

STUDY OF THE HYDROGEN REACTION ON BISMUTH MODIFIED PLATINUM ELECTRODES BASED ON THE EQUILIBRIUM POLARISATION RESISTANCE

Quaino, P.M.; Gennero de Chialvo, M.R.; Chialvo, A.C.*

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, 3000 Santa Fe, Argentina. e-mail: achialvo@fiquis.unl.edu.ar

Received April 25, 2003. Accepted in Final Form June 24, 2003

Dedicated to Professor Dr. A.J. Arvia on occasion of his 75th Anniversary

Resumen

La reacción del electrodo de hidrógeno (HER) fue estudiada sobre electrodos de platino con diferentes cubrimientos superficiales de bismuto adsorbido. Se demostró que, independientemente del grado de inhibición que produce el Bi_{ad} sobre los sitios de hidrógeno adsorbido H_{ad} (UPD), se establece el potencial reversible de hidrógeno y la resistencia de polarización de equilibrio resulta invariante. Se propone una interpretación cinética para explicar los resultados obtenidos, basada en un proceso de compensación de las dependencias de las constantes específicas de velocidad de reacción y del cubrimiento superficial de equilibrio con la energía libre standard del H_{ad} (OPD).

Abstract

The hydrogen electrode reaction (HER) was studied on platinum electrodes with different surface coverage of adsorbed bismuth. It was demonstrated that, independently of the degree of inhibition of the sites occupied by the adsorbed hydrogen H_{ad} (UPD) on the part of the Bi_{ad} atoms, the reversible hydrogen potential is established and the equilibrium polarisation resistance is invariant. The experimental results were interpreted on terms of a kinetic model based on the dependences of the specific kinetic constants and the hydrogen equilibrium surface coverage on the standard Gibbs free energy of H_{ad} on OPD sites.

Introduction

The irreversible adsorption of metallic atoms (Bi, Cd, Cu, etc.) on platinum electrodes is currently studied with the aim of developing a more efficient electrocatalytic material for the hydrogen electrode reaction (HER) [1-9]. Basically, these adatoms inhibit the adsorption of the underpotentially deposited hydrogen, the H_{ad} (UPD), and interact strongly with the substrate.

At the same time, experimental evidences would indicate that the HER on Pt involves an adsorbed reaction intermediate, the overpotentially deposited hydrogen H_{ad} (OPD), which equilibrium surface coverage would be very low [10]. Experiments also indicate that the reaction would take place through the Volmer-Tafel route rather than the Volmer-Heyrovsky route at low overpotential values [7,10]. Therefore, free adjacent sites are needed in order to make possible the occurrence of the Tafel step.

On this context, it should be of interest to understand the role played by the metallic atoms adsorbed on the UPD sites and their influence on the hydrogen atoms adsorbed on the OPD sites.

The electrocatalytic behavior of platinum electrodes modified by the adsorption of bismuth atoms, and the Pt/Bi_{ad} electrode, for the HER, have been studied by different authors [5,7-9]. Experiments carried out on Pt(111)/Bi_{ad} [7] and Pt (100)/Bi_{ad} [5] concluded that the rate of the hydrogen evolution reaction (*her*) was strongly reduced. However, it should be mentioned that the experimental conditions used in these studies were not appropriate, as the electrolyte solution was not saturated by dissolved hydrogen, originating strong uncertainties on the analysis of the experimental results. On the other hand, recent studies carried out under more rigorous experimental conditions indicate that the hydrogen oxidation reaction (*hor*) on Pt (111)/Bi_{ad} [8,9] would be less sensitive to the presence of Bi_{ad}, although there is a limiting kinetic current at high overpotentials which is lower than the limiting diffusional current recorded on pure platinum.

In spite of the studies carried out on this subject, there are many aspects that must be carefully analysed in order to improve the understanding of the role played on the HER by the adsorption of bismuth on platinum. On this basis, the present work deals with the study of the HER on polycrystalline Pt/Bi_{ad} through the evaluation of the dependence of the equilibrium polarisation resistance (R_p) on the bismuth surface coverage (θ_{Bi}). This scarcely used technique [11-14] is useful for the study of electrochemical reactions on materials where the reversible electrode potential is perfectly defined (absence of corrosion processes). On such conditions, each elementary step of the reaction takes place with similar values of the forward and backward reaction rates and consequently the whole behaviour of the electrode reaction can be appropriately characterised.

