SHORT COMMUNICATIONS

COADSORPTION PHENOMENA AND ADSORBATE COMPETITION IN SURFACE ELECTROCHEMICAL REACTIONS INVOLVING CARBON MONOXIDE AND OTHER ORGANIC RESIDUES

M. C. Arévalo, E. Pastor, S. González and A. J. Arvia*

Departamento de Química Física, Universidad de La Laguna, Tenerife, Spain

Recent surface science studies at metal–gas interfaces have demonstrated the existence of the coadsorption bond[1, 2]. In principle, it should be expected that coadsorption phenomena may contribute in a number of electrocatalytic reactions, particularly those involving multicomponent systems. As a matter of fact, there are several reaction mechanisms derived from electrochemical kinetic studies which describe either reaction stages with two adsorbate species appearing simultaneously on the electrode surface or the formation of intermediates under the form of complex ensembles of atoms and molecules interacting with the active surfaces sites[3, 11]. However, although these facts point out coadsorbate formation, and adsorbate competition, the matter deserves further consideration from the standpoint of distinguishing more clearly between coadsorption phenomena and competitive adsorption processes. Electrochemical evidence of coadsorption phenomena could be very useful to conjecture possible configurations and stoichiometries of the coadsorbates as a function of both the applied potential and the composition of the electrolyte solution.

The present work reports a number of preliminary electrochemical experiments performed on polycrystalline Pt(pc) electrodes in acid solution by using an electrochemical flow cell technique and adequately selected combined potential routines. From these results the voltammetric behaviour of different co-adsorbates as well as the participation of competitive adsorption in several electrochemical surface reactions can be observed.

Complex adsorbed residues on Pt(pc) were formed in 0.5 M H_2SO_4 from the sequential adsorption/ electroadsorption processes involving two different substances. Subsequently, the characteristics of adsorbed residues could be followed through the corresponding anodic stripping voltammograms. The following four groups of substances were investigated: (i) CO and propargyl alcohol (PA); (ii) methanol (MeOH) and PA; (iii) CO and allyl alcohol (AA); (iv) MeOH and AA. The electrochem-

ical behaviour of the chosen substances was also separately determined to confirm previously reported data[12, 13].

The electrochemical measurements were performed in a flow-type electrochemical cell containing 50 ml of the electrolyte solution with the usual arrangement of three electrodes. Most of the work was made with a Pt plate working electrode encased into a glass holder which offered a bright metal active plane of $0.26 \, cm^2$ geometric area. A $Hg/Hg_2SO_4(s)/K_2SO_4(sat)/0.5 \, M \, H_2SO_4$ reference electrode (*sse*), $(e/v(nhe) = 0.659)$ was employed. Potentials in the text are referred to the *sse*. The counter electrode pretreatment consisted of a potential cycling in 0.5 M H_2SO_4 in the −0.660–0.800 V range at 0.2 V s^{-1}.

The base electrolyte was 0.5 M H_2SO_4, which was prepared from 98% H_2SO_4 (Merck p.a.) and Millipore-Milli-Q* water. The solutions of the different alcohols (PA, AA and MeOH) were made from chemicals (p.a.) previously distilled to obtain the highest degree of purity as determined through NMR and gas chromatography. CO was prepared from 98% H_2SO_4 (Merck p.a.) and formic acid (Merck p.a.). Runs were made at 25°C. The entire experiments were run under a continuous Ar atmosphere, except when CO saturation was used for producing the corresponding adsorbed residue.

The sequential adsorption of the two substances proceeded in all cases at a constant preset adsorption potential, $E_{ad} = -0.250$ V, located in the double-layer potential region of the Pt/0.5 M H_2SO_4 interface.

Each electrochemical run comprised the following consecutive stages. Firstly, the behaviour of the H-atoms electrosorption voltammogram under potential cycling was recorded. The stability of this voltammogram was taken as a purity test of the Pt/0.5 M H_2SO_4 system, according to the criterion reported in the literature[14]. Then, the potential was set at E_{ad}, and once the null current was reached the addition of either CO (under gas saturation) or 2 ml 0.1 M MeOH (by means of a glass syringe) was made to form the first electroadsorbed residue. The adsorption time (first adsorption time) in these cases was

*Visiting Professor, INIFTA, Universidad Nacional de La Plata, Argentina.

