DOI: 10.1002/cctc.201200687

Unusually high activity of Pt islands on Rh(111) electrodes for ethanol oxidation

Vinicius Del Colle,^[b] Vitali Grozovski^[a], Enrique Herrero^{[a]*} and Juan M. Feliu^[a]

The electrooxidation of ethanol has been widely studied since its possible application in PEM cells. Many efforts have been devoted to disentangle its oxidation mechanism and how this mechanism depends on the ethanol concentration and the surface structure and composition of the electrode.^[1–4] The goal is to obtain CO₂ as final product at the lowest potential and the highest current. In the oxidation mechanism, three different products can be obtained: acetaldehyde, acetic acid and CO₂, exchanging 2, 4 and 12 electrons respectively. Acetic acid is a stable product since its oxidation takes place at very high potentials^[5], thus the challenge is to break the C-C bond either in ethanol^[6, 7] or acetaldehyde^[8] to obtain CO₂.

Among pure metals, platinum has the highest catalytic activity in acid media, but the final product in the oxidation is mixture of CO₂ and acetic acid, whose ratio strongly depends on the surface structure.^[9] In order to increase the activity of platinum, other metals, namely, Ru,^[8, 10] Os,^[11, 12] Sn^[7] and Rh^[13] have been added to the surface to diminish the overpotentials and to increase the selectivity of the oxidation towards the formation of CO₂. The effect of these metals in the oxidation mechanism has been explained on the basis of the bifunctional mechanism^[14] and ligand effect.^[15] From previous results, it seems clear that the only surface modifier that increases the CO₂/acetaldehyde ratio is Rh,^[13] although the overall reaction rate is lower. On the other hand, the opposite combination, Pt deposited on Rh electrodes has not been studied yet. Rh electrodes are not active for the oxidation of ethanol. However, it has been shown that a single layer (or submonolayer) of a metal deposited on a different substrate can have electrocatalytic activities larger than any of the two bulk metals.^[16, 17] In general, the metal overlayer has interatomic distances that are different from the bulk metal, since it accommodates its structure to that of

the underneath substrate. This effect causes a change in the electronic properties of the overlayer and can increase (or decrease) the catalytic properties.^[18] The aim of this work is to determine the electrochemical behaviour of Rh electrodes modified by Pt (sub)monolayers for ethanol oxidation, analysing the effect of the surface composition on the mechanism using *in situ* FTIR spectroscopy.

Figure 1 shows the cyclic voltammograms for three different Pt coverages on the Rh(111) electrode. The deposition of trace amounts of Pt on the Rh(111) surface triggers a significant change in the voltammogram of the Rh(111) electrode.^[19] For the clean Rh(111) electrode, the voltammogram in sulphuric acid solution shows a pair of quasi-reversible peaks at 0.15 and 0.06 V, which are associated to the competitive adsorption of hydrogen/sulphate on the electrode surface.^[20, 21] In the initial deposition stages of Pt, these peaks become significantly sharper and more reversible. Although the explanation on the origin of such change is beyond the scope of this manuscript, it should be recalled that the interaction of water with adsorbates is different on platinum and rhodium. For instance water and CO adsorbed on Pt(111) show repulsive interactions whereas attractive interactions are measured on Rh(111) electrodes.^[22] Changes in the net interaction of the water molecules with the adsorbates (sulphate or hydrogen) should lead to changes in the voltammogram.