Experimental

Cell description: The experimental determinations were carried out in three-electrodes Pyrex glass cells. Three different cells were used, one for the Bi adsorption, another for the voltammetric characterisation and the last one for the polarisation resistance measurements under hydrogen gas bubbling. Large area platinum counterelectrodes and hydrogen bubble reference electrodes immersed in the same solution were used in all of them. Special attention was paid to the purity of the electrolyte solutions, which was verified by essays of adsorption-oxidation before each experimental run.

Preparation of Pt/Bi_{ad} electrodes: The irreversible adsorption of bismuth on a clean platinum electrode was carried out potentiostatically in a $5 \cdot 10^{-4}$ M Bi₂(SO₄)₃ solution prepared from Bi₂O₃ dissolved in 0.5 M H₂SO₄ solution. The adsorption processes were carried out in the range of potentials $-0.05 \text{ V} \leq E_{ad} \leq 0.75 \text{ V}$. It should be noticed that at $E_{ad} < -0.05 \text{ V}$ the massive deposition of Bi is produced. The time of application of the adsorption potential was varied in the range $30 \text{ s} \leq t_{ad} \leq 600 \text{ s}$. The electrodes were then removed from the cell at closed circuit and immediately washed in order to avoid adsorption by contact.

Treatment of Pt electrodes: The platinum electrodes which were subjected to a bismuth adsorption process cannot be recovered through conventional pretreatments such as anodic electrodesorption, as the Bi_{ad} cannot be eliminated from the electrode surface yet after a large number of desorption cycles. Therefore, a new procedure was developed in order to obtain Pt electrodes free from Bi_{ad} , with a reproducible voltammetric shape independently of their previous history. This experimental treatment consisted in the following steps: (i) polishing with emery paper 2500; (ii) polishing with alumina powder 0.5 μm ; (iii) growth of a PtO_2 layer in acid solution through the application of periodic potential signals of high amplitudes and frequencies [15] and (iv) reduction of this oxide film. The time used for the oxide film growth was varied in order to obtain working electrodes with a roughness factor of approximately 20 to 50.

Voltammetric characterisation: The working electrodes were subjected to cyclic voltammetry in a three-electrodes cell in a 0.5 M H_2SO_4 solution free from Bi^{3+} ions at a sweep rate of 0.025 V s^{-1} . The aim of these voltammetric runs were: (i) characterisation of Pt and Pt/ Bi_{ad} electrodes; (ii) verification of the purity of the electrolyte solutions and (iii) quantification of the amount of Bi_{ad} . In the first case, the potentiodynamic sweep was applied between the potentials $E_{\text{low}} = 0.0 \text{ V}$ and $E_{\text{up}} = 1.5 \text{ V}$ in order to obtain the corresponding voltammogram and also in the range $E_{\text{low}} = 0.0 \text{ V}$ and $E_{\text{up}} = 0.425 \text{ V}$ for the evaluation of the voltammetric charge related to the electroadsorption of H atoms within the UPD potential domain.

The verification of the purity of the electrolyte solutions was made through the application of two consecutive steps of potentiostatic adsorption under nitrogen bubbling at -0.05 V during 5 min and 0.0 V during another 5 min, respectively. Immediately after the adsorption and without interrupting the electric circuit, a potentiodynamic sweep in the anodic direction was applied up to $E_{\text{up}} = 1.5 \text{ V}$, returning then to $E_{\text{low}} = 0.0 \text{ V}$ and after that applying repetitive cycles between these limiting potential values. The purity of the solution is determined by the absence of peaks or electrooxidation processes different from those characteristics of the Pt electrode and/or the inhibition of the current peaks related to the H and O UPD electroadsorption (see Figure 1).

Finally, in order to quantify the amount of Bi_{ad} , the inhibition of the H_{ad} (UPD) sites was evaluated. The charge of H_{ad} obtained in presence and in absence of Bi_{ad} was evaluated through potentiodynamic cycles run between $E_{\text{low}} = 0.0 \text{ V}$ and $E_{\text{up}} = 0.425 \text{ V}$ before and after the Bi adsorption.