10 min. For the case of MeOH addition, the current transient of the electroadsorption process was simultaneously recorded. Subsequently, the electrolyte solution in the cell was replaced with fresh 0.5 M H_2SO_4 by keeping the working electrode potential at the same value. Immediately afterwards 2 ml of either 0.1 M AA or 0.1 M PA were added to produce the complex adsorbate at E_{ad}, and simultaneously, the current transient of the second electroadsorption process was recorded for obtaining the total electroadsorption charge resulting from the addition of either AA or PA. The time spent for this stage (second adsorption time) was changed from 15 min (short time range adsorption) to 90 min (long time range adsorption). Finally, the electrolyte solution was replaced again by plain 0.5 M H_2SO_4, and the stripping voltammogram of the complex adsorbed residue was obtained as indicated elsewhere[15].

Blank experiments were systematically made by using each one of the above-mentioned substances independently (Fig. 1). These results confirmed data already reported in the literature.

Let us first consider the short time range adsorption experiments. Runs were made at E_{ad} by firstly adsorbing CO until the surface saturation coverage was reached, and afterwards by electroadsorbing PA (Fig. 2a). In this case the corresponding stripping voltammogram of the adsorbed residue exhibits two anodic peaks, but they differ from those described in the literature for the separate substances[8, 15]. Nevertheless, the anodic stripping charge remains about the same as the sum of the charges determined for the separate substances on the same electrode under comparable conditions, at least within the error of the present experiments (Table 1). The corresponding charge balance was made on the basis of the following reactions

CO adsorption on Pt:

$$CO(gas) \rightleftharpoons CO(solution) + Pt = Pt(CO) \quad (1a)$$

CO anodic stripping:
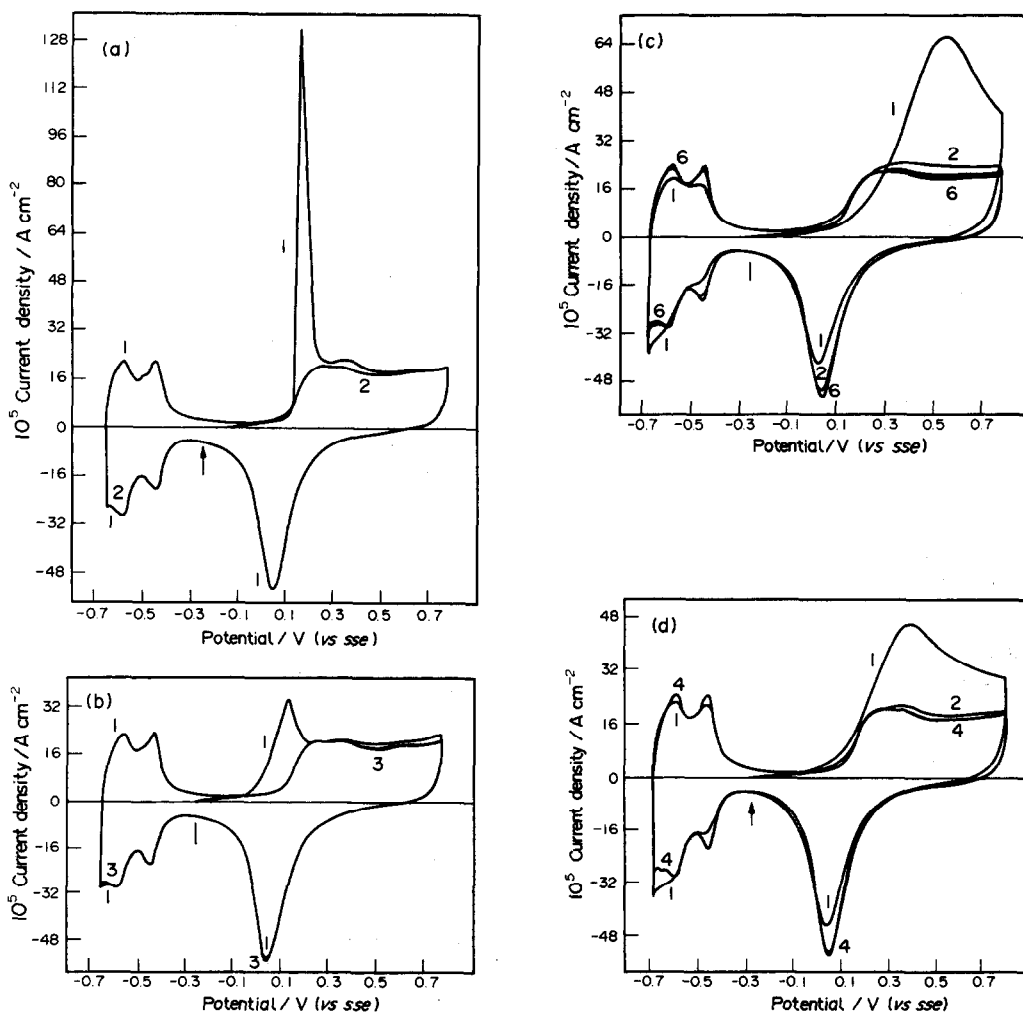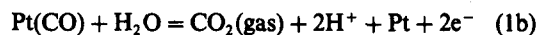
$$Pt(CO) + H_2O = CO_2(gas) + 2H^+ + Pt + 2e^- \quad (1b)$$

