Intermetallic junction contribution to the CO electrooxidation on a Pt/Au electrode: the excess voltammetric current

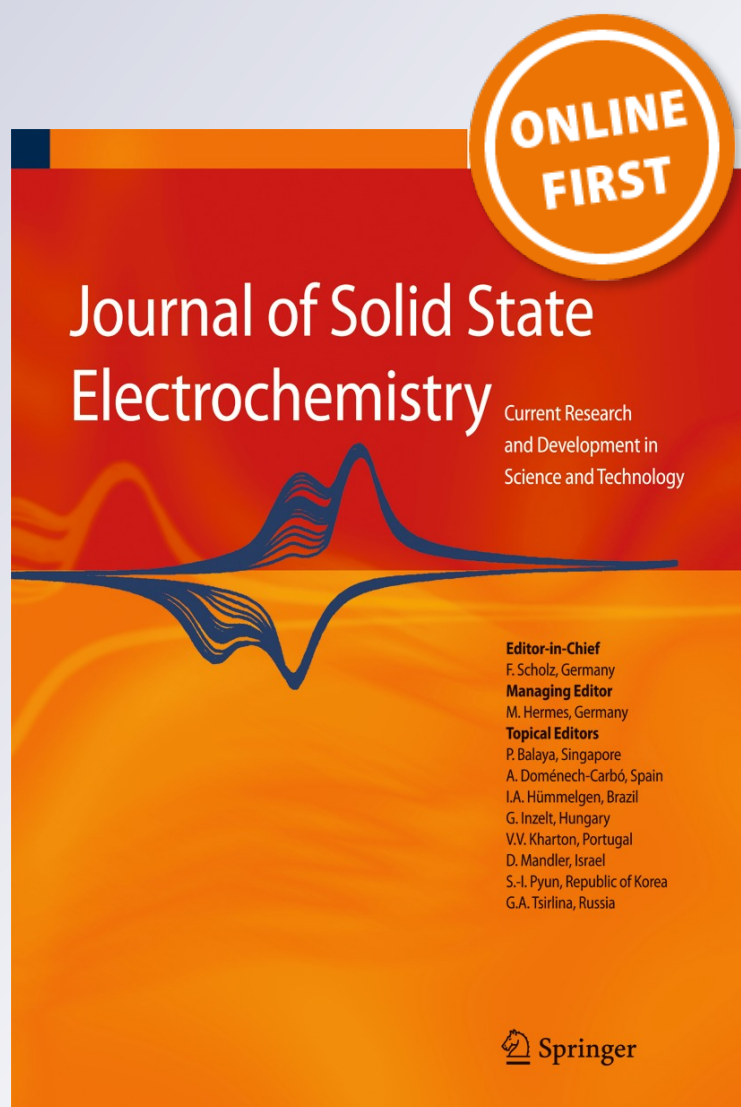## Gisela C. Luque, Maria R. Gennero de Chialvo & Abel C. Chialvo

Journal of Solid State Electrochemistry

Current Research and Development in Science and Technology

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ORIGINAL PAPER

Intermetallic junction contribution to the CO electrooxidation on a Pt/Au electrode: the excess voltammetric current

Gisela C. Luque[1] · Maria R. Gennero de Chialvo[1] · Abel C. Chialvo[1]

Abstract The contribution of the intermetallic junction to the electrocatalytic activity of a Pt/Au electrode for the carbon monoxide oxidation reaction (COOR) in alkaline solution is evaluated on the basis of the excess voltammetric current. This contribution is measured on a new type of bimetallic electrode characterized by a large ratio between the total intermetallic perimeter and the electrode area. The results obtained demonstrate that Pt/Au heterojunction enhances the reaction rate in two potential regions. This improvement is explained on the basis of the spillover of the CO adatoms from one side of the intermetallic junction to the other.