Electrochemical measurements: The polarization resistance of the hydrogen electrode reaction was measured on Pt and Pt/ Bi_{ad} electrodes through galvanostatic polarization pulses applied near the equilibrium potential ($|\eta| \leq 10 \text{ mV}$). Measurements were carried out in 0.5 M H_2SO_4 solutions saturated with hydrogen at a pressure of 1 atm. The measurements were made using a potentiostat-galvanostat Radiometer PGP201, controlled by a data generation/acquisition card Advantech PCL-818 and the software Labtech Notebook[®]. Current steps lasting 30 s were applied, registering continuously the variation of potential on time, which always returned to the resting potential value. For each step, 100 potential measurements were made and the average value (η) was assigned

to the current (I) of the analysed step. In this way the dependence $I(\eta)$ was obtained, being all experiments carried out at $30 \pm 1^\circ\text{C}$.

The equilibrium polarisation resistance (R_p) was evaluated from the regression of the dependences $I(\eta)$ by a second or third order polynomial. The linear coefficient of such fitting polynomial corresponds to the polarisation resistance value

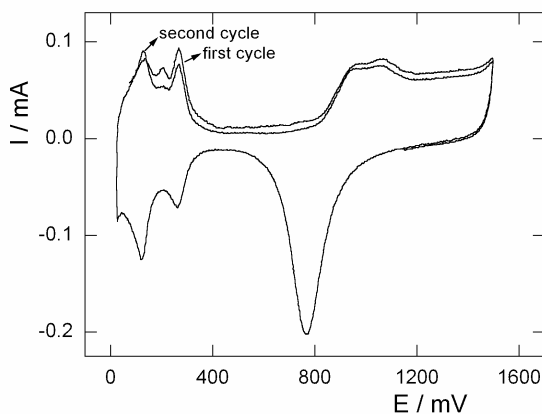


Figure 1: Voltammogram of a Pt electrode recorded for the verification of the solution purity. $0.5\text{M H}_2\text{SO}_4$; $v = 0.025\text{ V s}^{-1}$; 30°C .

Results

Bismuth adsorption on platinum: The voltammetric behaviour of the $\text{Pt}/\text{Bi}_{\text{ad}}$ was almost independent of the adsorption potential, although the amount of Bi_{ad} quantified as the amount of inhibited H_{ad} (UPD) depends upon time and adsorption potential. Figure 2 (line a) shows the voltammetric response of a Pt electrode between 0.0 V and 1.5 V. Figure 2 (line b) is the profile obtained after a Bi adsorption at $E_{\text{ad}} = -0.050\text{ V}$ during 30 s between 0.0 V and 0.425 V, recorded for the evaluation of the degree of inhibition of the H_{ad} (UPD). Finally, Figure 2 (line c) is the response obtained after (b) when the potentiodynamic sweep is extended to 1.5 V (first and second cycle). This profile shows a current peak at 0.90 V during the anodic sweep and a significant increase of the cathodic charge corresponding to the electroreduction of O_{ad} . It should be mentioned that this effect depends strongly on the time and the potential of adsorption. The opposite behaviour, that is a decrease of the electroreduction charge of O_{ad} , can be also obtained without appreciable effect on the anodic shape of the voltammogram. Another important aspect is that the repetitive cycling between 0.0 V and 0.425 V does not change the voltammetric profile, whereas the potentiodynamic sweep between 0.0 V and 1.5 V produces a continuous decrease cycle by cycle of the anodic peak located at 0.90 V and a lesser inhibition of the H_{ad} (UPD).

All the studies carried out on the $\text{Pt}/\text{Bi}_{\text{ad}}$ electrodes indicate that while the electrode potential is held below 0.75 V, the Bi_{ad} layer is highly stable.

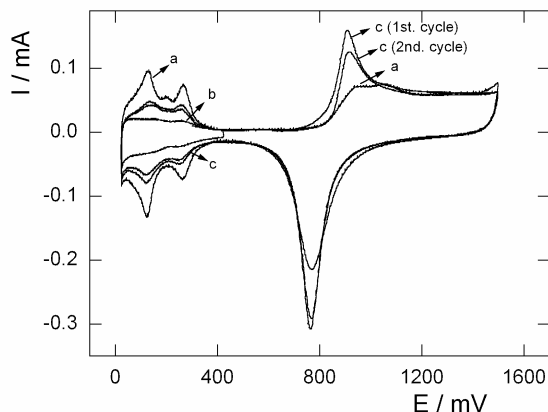
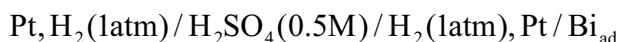


Figure 2: Voltammograms of a Pt electrode. (a) Blank; (b) After Bi adsorption, $\theta_{\text{H}_{\text{ad}}}^{\text{inh}} = 0.742$; (c) first and second extended cycle after (b). $0.5\text{M H}_2\text{SO}_4$; $\nu = 0.025\text{ V s}^{-1}$; 30°C .