Fig. 1. Voltammograms resulting for the blanks. $E_{ad} = -0.250$ V; 0.5 M H_2SO_4; 0.2 V s^{-1}; 25°C. The anodic stripping voltammogram of the adsorbed residues started at E_{ad} (see arrow). The numbers identify the successive potential cycle runs between -0.660 and 0.800 V. As indicated by the arrow, in a few cycles the voltammogram approaches that of base Pt in 0.5 M H_2SO_4. (a) CO, (b) MeOH, (c) PA, (d) AA.
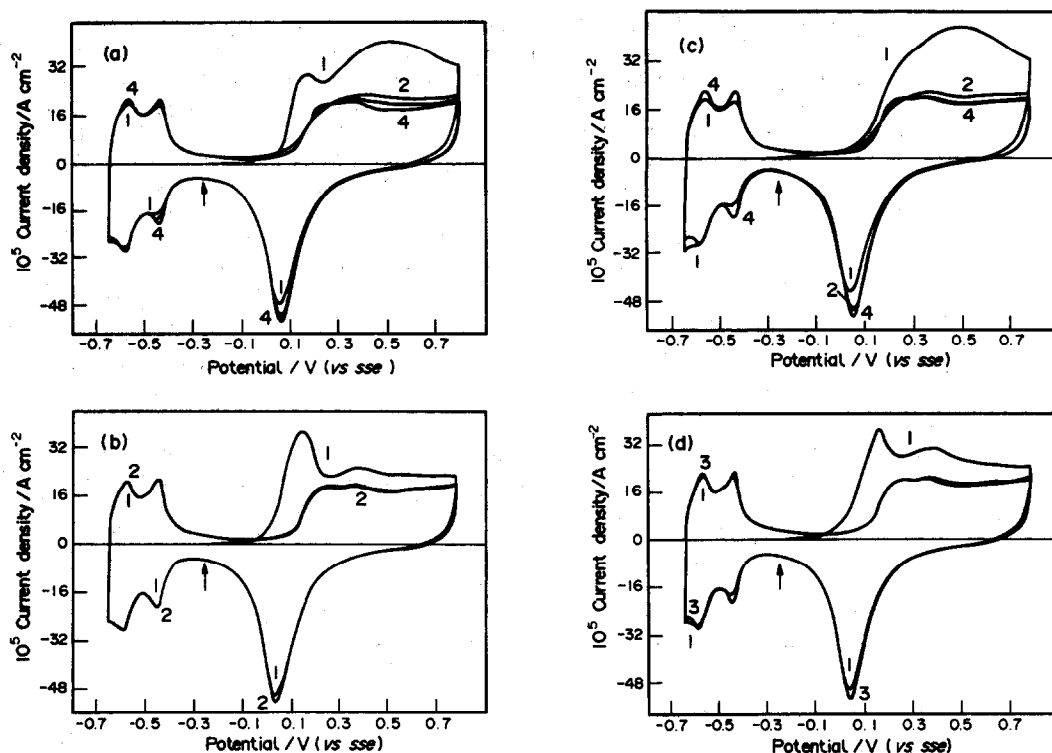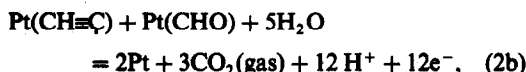
Fig. 2. Voltammograms resulting for the sequential adsorption (short time range adsorption) of different substances. $E_{ad} = -0.250$ V; 0.5 M H_2SO_4; 0.2 V s^{-1}; 25°C. The cyclic voltammogram is started at E_{ad} and later continued between -0.660 and 0.800 V. The numbers in the figure identify the successive potential cycles. (a) CO and PA, (b) CO and AA, (c) MeOH and PA, (d) MeOH and AA.