Increasing the Pt coverage leads to the diminution of the sharp peaks and the increase of a broad signal between 0.06 and 0.35 V characteristic of hydrogen adsorption on platinum (fig. 1B). As shown by STM, the total Pt amount on the surface cannot be determined directly by voltammetry,^[19] since platinum deposition follows a Volmer-Weber island growth mechanism.^[23] At the initial stages of Rh deposition, Pt forms monoatomic-high islands, but as the deposition progress, multiatomic high islands appear. In spite of that, the changes in the coverage can be characterized voltammetrically. When the Rh(111) electrode is cycled up to 1 V, some surface oxides are formed above 0.8 V, without apparent difference in the surface structure. These oxides are reduced in a single peak at 0.70 V in the negative going scan. As can be seen in the inset of figure 1A, the charge under this peak diminishes as the Pt coverage increases and can be used to characterize the area of the electrode covered by platinum. The three coverages are then 0.05, 0.047 and 0.89. The value measured for the low platinum coverage sample (0.05) is in agreement with that obtained by the STM using identical conditions.^[19] For the other

[a] Dr. V. Grozovski, Prof. E. Herrero, Prof. J.M. Feliu
Instituto de Electroquímica,
Universidad de Alicante,
Apartado 99, E 03080 Alicante, Spain.
Tel: +34-965 909814,
Email: herrero@ua.es

[b] Dr. V. Del Colle
Departamento de Química,
Universidade Federal de Alagoas-Campus Arapiraca,
Av. Manoel Severino Barbosa S/N, Bom Sucesso 57309-005 -
Arapiraca (AL), Brazil

Supporting information for this article is available on the WWW
under <http://dx.doi.org/10.1002/cctc.201200687>

two surfaces the total platinum amount should be higher, since multiatomic-high platinum islands are observed by STM and the present values should be considered as the lower limit.

Figure 1. **A)** Cyclic voltammograms of Rh(111) and Pt-Rh(111) electrodes in 0.1 M H_2SO_4 with three different Pt coverage. Inset: enlargement of the oxide reduction peak. **B)** Enlargement of the potential region between 0.05 and 0.35 V. Scan rate: 50 mV s^{-1} .

The other parameter that can be used to characterize the electrode is the charge under the peak at low potentials (figure 1B). For all the electrodes, this charge is associated with the adsorption of hydrogen and sulphate. In the case of the Rh(111) this charge is $316 \mu\text{C cm}^{-2}$, whereas the charge for the Pt(111) electrode is $241 \mu\text{C cm}^{-2}$. In an epitaxial growth of the Pt layer, it is expected that the total charge for hydrogen/sulphate adsorption diminishes. On the other hand, if multiatomic-high islands appear, the charge should increase due to the formation of a non-flat interface. For the low Pt coverage, the charge slightly diminishes, ($310 \mu\text{C cm}^{-2}$), which is in agreement with the formation of an epitaxial Pt layer at very diluted coverage. For the other two coverages, the charge increases to 320 and $472 \mu\text{C cm}^{-2}$, respectively. In this latter case, the Rh(111) surface is almost covered by Pt, and a charge of $241 \mu\text{C cm}^{-2}$ would have been expected for an epitaxial growth. Thus, the measured charge indicates that the obtained surface roughness is equivalent to a platinum surface with a roughness factor of 2. In fact, the voltammetric profile of this electrode resembles that of a polycrystalline platinum electrode.

The activity of these electrodes for ethanol oxidation was studied by cyclic voltammetry (Fig. 2A) in which the voltammograms for the Pt(111), Pt poly and Rh(111) electrodes have been added for a better comparison. As expected, the currents for the Rh(111) electrode are negligible. When the Rh(111) electrode is modified with small amounts of Pt, the activity of the electrode increases significantly. It should be highlighted that the coverage in this case is only 0.05 and the

currents densities (calculated according to the area of the Rh(111) electrode) are higher than those measured for the Pt(111) electrode, although the onset of ethanol oxidation is slightly more positive. Since Rh atoms are completely inactive for the oxidation of ethanol, only 5% of the surface atoms are active. For a real comparison with the Pt electrodes, the current density should be referred to the platinum active area, i.e., dividing the measured current density for this electrode by 0.05. When this current density is calculated (figure 2B), it can be observed that the activity of this electrode is more than 20 times higher than that measured for the Pt poly electrode, which is indeed higher than that of the Pt(111) electrode.^[9]

Figure 2. **A)** Cyclic voltammograms of ethanol oxidation on Rh(111), Pt(111), Pt poly and Pt-Rh(111) with different Pt coverages in 0.1 M H_2SO_4 + 0.5 M EtOH. The current densities are calculated according to the area of the electrodes. Scan rate 50 mV s^{-1} . **B and C)** Same as figure 2A for selected electrodes but the current density is calculated according to the platinum active area of the electrodes.