Hydrogen electrode potential on Pt-Bi_{ad} electrodes: In order to study the HER through the measurement of the equilibrium polarisation resistance, it is necessary that the Pt/Bi_{ad} electrode defines the reversible potential. Therefore, the following equilibrium cell was performed,



The reversible potential of this cell was, for any value of the corresponding surface coverage of Bi_{ad}, $E \leq \pm 1\text{ mV}$. Therefore, it can be concluded that the Pt/Bi_{ad} electrode defines the hydrogen reversible potential.

Evaluation of the behaviour of the HER near the equilibrium potential: In order to evaluate the polarisation resistance, the current-potential dependence near the equilibrium potential was evaluated by the application of current pulses. Figure 3 illustrates the applied current signal as well as the corresponding potential response. Some of the experimental current-potential curves $I(\eta)$ obtained from these measurements can be observed in Figures 4-7. The values corresponding to the Pt electrode free from Bi are indicated as open circles ($I(\eta)_{\text{Pt}}$) and the dashed line is the corresponding regression curve. After the irreversible adsorption of bismuth, the evaluation of the dependences $I(\eta)_{\text{Pt-Bi}}$ were carried out, which are shown in the Figures 4-7 as filled circles, being the continuous line the corresponding regression curve.

A cyclic voltammogram between 0.0 V and 0.425 V was recorded in order to determine the surface coverage of Bi_{ad} through the degree of inhibition of the H_{ad} (UPD), as it is illustrated in the Figure 2 (line b). Figures 4-7 correspond to different degrees of inhibition and it can be observed that, although the cases under analysis involve values comprised between 30 to 92 %, the differences between the dependences $I(\eta)_{\text{Pt-Bi}}$ and $I(\eta)_{\text{Pt}}$ are almost negligible.

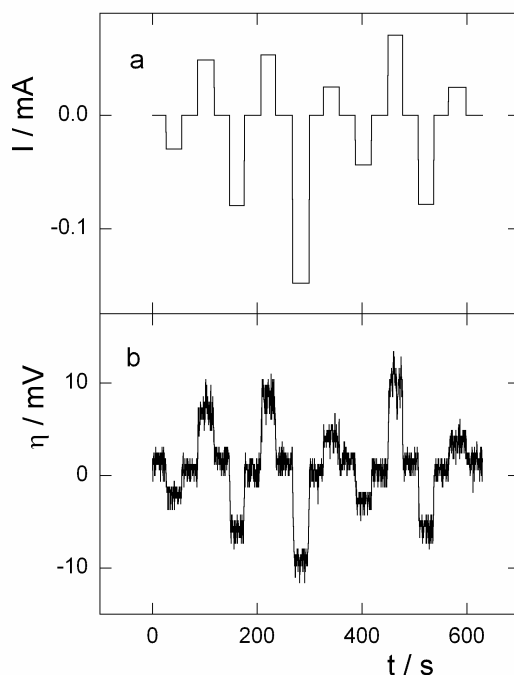


Figure 3: (a) Galvanostatic pulses perturbation; (b) Potential response of a Pt/Bi_{ad} electrode. $\theta_{\text{H}_{\text{ad}}}^{\text{inh}} = 0.348$; 0.5M H₂SO₄; 30°C.

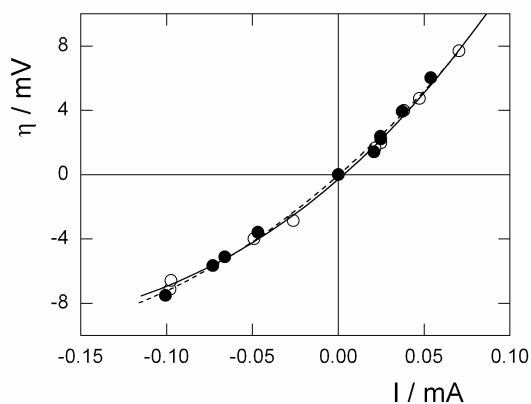


Figure 4: Experimental $\eta(I)$ dependences: (●) Pt/Bi_{ad}, $\theta_{\text{H}_{\text{ad}}}^{\text{inh}} = 0.42$; (○) Pt. Regression curves: (---) Pt/Bi_{ad}; (—) Pt. 0.5M H₂SO₄; 30°C.