PA electroadsorption at $E_{ad} = -0.250$ V[15]:

$$2Pt + CH{\equiv}C{-}CH_2OH = Pt(CH{\equiv}C)$$
$$+ Pt(CHO) + 2H^+ + 2e^- \quad (2a)$$
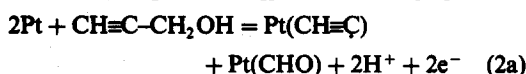
and the anodic stripping of PA residues:

$$Pt(CH{\equiv}C) + Pt(CHO) + 5H_2O$$
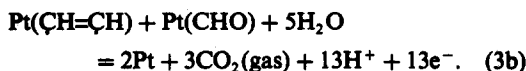$$= 2Pt + 3CO_2(gas) + 12H^+ + 12e^-, \quad (2b)$$

where the parentheses denote adsorbed species. It should be noted that when the present experiments were started by firstly adsorbing PA and later CO, the anodic stripping voltammogram of the electro-adsorbed residues was the same as that already reported for PA alone[15].

A similar type of experiment was run with CO and AA (Fig. 2b). In this case results resemble largely those above described for PA, although the anodic stripping voltammogram of the adsorbed residues exhibits a complex peak which differs consider-ably from that expected for a direct addition of the blank voltammograms. The corresponding charge balance was made by considering reactions (1a), (1b), together with the following reactions[16]:

AA electroadsorption at $E_{ad} = -0.250$ V:

$$2Pt + CH_2{=}CH{-}CH_2OH$$
$$= Pt(CH{=}CH) + Pt(CHO) + 3H^+ + 3e^- \quad (3a)$$
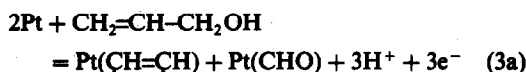
and the anodic stripping of AA residues:

$$Pt(CH{=}CH) + Pt(CHO) + 5H_2O$$
$$= 2Pt + 3CO_2(gas) + 13H^+ + 13e^-. \quad (3b)$$

The corresponding charge balance data (Table 1) suggests that in the present case another complex adsorbed residue has been formed.

Similar runs were made by replacing CO by MeOH as the first adsorbate forming substance, and by using again for the complex adsorbate formation either PA (Fig. 2c) or AA (Fig. 2d). The anodic stripping voltammograms for both coadsorbates exhibit specific characteristics, namely two anodic current peaks different from those seen for the blanks. The charge balances (Table 1) were derived from the following reactions[16]:

MeOH electroadsorption at $E_{ad} = -0.250$ V

$$Pt + CH_3OH = Pt(CO) + 4H^+ + 4e^- \quad (4a)$$
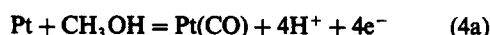
and MeOH residue anodic stripping

$$Pt(CO) + H_2O = Pt + CO_2(gas) + 2H^+ + 2e^-, \quad (4b)$$

together with either reactions (2a) and (2b) or (3a) and (3b), for PA and AA, respectively.