Keywords Intermetallic junction · Pt/Au electrode · CO oxidation reaction · Excess voltammetric current

Introduction

Adsorbed carbon monoxide is the common reaction intermediate in the electrooxidation of methanol, ethanol, etc., being a strong inhibitor of the reaction sites. Therefore, the search of alternatives for the improvement of its oxidation is essential in the development of direct alcohol fuel cells. In the search for high performance electrocatalysts, it has been proposed surface decoration [1–3], core-shell type nanoparticles [4–6] and bimetallic electrodes [7–9], amongst other alternatives. In this last case, alloy structures were employed, being the enhancement on the electrocatalytic activity mainly due to changes in the electronic states of the heteroatoms in the solid solution. An interesting alternative is the preparation of bimetallic electrodes constituted by a mosaic structure, which exhibit surface discontinuities of chemical nature. This interfacial region (bimetallic junction) could contribute to the kinetics of a given electrochemical reaction in an extension that should be evaluated. The conditions under which the reaction takes place on such region can be markedly different with respect to those on the monometallic regions, particularly when two or more reaction intermediates are involved. One reason for this behaviour is the difference between the electronic properties of this metallic ribbon of a few nanometers wide and those of the rest of the electrodic surface. Moreover, adsorbed reaction intermediates located at one side of the interfacial region, with specific concentrations and properties, can react with others located on the other side, existing also the possibility of spillover of the adsorbed species [10, 11]. Therefore, the evaluation of the contribution of the bimetallic junction deserves a special treatment. Thus, the concept of the voltammetric excess current (I_{exc}) is proposed for a fast and accurate determination of the contribution of the interfacial region between two metals with different electrocatalytic properties. This concept is applied to the carbon monoxide oxidation reaction (COOR). It involves the reaction intermediates CO_{ad} and OH_{ad}, which exhibit markedly different adsorption properties, strongly dependent of the electrode material [12]. For the calculation of I_{exc}, a bimetallic electrode with a mosaic type surface is used, constituted by a metal M_1 occupying an area A_1 and a metal M_2 occupying an area A_2. The excess voltammetric current due to the intermetallic junction is defined as the difference between the current measured in the bimetallic electrode of area ($A_1 + A_2$), and the sum of the

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current values measured at the electrodes constituted by the metals M_1 and M_2 with areas A_1 and A_2, respectively, operating under equal reaction conditions. Being the excess voltammetric current proportional to the length of the intermetallic junction, it should be important to obtain a high ratio between the junction perimeter and the electrode area. Clearly, if this excess current is zero, the intermetallic region does not influence the kinetic of the reaction. On the contrary, if it is positive or negative, it will be a case of catalysis or inhibition respectively originated in the junction. Consequently, this technique gives information related to the role of the intermetallic region on the electrode reactions, which cannot be obtained by conventional methods. On this context, the present work evaluates the excess voltammetric current for the carbon monoxide electrooxidation on a rotating bimetallic Pt/Au electrode in 0.1 M NaOH solution saturated with CO gas.

Previous considerations

As it was already mentioned in the "Introduction" section, the bimetallic electrode must have a long intermetallic junction in order to obtain a measurable contribution to the electrode current. This condition is fulfilled by a mosaic-like structure constituted by islands of metal M_1 on a substrate of metal M_2. It should be also important that the areas A_1 and A_2 have similar values in order to guarantee equal reaction conditions than those on a monometallic electrode. Moreover, a linear diffusion towards each metal must be ensured. Criteria for this linear diffusion were developed for particle arrays supported on an inert substrate [13]. Although in the bimetallic electrode all the surface is active, it can be considered the most unfavourable situation, where one of the metals is inactive. In such a case, electrode can be assimilated to an array of islands with radius (r). Diffusion over the islands will be linear when the relationship between the thickness of the Nernst diffusion layer (δ) and r is $\delta/r<0.3$ [13]. The thickness δ is determined by the electrode rotation rate (ω) according to the Levich equation: δ [cm]$=0.0482\ \omega^{-1/2}$ [rpm$^{-1/2}$] [13]. Thus, it can be concluded that for islands with a radius of approximately 50 μm, the relationship $\delta/r<0.3$ is fulfilled with a rotation rate $\omega>1000$ rpm.