Equilibrium polarisation resistance: The results described in the previous item can be more adequately analysed through the evaluation of the relationship $\omega = R_p(\text{Pt}) / R_p(\text{Pt}/\text{Bi}_{\text{ad}})$ as a function of the degree of inhibition ($\theta_{\text{H}_{\text{ad}}}^{\text{inh}}$) of the H_{ad} (UPD) sites. This

variable was calculated as follows: $\theta_{H_{ad}}^{inh} = (Q_{H_{ad}}^{Pt} - Q_{H_{ad}}^{Pt-Bi}) / Q_{H_{ad}}^{Pt}$, being $Q_{H_{ad}}^{Pt-Bi}$ the voltammetric charge of H_{ad} (UPD) with adsorbed bismuth and $Q_{H_{ad}}^{Pt}$ that corresponding to pure platinum. It can be clearly appreciated in Figure 8 that the experimental relationship ω is independent of the degree of inhibition of the H_{ad} (UPD), being $\omega \cong 1$.

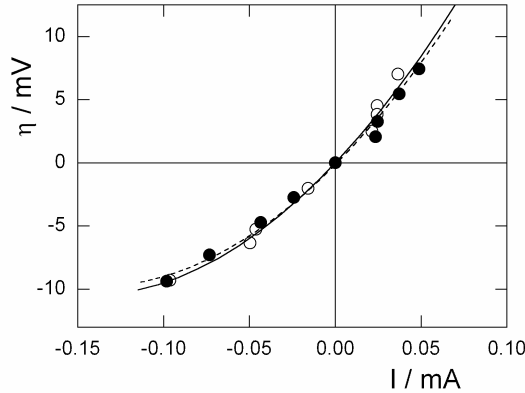


Figure 5: Experimental $\eta(I)$ dependences: (●) Pt/Bi_{ad} , $\theta_{H_{ad}}^{inh} = 0.61$; (○) Pt . Regression curves: (---) Pt/Bi_{ad} ; (—) Pt . $0.5M H_2SO_4$; $30^\circ C$.

This result was quite different from the expected value according to a model of inhibition described in the literature [7,10]. This model considers as a first approximation that the current of the *her* depends on bismuth coverage as follows:

$$I = I_{(o)}(1 - \theta_{Bi})^m \quad (1)$$

The corresponding expression for the polarisation resistance is:

$$\frac{R_p^o}{R_p} = \omega = (1 - \theta_{Bi})^m \quad (2)$$

which gives a ω value much less than unity yet at low bismuth surface coverage, because, for example, $m = 24$ for the case of $Pt(111)$ [7].

Discussion

The present study demonstrates that the equilibrium polarisation resistance of the hydrogen electrode reaction (HER) on platinum is insensitive to the existence of bismuth atoms irreversibly adsorbed on the electrode surface. This experimental result is obtained yet at degrees of inhibition of the UPD hydrogen atoms greater than 90%. A straightforward consequence of this study is that the HER requires adsorption sites different from the UPD sites. Nevertheless, several considerations should be made.

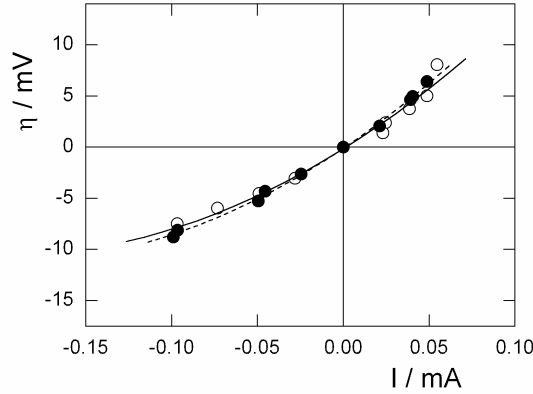


Figure 6: Experimental $\eta(I)$ dependences: (●) Pt/Bi_{ad}, $\theta_{\text{H}_{\text{ad}}}^{\text{inh}} = 0.73$; (○) Pt. Regression curves: (---) Pt/Bi_{ad}; (—) Pt. 0.5M H₂SO₄; 30°C.