Let us now consider the long time range adsorption experiments. In this case there is a clear influence of the adsorption time on the anodic stripping voltam-mogram of the second adsorbed residue. As the second adsorption time increases, the anodic strip-ping voltammogram tends to coincide with that of the blank for the second adsorbate forming substance (Fig. 3).

On the other hand, short time range adsorption experiments show that coadsorbed species can be produced on a Pt electrode in acid solution, when the metal under a preset applied potential is placed in
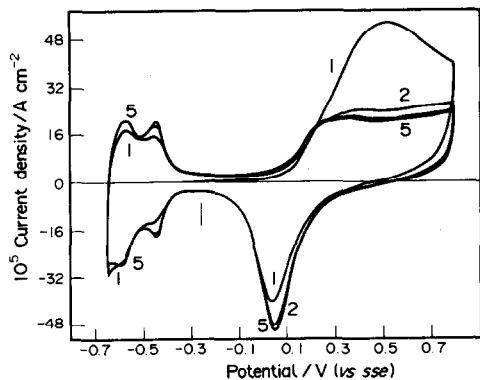
Fig. 3. Voltammograms resulting for the sequential adsorption (long time range adsorption) of CO and PA. $E_{ad} = -0.250$ V; 0.5 M H_2SO_4; 0.2 V s^{-1}; 25°C. The cyclic voltammogram is started at E_{ad} and later continued between -0.660 and 0.800 V. The numbers in the figure identify the successive potential cycles.

teristic broad single anodic stripping peak. The potentials of these peaks comprise values ranging between the anodic stripping peak potential values of adsorbates produced from the separate adsorbate-forming substances. Likewise, the shape of the anodic stripping peaks suggests that either the adsorbate ensemble implies a sequential electro-oxidation process of different potential-dependent structures or that the complex distribution of crystallographic faces at Pt(pc) is being reflected in the voltammograms, as is known from surface electrochemical reactions on Pt single crystal, for instance, the electrochemical oxidation of CO adsorbed residues[19–21].

Otherwise, from long and short time range experiments one can conclude that coadsorption phenomena behave dynamically, so that they also exhibit a contribution of competitive adsorption of the two adsorbates. However, for those systems investigated in the present work, coadsorbate displacement can be imagined as an alternative process, the initial rate of the former being much larger than that of the latter.

Further details about the preceding coadsorption processes as well as other ones directly related to electrocatalysis will be described in a more extended forthcoming publication.

contact with the adsorbate producing substances following a certain sequence, and providing that the first metal–adsorbate interaction involves the most easily adsorbed/electroadsorbed residue. This fact, however, does not preclude the possibility that coadsorption phenomena would also appear under certain conditions even when both substances interact simultaneously with the metal[17].

Coadsorption phenomena should result from an interplay between the repulsive interadsorbate forces and changes in the structure of the adsorbate ensemble. From the structural standpoint, the coadsorbate ensemble can be formally described, neglecting the participation of the solution components, as a complex $(R_1 R_2)$(Pt sites), where R_1 stands for that part of the coadsorbed residue originated from either CO or MeOH, and R_2 denotes that part produced on the R_1-covered Pt surface when the electroadsorption of either AA or PA takes place. It is possible that well-defined potential dependent coadsorbate structures could be formed on crystallographically well-determined surface domains of the substrate as it occurs in metal single crystal/gas phase interfaces[18].

For all the reactions investigated in the present case, each coadsorbate appears to involve a charac-

REFERENCES

1. C. M. Mate and G. A. Somorjai, *Surf. Sci.* **160**, 542 (1985).
2. M. A. Van Hove, R. F. Lin and G. A. Somorjai, *J. Am. chem. Soc.* **108**, 2532 (1986).
3. J. K. Sass and K. Bange, *Electrochemical Surface Science* (Edited by M. P. Soriaga), ACS Symposium Series 378, Ch. 4, p. 54. The American Chemical Society, Washington, DC (1988).
4. S. A. Bilmes and A. J. Arvia, *J. electroanal. Chem.* **198**, 137 (1986).
5. S. A. Bilmes, M. C. Giordano and A. J. Arvia, *J. electrochem. Soc.* **225**, 183 (1987).