Experimental details

Electrode preparation and characterization

Discs of Pt and Au of 1 cm diameter supported in Teflon holders, with an exposed geometric area of 0.23 cm^2, were used as rotating working electrode. The polycrystalline Pt disc were polished with 1 μm alumina powder and its purity was verified by cyclic voltammetry in 0.1 M HClO$_4$ solution. The

Au electrode was prepared by electrodeposition on the Au disc substrate in order that its surface morphology be the same as that of the gold phase in the bimetallic electrode. The electrodeposition was carried out in a 0.095 M HAuCl$_4$ solution by the application of a current density of 5 mA cm^{-2} during 2 h. Finally, the bimetallic Pt/Au electrode was prepared with a Pt disc equal to that described previously, which was covered with a commercial screen printing polyester mesh of 80 thread count. This mesh was pressed against the Pt substrate at 180 °C during 30 min. After being removed from the press and cooled to room temperature, it was subjected to an electrodeposition process in the same bath and conditions as described above in order that the electrocatalytic properties of the gold phase in the bimetallic electrode be the same as those of the Au electrode. After electrodeposition, the electrode was immersed in toluene where the polyester mesh is detached. Then, it was repeatedly rinsed first with acetone and then with water. After that, the bimetallic electrode was subjected to a cleaning process consisting in an immersion in concentrated hot H$_2$SO$_4$ during 30 min. Finally, it was rinsed with ultrapure water.

The surface morphologies of the electrodeposited electrodes were characterized by scanning electron microscopy (SEM). They were also electrochemically characterized by cyclic voltammetry in 0.1 M HClO$_4$ solution at 0.10 V s^{-1}. The corresponding electrochemical electrode areas were evaluated from the potentiodynamic profiles.

COOR kinetic measurements

The experimental determination of the voltammetric current for the CO oxidation reaction was carried out in a three electrode cell specially built for the use of a rotating electrode. The counter electrode was a large area Pt electrode located externally to the cell. A reversible hydrogen electrode in the same solution (RHE) was used as reference electrode, placed in a holder connected to a Luggin capillary of 0.2 mm diameter, located in the centre and at a distance of 0.2 mm from the working electrode surface. This configuration ensures that the ohmic effects are negligible in the experimental conditions and that the hydrodynamics of the solution near the rotating electrode is not affected. The potentiodynamic sweeps were applied by a potentiostat-galvanostat TEQ4. The working electrode was rotated employing a Radiometer EDI 10000 system at 1600 rpm. The electrolyte was 0.1 M NaOH (Merck pro analysis) prepared with ultrapure water (PureLab, Elga LabWater), which was subjected to a continuous and efficient carbon monoxide bubbling at $p=1$ atm. The CO oxidation was carried out by repetitive potentiodynamic sweeps run at 0.01 V s^{-1}, in the potential range comprised between 0.3 and 1.4 V.