The modified electrode with a high platinum coverage has the highest current density of all the studied electrodes. As aforementioned, multiatomic-high Pt islands are present on the electrode surface, which leads to an apparent roughness factor of two for the Pt islands. If this surface area of platinum is taken into account (figure 2C), the activity of the electrode is almost identical to that measured for the Pt poly electrode. These results demonstrate, first of all, that the catalytic activity of small platinum islands completely surrounded by rhodium atoms are 20 times more reactive for ethanol oxidation than the pure platinum electrode. The increase in reactivity is probably associated to a modification on the electronic properties of the platinum electrode,

which increases its reactivity towards ethanol oxidation. In this case, the Pt islands are expected to have lower Pt-Pt distances than those measured on a Pt bulk electrode, since the Rh-Rh distances on the Rh(111) surface (0.269 nm) are smaller than the Pt-Pt distances on the bulk metal (0.277 nm). Thus, the formation of a compressed Pt layer seems to increase the catalytic activity, by changing the electronic properties.^[18] It is also possible that the active site for the reaction is the ensemble Pt-Rh, as has been shown for other adlayers and reactions.^[24] To fully understand the effect, a more detailed study is being carried out including other electrode surfaces and different coverages. Second, the multiatomic-high islands have the same activity than the polycrystalline platinum, and the presence of an underlayer of rhodium has no significant effect on the electrocatalytic activity for ethanol oxidation. It is well known that the special electrocatalytic properties of monolayers almost disappear when the second layer is deposited on top due to the relaxation of the distances in the second layer.^[25]

FTIR experiments were carried out for the same coverages to determine whether the cleavage of the C-C bond takes place or only acetaldehyde and acetic acid are formed. The spectra are qualitatively the same for all the Pt coverages (fig. S1), showing bands at 2342 cm⁻¹ for CO₂, at 2050 cm⁻¹ for adsorbed linear CO, at 1713 for the -COOH and CHO groups in acetic acid and acetaldehyde and several bands between 1420-1200 cm⁻¹, for different vibrational modes of acetic acid and acetaldehyde.^[9] As expected, the spectra for the Rh(111) are featureless, due to its inactivity towards the oxidation reaction of ethanol. The intensities of some of those bands normalized to the coverage values determined previously are plotted in figure 3A-C. As can be seen, adsorbed CO is observed in all cases at potential below 0.6 V (figure 3A), potential at which adsorbed CO is oxidized to CO₂. When the three electrodes are compared, the normalized intensity for the electrode with the lower coverage has the highest intensity. This fact indicates that the Pt islands present on the Rh(111) surface retain their ability to break the C-C bond, since CO originates from the cleavage of the C-C bond. As has been shown, when the C-C bond is broken, the -CH₂OH fragment is immediately transformed into adsorbed CO.^[6] Moreover, their electrocatalytic activity for the cleavage is significantly higher than the multiatomic-high Pt islands. As aforementioned, CO is oxidized to CO₂ above 0.6 V, and therefore in parallel to the disappearance of the CO band, the CO₂ band appears at 0.60 V. As before, the relative intensity of this band is higher for the surfaces with the lowest Pt coverage. Finally, the band related with the carbonyl/carboxyl follows the same trend for the other two previous bands.

Figure 3. Integrated band intensity normalized to the Pt coverage for (A) adsorbed CO_{linear} at 2040 cm⁻¹, (B) CO₂ at 2340 cm⁻¹ and (C) C=O group from acetaldehyde and acetic acid at 1724 cm⁻¹ as a function of the potential on the Rh(111) electrode with different Pt coverages.