It is known and accepted that the surface coverage of H_{ad} (OPD) near the equilibrium potential is very low and that in the low overpotentials region the hydrogen evolution reaction (*her*) on platinum is produced mainly through the Volmer-Tafel route [7,11]. On this context, the invariability of the polarisation resistance with the Bi_{ad} surface coverage varying from zero to values that produce the complete inhibition of the H_{ad} (UPD) is an unexpected result. Therefore, a thorough analysis of the equilibrium polarisation resistance from the kinetic point of view should be made in order to understand the origin of this behaviour. The relationship of R_p with the equilibrium reaction rates of the elementary steps of the Volmer-Heyrovsky-Tafel mechanism can be written as follows [16],

$$R_p = \frac{RT}{4F^2} \left(\frac{4v_T^e + v_H^e + v_V^e}{v_V^e v_H^e + v_V^e v_T^e + v_H^e v_T^e} \right) \quad (3)$$

If the Heyrovsky step does not contribute significantly to the HER near the equilibrium potential, equation (3) can be written as,

$$R_p \cong \frac{RT}{F^2} \left(\frac{1}{v_V^e} + \frac{1}{4v_T^e} \right) \quad (4)$$

Therefore, the invariability of the polarisation resistance implies the constancy of the equilibrium reaction rate of the Volmer and Tafel steps. This could be explained on the basis of a small influence of the bismuth atoms adsorbed on the UPD sites on the OPD sites. This is equivalent to assume that the standard Gibbs free energy of the hydrogen adsorbed on the OPD sites ($\mu_{\text{H}(\text{o})}^{\circ}$) does not depend on the Bi surface coverage and therefore the behaviour of H_{ad} (OPD) would be the same as on a pure platinum electrode. This approximation seems to be unlikely due to the wide range of inhibition of the UPD sites. An electronic effect on the OPD sites should be reasonable when the Bi surface coverage is high. Some evidence in favour of a strong interaction between Pt and Bi was postulated by Hamn *et al.* [17], who analysed the Bi(4f) binding energy of the XPS signal of this electrode. Therefore, it seems more appropriate to consider the existence of

a distribution of the standard Gibbs free energy of H_{ad} (OPD) around each Bi_{ad} (UPD). Using the approximation of patches of sites of equal energy $\mu_{H(p)}^o$ [18,19], the system can be described considering that each patch obeys the Langmuir isotherm. Consequently, the equilibrium reaction rate ($v_{i(p)}^e$) of the step i ($i = V, T$), the equilibrium surface coverage of H_{ad} ($\theta_{(p)}^e$) and the specific kinetic constants of the forward ($k_{+i(p)}$) and backward ($k_{-i(p)}$) reaction of the step i on each patch (p) are related by the following expressions [14],

$$v_{V(p)}^e = k_{+V(p)} (1 - \theta_{(p)}^e) = k_{-V(p)} \theta_{(p)}^e \quad (5a)$$

$$v_{T(p)}^e = k_{+T(p)} (\theta_{(p)}^e)^2 = k_{-T(p)} (1 - \theta_{(p)}^e)^2 \quad (5b)$$