Results and discussion

Electrode characterization

The surface morphology was characterized by scanning electron microscopy (SEM). Figure 1a shows a SEM micrograph of the bimetallic electrode. It can be observed the Pt islands, originated in the contact between the mesh and the Pt substrate, with an elliptical shape of approximately 110–120 μm (major axis) and 80–90 μm (minor axis). These islands are surrounded by electrodeposited Au, configuring a surface structure with a long length of the Pt/Au junction. Meanwhile, Fig. 1b illustrates the surface morphology of the Au electrodeposit, with crystallites size of 1 μm superficially oriented on high Miller indices. As expected, this type of morphology is observed in both, bimetallic Pt/Au and monometallic Au electrodes. It should be important to note that the surface roughness of the electrodeposit is more than one order of magnitude lower than the diffusion layer ($\delta=12$ μm) and thus there is no effect of crystallite size on the current-potential response.
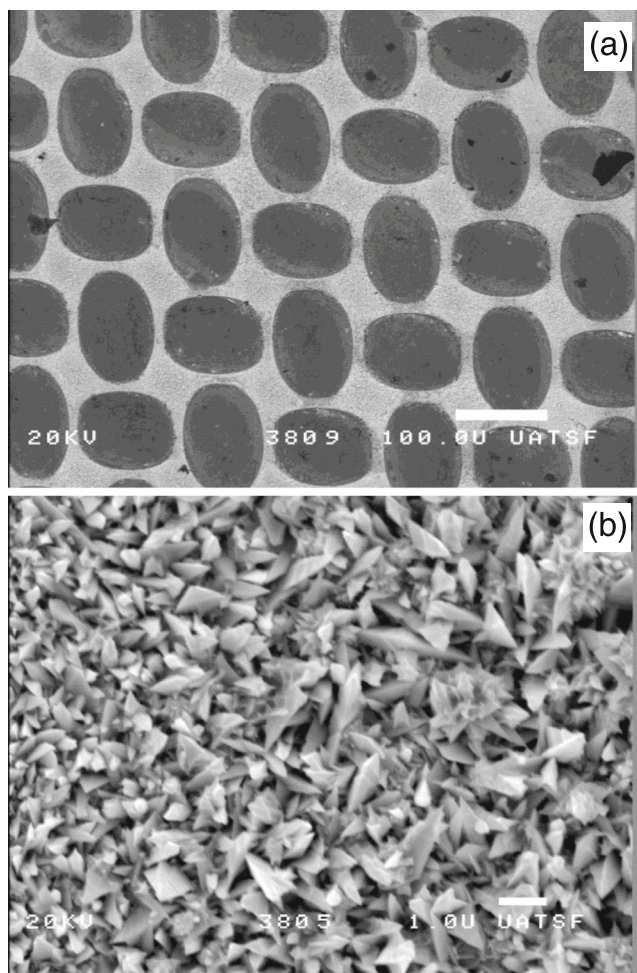
Fig. 1 SEM micrographs of **a** Pt/Au electrode, *scale bar*: 100.0 μm; **b** electrodeposited Au electrode, *scale bar*: 1.0 μm

Electrodes were also characterized electrochemically by cyclic voltammetry carried out in 0.1 M $HClO_4$ solution at a sweep rate of 0.1 V s^{-1}. The voltammetric profile of the Pt/Au electrode in 0.1 M $HClO_4$ solution, run at 0.1 V s^{-1}, in the potential range comprised between 0.05 and 1.40 V, is depicted in Fig. 2. The voltammogram is similar to those previously obtained by other authors [14, 15]. It can be observed the two peaks characteristic of the electroreduction of gold oxide (1.16 V) and Pt oxide (0.63 V), as well as the peaks corresponding to the adsorption/desorption of H_{UPD} on Pt. These voltammetric peaks were employed for the evaluation of the electrochemical area corresponding to the surface fraction covered by Au and Pt. The determination of the electrochemical area of the Pt and Au electrodes were carried out in a similar way.