These results corroborate the significantly higher activity of the Pt monoatomic islands on the Rh(111) surface and that those islands are able to cleave the C-C bond. In addition, it opens up new possibilities for developing more efficient electrocatalyst for ethanol oxidation by depositing Pt on a metal in which the Pt-Pt distances are compressed.

Experimental Section

Rh(111) and Pt(111) electrodes were cut and polished from a small single crystal bead following the procedure described by Clavilier.^[26] After that, they were cleaned by flame annealing and cooled down in H₂/Ar and protected with water in equilibrium with this gas mixture to prevent contamination and surface oxidation before immersion in the electrochemical cell, as described elsewhere.^[27] A rhodium and platinum single crystal beads were used as a reproducible model of a polyoriented electrode. Platinum deposition on the Rh electrodes was carried out by cycling the electrode in solutions containing 10⁻⁶ - 10⁻⁴ M Na₂PtCl₆ + 0.1 M H₂SO₄ in potential range between 0.05 - 0.80 V for Rh poly and 0.05 - 1.00 V for Rh(111) at a scan rate of 0.050 V s⁻¹. Under those circumstances, the Pt deposition is a mass controlled process that takes place in the whole potential window. The ethanol oxidation studies were carried out in second cell with a 0.5 M C₂H₅OH + 0.1 M H₂SO₄ solution. For the chronoamperometric studies, the curves for ethanol oxidation were recorded for 300 seconds, applying successive potential steps of 0.050 V in the positive direction from 0.55 to 1.0 V vs. RHE.

Spectroelectrochemical experiments were carried out with a Nicolet Magna 850 spectrometer equipped with a narrow-band MCT detector, as described elsewhere^[7]. The reference spectra was acquired at 0.050 V whereas the sample spectra were recorded after applying successive potential steps of 50 mV in the positive and negative directions from 0.05 to 1.0 V vs. RHE.

Experiments were carried out at room temperature, 22-25 °C, in a classical two-compartment electrochemical cell including a platinum counter electrode and a reversible hydrogen electrode (RHE) as reference. Solutions were prepared from sulphuric acid (Merck suprapur®), ethanol (Merck p.a.), ultrapure water from a Purelab Ultra (Elga-Vivendi) system. H₂ and Ar were also employed (N50, Air Liquide). The cleanliness of the solutions was tested by the stability of the characteristic voltammetric features of well-defined single crystal electrodes.

Acknowledgements

Financial support by the MICINN (Spain) (project CTQ2010-16271) and Generalitat Valenciana (project PROMETEO /2009/045, FEDER) is acknowledged. V. Del Colle thanks the Universidad de Alicante by the financial support during his stay as invited researcher.

Keywords: Platinum • rhodium • ethanol oxidation • electrocatalysis • island deposition

- [1] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, 8, 621-629.
- [2] G. A. Camara, T. Iwasita, *J. Electroanal. Chem.* **2005**, 578, 315-321.
- [3] J. Souza-Garcia, E. A. Ticianelli, V. Climent, J. M. Feliu, *Chem. Sci.* **2012**.
- [4] D. J. Tarnowski, C. Korzeniewski, *J. Phys. Chem. B* **1997**, 101, 253-258.