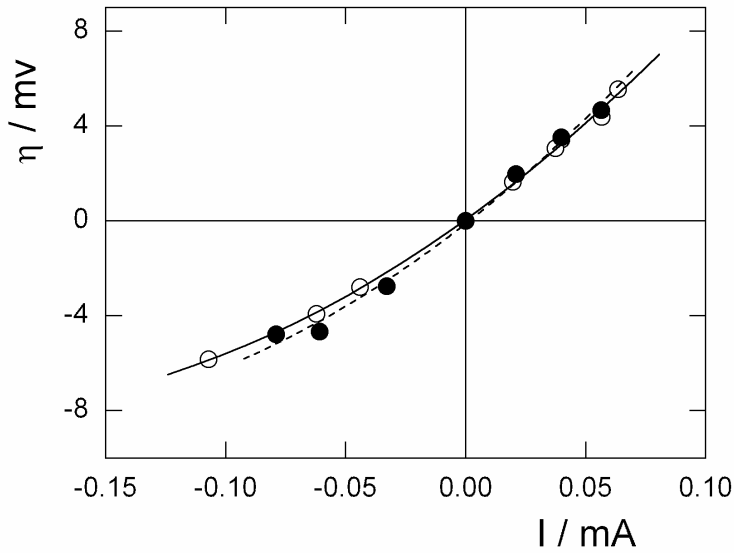


Figure 7: Experimental $\eta(I)$ dependences: (●) Pt/Bi_{ad} , $\theta_{H_{ad}}^{inh} = 0.90$; (○) Pt . Regression curves: (---) Pt/Bi_{ad} ; (—) Pt . $0.5M H_2SO_4$; $30^\circ C$.

A local variation of the standard Gibbs free energy of the H_{ad} (OPD) with the distance with respect to an UPD site $\mu_{H(p)}^o = \mu_{H(o)}^o + \Delta\mu_{(p)}^o$ is considered, being $\mu_{H(p)}^o$ the energy value of an OPD site adjacent to an UPD site and $\mu_{H(o)}^o$ the corresponding energy of the OPD site far from UPD sites. Expressions of θ^e and $k_{\pm i}$ as a function of $\Delta\mu^o$ were previously deduced [18,19],

$$\theta_{(p)}^e = \frac{\theta_{(o)}^e}{\theta_{(o)}^e + (1 - \theta_{(o)}^e) e^{\Delta\mu_{(p)}^o/RT}} \quad (6)$$

$$k_{+V(p)} = k_{+V(o)} e^{-\beta\Delta\mu_{(p)}^o/RT} \quad (7a)$$

$$k_{-V(p)} = k_{-V(o)} e^{(1-\beta)\Delta\mu_{(p)}^o/RT} \quad (7b)$$

$$k_{+T(p)} = k_{+T(o)} e^{2(1-\beta)\Delta\mu_{(p)}^o/RT} \quad (8a)$$

$$k_{-T(p)} = k_{-T(o)} e^{-2\beta\Delta\mu_{(p)}^o/RT} \quad (8b)$$

where β is the symmetry factor associated to the variation of the adsorption activation energy with $\mu_{H(p)}^o$. The substitution of equations (6-8) into equations (5a) and (5b) leads to the conclusion that the influence of $\mu_{H(p)}^o$ on the equilibrium reaction rates can be considered negligible, due to compensation process between θ^e and $k_{\pm i}$. Moreover, if the adsorption process is considered barrierless $\beta \cong 0$ and on the basis of experimental results it can be assumed that $\theta_{(o)}^e \ll 1$, equations (5a) and (5b) can be written as,

$$v_{V(p)}^e \cong k_{+V(o)} (1 - \theta_{(o)}^e) = k_{-V(o)} \theta_{(o)}^e = v_{V(o)}^e \quad (7a)$$

$$v_{T(p)}^e \cong k_{+T(o)} (\theta_{(o)}^e)^2 = k_{-T(o)} (1 - \theta_{(o)}^e)^2 = v_{T(o)}^e \quad (7b)$$

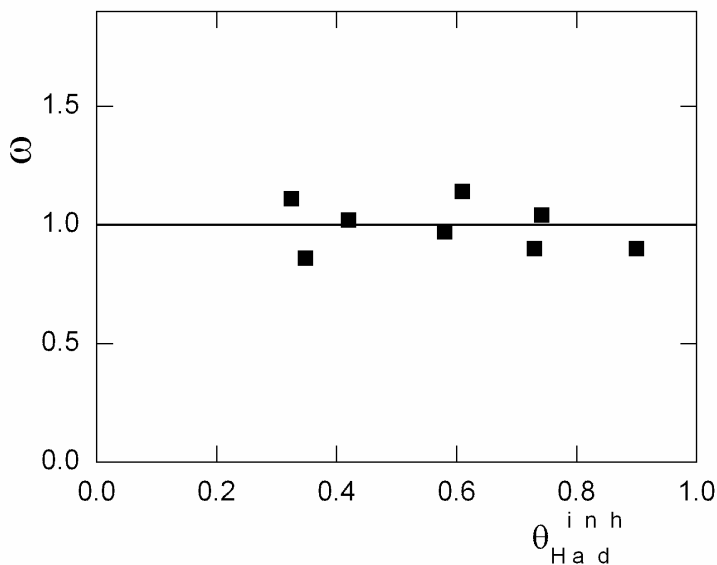


Figure 8: Dependence of $\omega = R_p(Pt) / R_p(Pt/Bi_{ad})$ on the degree of inhibition of H_{ad} UPD ($\theta_{H_{ad}}^{inh}$).