Voltammetric CO electrooxidation

CO electrooxidation on Pt Previous to the COOR study, the electrodic area was evaluated from the H_{UPD} voltammetric charge in acid solution and the resulting value was 0.51 cm^2. The anodic part of the potentiodynamic profile resulting from a repetitive voltammetric sweep at 0.01 V s^{-1} applied to the Pt electrode in alkaline solution saturated with CO can be appreciated in Fig. 3a. It can be observed an exponential increase of current density up to the peak at 0.7 V, which is followed by a second broad peak and then reaching current density values near zero at 1.4 V. The mechanism of COOR on Pt in alkaline solution remains uncertain, with different proposals [15–22]. All of them begin with the adsorption of CO, but they differ in the reaction of CO_{ad} with OH species. It could be the hydroxyl ion in solution (OH$^-$) [16, 17], adsorbed hydroxyl (OH$_{ad}$) [17–20] and also the hydroxyl ion specifically adsorbed (OH$_{ad}^-$) [21, 23]. Moreover, it is considered that the surface diffusion of CO_{ad} depends on the crystallographic orientation
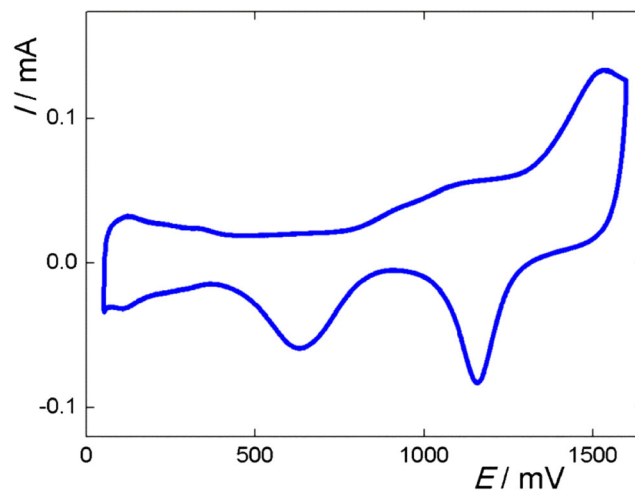
Fig. 2 Potentiodynamic profile of the Pt/Au electrode in 0.1 M $HClO_4$ solution, run at 0.1 V s^{-1}, 25 °C
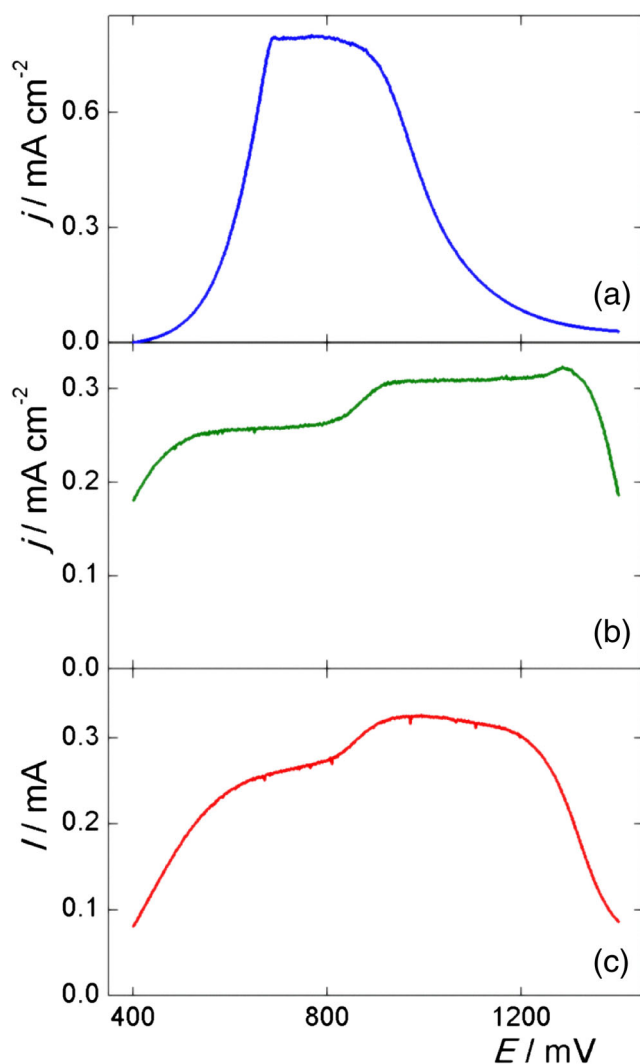
Fig. 3 Anodic voltammetric profiles in 0.1 M NaOH solution saturated with CO gas, run at 0.01 V s^{-1}, 25 °C. Electrodes: **a** Pt; **b**, Au; **c** Pt/Au

Pt(hkl) [18, 23], but this effect would be significantly lower than in acid solutions [20].

CO electrooxidation on Au Figure 3b exhibits the anodic voltammetric profile of the Au electrode obtained in the 0.1 M NaOH solution saturated with CO, resulting from the application of cyclic voltammetry at a sweep rate of 0.01 V s^{-1}. This profile shows differences with respect to that on Pt. It can be observed two plateaus, the first one is preceded by a fast current density increase since 0.4 V and it is extended up to 0.8 V. Then there is an increase of current up to the second plateau, which is extended up to 1.2 V. The transition between the two plateaus is observed only under rotation and its origin cannot be explained yet. It was also observed in the response of Au(hkl) of low indexes [20, 24]. Taking into account that the voltammogram obtained in the same conditions but in absence of CO exhibits a small shoulder at 0.8 V, it can be considered that at this potential, it is produced the discharge

of the specifically adsorbed hydroxyl ion ($OH_{ad}^{-} \rightarrow OH_{ad} + e^{-}$). It should be noticed that the species OH_{ad}^{-} provides only little charge donation to the Au surface, as it has been shown by surface-enhanced Raman spectroscopy [25]. Additionally, a change in the superficial atomic order could take place due to the CO adsorption [25, 26]. All these phenomena would lead to differences in the behaviour of the COOR depending on the potential range analyzed. On the other hand, the corresponding Au electrode area was determined previously from the oxide electroreduction charge in 0.1 M HClO$_4$ solution [27], which was equal to 1.42 cm^2. The corresponding current densities were calculated with this value.