Table 1. Charge density balance for the adsorbate residues. Pt(pc); 0.5 M H_2SO_4; $E_{ad} = -0.250$ V; $c_{PA} = c_{AA} = c_{MeOH} = 0.5$ mM; 25°C

Adsorbates	Surface electrode	$q_t/\mu C$ cm^{-2}*	$q_s/\mu C$ cm^{-2}*	n	$q_s^{th}/\mu C$ cm^{-2}*
CO	Pt	—	460	—	—
PA	Pt	176	910	—	—
AA	Pt	216	850	—	—
MeOH	Pt	640	320	—	—
PA	Pt(CO)	35	675	5	642
AA	Pt(CO)	18	490	12	531
PA	Pt(MeOH residue)	82	786	2	775
AA	Pt(MeOH residue)	60	494	3.6	556

q_t = charge density from the electroadsorption current transient.
q_s = charge density from the anodic stripping voltammogram.
$n = (q_t)_X$(blank)/$(q_t)_X$(Pt(Y)).
$q_s^{th} = (q_s)_Y$(blank) + $((q_s)_X$(blank)/n).
X = AA, PA; Y = CO, MeOH residue.
*Maximum estimated error 10%.

6. F. T. Wagner and T. E. Moylan, *Surf. Sci.* **182**, 409 (1986); **191**, 121 (1987).
7. M. L. Marcos, J. M. Vara, J. González Velasco and A. J. Arvia, *J. electroanal. Chem.* **224**, 189 (1987).
8. F. T. Wagner, T. E. Moylan and S. J. Schmieg, *Surf. Sci.* **195**, 403 (1988).
9. F. T. Wagner and T. Moylan, *Electrochemical Surface Science* (Edited by M. P. Soriaga), ACS Symposium Series 378, Ch. 5, p. 65. The American Chemical Society, Washington, DC (1988).
10. R. R. Rodriguez, W. J. Tornquist, F. Guillaume and G. L. Griffin, *Electrochemical Surface Science* (Edited by M. P. Soriaga, ACS Symposium Series 378, Ch. 25, p. 369. The American Chemical Society, Washington, DC (1988).
11. M. L. Marcos, J. González Velasco, M. C. Giordano and A. J. Arvia, *J. electroanal. Chem.* **270**, 205 (1989).
12. E. Gileadi, *Modern Aspects of Electrochemistry* (Edited by J. O'M. Bockris), no. 4, p. 47. Butterworth, London (1966).
13. J. O'M. Bockris and S. Srinivasan, *Fuel Cells: Their Electrochemistry*. McGraw-Hill, New York (1969).
14. H. Angerstein Kozlowska, W. B. A. Sharp and B. E. Conway, *J. electroanal. Chem.* **43**, 9 (1973).
15. M. C. Arévalo, E. Pastor, S. González, A. Arévalo, M. C. Giordano and A. J. Arvia, *J. electroanal. Chem.* **281**, 245 (1990).
16. E. Pastor, M. C. Arévalo, S. González and A. J. Arvia, *Electrochim. Acta* **36**, 2003 (1991).
17. M. C. Arévalo, E. Pastor, S. González and A. J. Arvia, submitted.
18. J. Somers, T. Linder and A. M. Bradshaw, *Electrochemical Surface Science* (Edited by M. P. Soriaga), ACS Symposium Series 378, Ch. 8, p. 111. The Electrochemical Society, Washington, DC (1988).
19. B. Beden, S. Bilmes, C. Lamy and J. M. Léger, *J. electroanal. Chem.* **149**, 295 (1983).
20. C. Lamy, J. M. Léger, J. Clavilier and R. Parsons, *J. electroanal. Chem* **150**, 71 (1983).
21. J. M. Léger, B. Beden, C. Lamy and S. Bilmes, *J. electroanal. Chem.* **170**, 305 (1984).