Therefore, in spite of the approximations made, a reasonable kinetic interpretation of the experimental behaviour has been given. Furthermore, preliminary results obtained in this laboratory indicate that in the overpotentials region $-0.05 \text{ V} \leq \eta \leq 0.0 \text{ V}$ the *her* does not depend on the presence of adsorbed bismuth atoms. Nevertheless, it is likely that at high overpotential values the effect of lateral interactions could produce

significant differences between the $I(\eta)$ dependences corresponding to Pt and Pt/Bi_{ad} electrodes.

Conclusions

The main conclusions of the present work can be summarised as follows:

- (i) Pt/Bi_{ad} electrodes define the reversible hydrogen potential independently of the value of the surface coverage of adsorbed bismuth.
- (ii) Near equilibrium, the hydrogen electrode reaction is insensitive to the presence of Bi atoms adsorbed on the UPD sites on platinum.
- (iii) It was demonstrated that the reaction intermediate of the HER is adsorbed on superficial sites different from the H_{ad} (UPD).

Acknowledgements

This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Agencia Nacional de Promoción de la Investigación Científica y Tecnológica (ANPCYT) and Universidad Nacional del Litoral (UNL).

References

- [1] Furuya, N.; Motoo, S. *J. Electroanal. Chem.* **1976**, *72*, 165.
- [2] Adzic, R.R.; Spasojevic, M.D.; Despic, A.R. *Electrochim. Acta* **1979**, *24*, 569.
- [3] Adzic, R.R.; Spasojevic, M.D.; Despic, A.R. *Electrochim. Acta* **1979**, *24*, 577.
- [4] Clavilier, J.; Feliu, J.M.; Fernandez-Vega, A.; Aldaz, A. *J. Electroanal. Chem.* **1990**, *294*, 193.
- [5] Gomez, R.; Fernandez-Vega, A.; Feliu, J.M.; Aldaz, A. *J. Phys. Chem.* **1993**, *97*, 4769.
- [6] Gao, L.J.; Conway, B.E. *J. Electroanal. Chem.* **1995**, *395*, 261.
- [7] Gomez, R.; Feliu, J.M.; Aldaz, A. *Electrochim. Acta* **1997**, *42*, 1675.
- [8] Schmidt, T.; Stamenkovic, V.; Lucas, C.A.; Markovic, N.M.; Ross, P.N. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3879.
- [9] Schmidt, T.; Grgur, B.N.; Behm, R.J.; Markovic, N.M.; Ross, P.N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4379.
- [10] Markovic, M.N.; Sarraf, S.T.; Gasteiger, H.A.; Ross, P.N. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3719.
- [11] Fernández, J.L.; Gennero de Chialvo, M.R.; Chialvo, A.C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2875.
- [12] Fernández, J.L.; Gennero de Chialvo, M.R.; Chialvo, A.C. *Electrochim. Acta* **2002**, *47*, 1129.
- [13] Fernández, J.L.; Gennero de Chialvo, M.R.; Chialvo, A.C. *Electrochim. Acta* **2002**, *47*, 1137.
- [14] Fernández, J.L.; Gennero de Chialvo, M.R.; Chialvo, A.C. *Electrochim. Acta* **2002**, *47*, 1145.
- [15] Chialvo, A.C.; Triaca W.E.; Arvia, A.J. *J. Electroanal. Chem.* **1983**, *146*, 93.
- [16] Gennero de Chialvo, M.R.; Chialvo, A.C. *J. Electroanal. Chem.* **1996**, *415*, 97.

[17] Hamm, U.W.; Kramer, D.; Zhai, R.S.; Kolb, D.M. *Electrochim. Acta* **1998**, 43, 2969.

[18] Gennero de Chialvo, M.R.; Chialvo, A.C. *J. Electroanal. Chem.* **1994**, 372, 209.

[19] Gennero de Chialvo, M.R.; Chialvo, A.C. *J. Electroanal. Chem.* **1995**, 388, 215.