CO electrooxidation on Pt-Au Finally, Fig. 3c shows the response to the application of the potentiodynamic sweep in alkaline solution saturated with CO to the bimetallic Pt/Au electrode. It should be taken into account that such response corresponds to the sum of the contributions of the area fraction of each metals and that of the intermetallic region. The area fractions were obtained from the voltammetric profile shown in Fig. 2, following the procedure described before. The area occupied by Pt was $A_{Pt}=0.17$ cm^2 and that occupied by Au was $A_{Au}=0.353$ cm^2.

From these three voltammetric profiles corresponding to the Pt, Au and Pt/Au electrodes, the specific contribution of the intermetallic region will be obtained by the evaluation of the excess voltammetric current, as it is described in the following item.

Excess voltammetric current (I_{exc}) The contribution of the intermetallic region to the current drained by the bimetallic electrode for the COOR can be evaluated by the following expression:

$$I_{exc} = I_{Pt/Au} - (j_{Pt}A_{Pt} + j_{Au}A_{Au}) \tag{1}$$

where $I_{Pt/Au}$ is the voltammetric current corresponding to the bimetallic electrode (Fig. 3c), j_{Pt} and j_{Au} are the current densities corresponding to Pt (Fig. 3a) and Au (Fig. 3b) electrodes respectively. Finally, A_{Pt} (0.17 cm^2) and A_{Au} (0.353 cm^2) are the corresponding areas of Pt and Au in the bimetallic electrode. The variation of I_{exc} on potential is illustrated in Fig. 4, where it can be appreciated two well defined positive regions. The first region is comprised between 0.40<E/V<0.68 and exhibits a peak around 0.56 V. The other region is comprised between 0.68<E/V<1.40 with a peak at 1.15 V. These results clearly show that the intermetallic junction contribute significantly to the global response to the COOR. At the potentials corresponding to the peaks, the contribution is equal to 40 and 50 % respectively of the total current (compare Fig. 4 with Fig. 3c). This implies that the reaction mechanism involves at least another reaction route, different from those verified on both metal phases. On the basis of these results, a kinetic
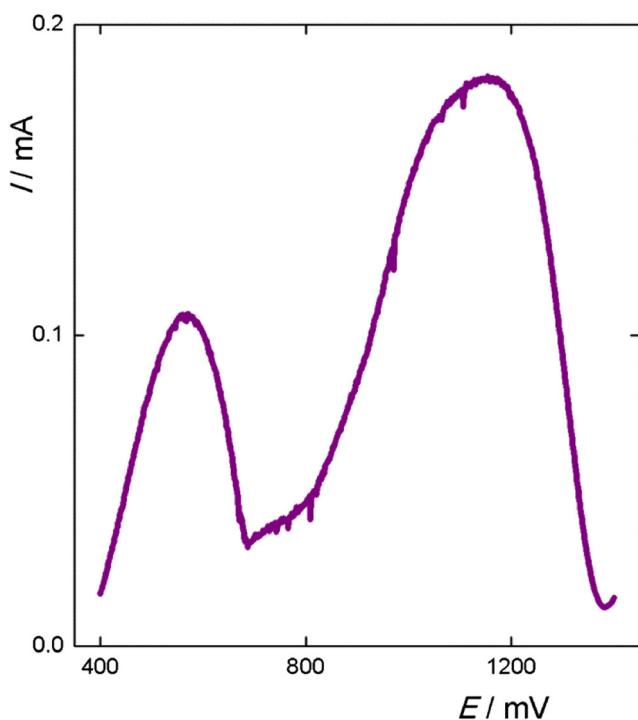
Fig. 4 Dependence of the excess voltammetric current on potential due to Pt/Au heterojunction

model is proposed to explain the effect of the bimetallic junction on the COOR. Moreover, the contribution of the junction is not only determined by the nature of this intermetallic region but also by its length.