- [5] A. Rodes, E. Pastor, T. Iwasita, *J. Electroanal. Chem.* **1994**, 376, 109-118.
- [6] J. Souza-Garcia, E. Herrero, J. M. Feliu, *ChemPhysChem* **2010**, 11, 1391-1394.
- [7] V. Del Colle, J. Souza-Garcia, G. Tremiliosi, E. Herrero, J. M. Feliu, *Phys. Chem. Chem. Phys.* **2011**, 13, 12163-12172.
- [8] S. C. S. Lai, S. E. F. Kleyn, V. Rosca, M. T. M. Koper, *J. Phys. Chem. C* **2008**, 112, 19080-19087.
- [9] F. Colmati, G. Tremiliosi-Filho, E. R. Gonzalez, A. Berna, E. Herrero, J. M. Feliu, *Faraday Discuss.* **2008**, 140, 379-397.
- [10] V. Del Colle, A. Berna, G. Tremiliosi, E. Herrero, J. M. Feliu, *Phys. Chem. Chem. Phys.* **2008**, 10, 3766-3773.
- [11] V. Del Colle, V. Santos, G. Tremiliosi-Filho, *Electrocatalysis* **2010**, 1, 144-158.
- [12] V. P. Santos, V. Del Colle, R. B. de Lima, G. Tremiliosi-Filho, *Langmuir* **2004**, 20, 11064-11072.
- [13] J. P. I. de Souza, S. L. Queiroz, K. Bergamaski, E. R. Gonzalez, F. C. Nart, *J. Phys. Chem. B* **2002**, 106, 9825-9830.
- [14] M. Watanabe, S. Motoo, *J. Electroanal. Chem.* **1975**, 60, 267-273.
- [15] T. Frelink, W. Visscher, J. A. R. Vanveen, *Surf. Sci.* **1995**, 335, 353-360.
- [16] M. J. Llorca, J. M. Feliu, A. Aldaz, J. Clavilier, *J. Electroanal. Chem.* **1994**, 376, 151-160.
- [17] L. A. Kibler, A. M. El Aziz, R. Hoyer, D. M. Kolb, *Angew. Chem., Int. Ed.* **2005**, 44, 2080-2084.
- [18] J. R. Kitchin, J. K. Nørskov, M. A. Barteau, J. G. Chen, *Phys. Rev. Lett.* **2004**, 93, 156801.
- [19] T. H. M. Housmans, J. M. Feliu, R. Gómez, M. T. M. Koper, *ChemPhysChem* **2005**, 6, 1522-1529.
- [20] Q. Q. Xu, U. Linke, R. Bujak, T. Wandlowski, *Electrochim. Acta* **2009**, 54, 5509-5521.
- [21] R. Gómez, J. M. Orts, J. M. Feliu, J. Clavilier, L. H. Klein, *J. Electroanal. Chem.* **1997**, 432, 1-5.
- [22] F. T. Wagner, T. E. Moylan, S. J. Schmieg, *Surf. Sci.* **1988**, 195, 403-428.
- [23] A. Cuesta, M. a. Escudero, B. Lanova, H. Baltruschat, *Langmuir* **2009**, 25, 6500-6507.
- [24] E. Leiva, T. Iwasita, E. Herrero, J. M. Feliu, *Langmuir* **1997**, 13, 6287-6293.
- [25] J. M. Feliu, B. Alvarez, V. Climent, A. Rodes, in *Thin Films: Preparation, Characterization, Applications* (Eds.: M. P. Soriaga, J. Stickney, L. A. Bottomley, Y. G. Kim), Kluwer Academic/Plenum Publ, New York, **2002**, pp. 37-52.
- [26] J. Clavilier, D. Armand, S. G. Sun, M. Petit, *J. Electroanal. Chem.* **1986**, 205, 267-277.
- [27] A. Rodes, M. A. Zamakhchari, K. Elachi, J. Clavilier, *J. Electroanal. Chem.* **1991**, 305, 115-129.

Received: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents (Please choose one layout only)

Layout 1:

COMMUNICATION

Text for Table of Contents.

((The TOC Graphic should not exceed the size of this area))

*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Layout 2:

COMMUNICATION

Monoatomic high platinum islands deposited on Rh(111) electrode have an electrocatalytic activity for ethanol oxidation that is 20 times higher than the one measured on platinum electrodes.

On these islands, CO₂ and acetic acid are the final products.

Vinicius Del Colle, Vitali Grozovski, Enrique Herrero and Juan M. Feliu*

Page No. – Page No.

Unusually high activity of Pt islands on Rh(111) electrodes for ethanol oxidation