It should be also emphasized that in this overpotential region Pt is completely inactive and therefore the reaction rate on Pt ( $v_{\text{Pt}}$ ) is null, as the surface is completely covered by CO<sub>ad</sub>.

4.4. Overpotential region:  $0.88 < \eta \leq 1.0 \text{ V}$

In this overpotential region, on the Pt surface the sites are covered by CO<sub>ad</sub> and OH<sub>ad</sub> species, which react according to step (4) to produce CO<sub>2</sub>, as it is described in Fig. 9(a). Meanwhile, at this high overpotential values, on the Ru surface the CO adsorption is completely inhibited by the electroadsorption of OH<sub>ad</sub> species, situation that is illustrated in Fig. 8(b). Then, as the possibility that the reaction between CO<sub>ad</sub> and OH<sub>ad</sub> could take place heterogeneously

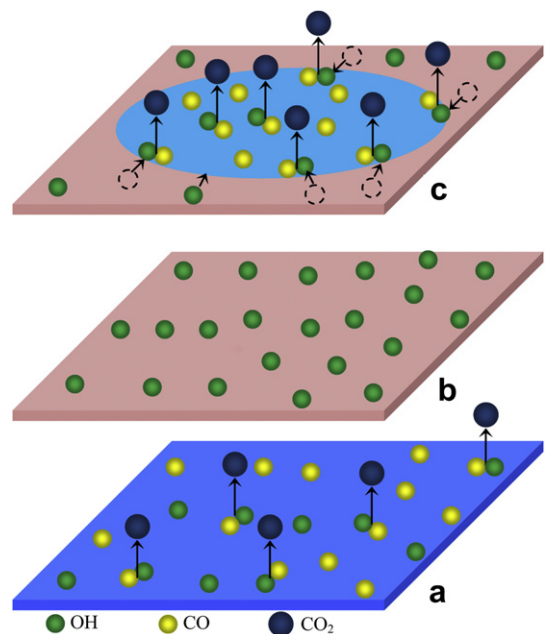
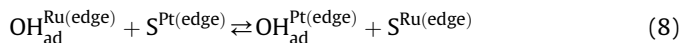


Fig. 9. Schemes of the electrode surface in the overpotentials range  $0.88 \leq \eta/V \leq 1.0 \text{ V}$ . (a) Pt; (b) Ru; (c) Pt/Ru.

was discarded, the excess in the electrocatalytic activity should be due in this case by the spillover of the  $\text{OH}_{\text{ad}}$ , which covers completely the Ru surface inhibiting the adsorption of CO, towards the free sites on the Pt side:



Step (8) allows the subsequent occurrence of step (4) on the Pt surface. This process implies that on Pt the  $\text{OH}_{\text{ad}}$  provided by the water electrosorption is complemented by the  $\text{OH}_{\text{ad}}$  coming from the Ru side due to the spillover. This situation is described in Fig. 8(c) and therefore the extensive overall net reaction rate of the CO oxidation on Pt/Ru for the region  $0.88 \leq \eta \leq 1.0 \text{ V}$  is given by the following contributions:

$$V = A_{\text{Pt}}v_{\text{Pt}} + I_{\text{Pt/Ru}}v_{\text{Pt/Ru}} \quad (9)$$

where  $A_{\text{Pt}}$  is the platinum surface area, being negligible the contribution of the ruthenium phase to the reaction rate.

On the basis of the model described, the reaction rate in the whole overpotentials region is determined by the contribution of three terms:

$$V = A_{\text{Pt}}v_{\text{Pt}} + A_{\text{Ru}}v_{\text{Ru}} + I_{\text{Pt/Ru}}v_{\text{Pt/Ru}} \quad (10)$$

being the electrode surface area  $A = A_{\text{Pt}} + A_{\text{Ru}}$ . It should be emphasizing that  $v_{\text{Pt}} \cong 0$  for  $0.6 \leq \eta/\text{V} < 0.82$  and  $v_{\text{Ru}} \cong 0$  for  $0.88 \leq \eta \leq 1.0 \text{ V}$ .

The analysis of the results obtained indicates that the carbon monoxide oxidation reaction takes place at low reaction rates on both Ru and Pt electrodes, but the spillover of  $\text{CO}_{\text{ad}}$  from Pt to Ru at low overpotentials and that of  $\text{OH}_{\text{ad}}$  from Ru to Pt at high overpotentials can explain the synergistic effect that enhances the overall reaction rate the positive excess electrocatalytic activity. Moreover, these processes can also explain the absence of this excess in the middle overpotential region. Thus, equation (10) clearly shows that the overall reaction rate must be analyzed considering the length of the intermetallic boundary.

Finally, it can be concluded that the design of the electrode surface that maximizes the intermetallic boundary region will lead to the best electrocatalysts for the CO electrooxidation reaction.

## 5. Conclusions

The present work provides direct experimental evidence about the contribution to the CO electrooxidation reaction of the intermetallic boundary region of a bimetallic electrode consisting in platinum islands deposited on ruthenium. From the comparison of the polarization curves obtained in steady state on the bimetallic electrode with those corresponding to the pure metals, it was possible to determine the excess electrocatalytic activity and thus it was demonstrated that the increase in the net current obtained is due to the contribution of the spillover of the adsorbed reaction intermediates located at the intermetallic region. It was also demonstrated that the direct reaction between the species

adsorbed on both sides of the edge is not feasible. Therefore, a surface configuration for a good electrocatalyst for the CO electrooxidation should consist in arrays of nanoislands of Pt (or Ru) on a Ru (or Pt) substrate, such that the intermetallic region is maximized.

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