Kinetic model for the COOR in the bimetallic junction

For the correct interpretation of the results obtained, it will be discussed at first the possibility of CO lateral diffusion when one of the metals are not active for the reaction. This condition is fulfilled at 0.4 V, where Pt can be considered inactive (Fig. 3a). It can be quickly appreciated that the excess current at this potential is 10 % of that corresponding to the maximum observed at $E=0.56$ V, being it the greatest value of the lateral diffusion contribution. Moreover, it should be noticed that at 0.58 V and at 1.05 V, both metals have the same current densities (Fig. 3a, b), condition in which the possibility of lateral diffusion vanishes. At these potential values, excess current is almost equal or quite similar to that of the corresponding peaks. Therefore, the excess current cannot be originated in diffusion contributions, but in processes taking place in the intermetallic junction.

Although the kinetic mechanism of the COOR in alkaline solution is a matter under discussion, it appears that its initiation is determined by the interaction of the adsorbed species CO_{ad} and OH_{ad} (or OH_{ad}^-). Thus, two hypotheses can be stated for the explanation of the excess current: (i) the COOR initiation through a Langmuir-Hinshelwood or Eley-Rideal

reaction type, involving the junction as a particular reaction environment, or (ii) the spillover of the reaction intermediates located at both sides of the junction promotes the COOR in the metallic phases. The first hypothesis has the difficulty to explain the existence of the two regions in the excess voltammetric current profile (Fig. 4), where it would be reasonable to expect only one current peak. On the other hand, the second hypothesis can explain the two regions on the basis of the spillover of the CO_{ad} species, together with differences in the behaviour of the adsorbed intermediates on the two metallic surfaces. It can be observed that the potential region corresponding to the first ($0.40<E$ / $V<0.68$) ends precisely when the current on Pt (Fig. 3a) reaches its maximum value ($E=0.68$ V). Moreover, from the comparison of Figs. 3a and 3b, it can be concluded that the CO consumption rate on Au is greater than on Pt. Thus, there is a driving force for the superficial diffusion (spillover) of CO_{ad} from Pt to Au, which can be described as follows.

$$CO_{ad}^{Pt} + S_{Au} \rightarrow CO_{ad}^{Au} + S_{Pt} \tag{2}$$

being S_{Pt} and S_{Au} free adsorption sites near the junction on Pt and Au respectively. Thus, step (2) promotes the COOR on the Au phase through the increase of amount of CO adsorbed on its surface. The sites liberated on the Pt surface are covered again by the CO from solution and thus contribute to the excess current involved in the first peak. On the other hand, in the potential region ($0.68<E$ / $V<1.40$) corresponding to the second peak (Fig. 4), a similar process should be verified, but in the opposite direction. The CO_{ad} surface coverage on Pt significantly decreases at the expense of a strong increase of the amount of OH_{ad}. Therefore, the process taking place in this potential region can be described as

$$CO_{ad}^{Au} + S_{Pt} \rightarrow CO_{ad}^{Pt} + S_{Au} \tag{3}$$

In other words, the excess voltammetric current would be originated in the different dependence of the CO_{ad} surface coverage on potential for each electrode surface. The instantaneous values of this coverage define the driving force and the direction of the surface diffusion processes.

Conclusion

The measurement of the excess voltammetric current allows demonstrating that the Pt/Au junction enhances the electrocatalytic activity of the bimetallic electrode for the CO oxidation reaction. This behaviour can be attributed to the contribution of the CO adatoms located near the interfacial region, which are able to diffuse and spill over the junction. Moreover, the existence of two potential regions on the profile of the excess voltammetric current would be determined by the direction of such spillover process, which depends on the electrode

potential. This result leads to the conclusion that a new family of bimetallic electrocatalysts for the COOR and other electrochemical reactions can be prepared through the correct selection of the metals and the increase of the junction extension with respect to the electrodic area.

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