Short communication

COMPETITIVE ELECTROFORMATION OF SILVER AND OXYGEN OVERLAYERS ON POLYCRYSTALLINE RHODIUM IN ACID

B.S. PARAJÓN COSTA, N.R. DE TACCONI, M.C. GIORDANO and A.J. ARVIA

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal 4, 1900 La Plata (Argentina)

INTRODUCTION

The stripping analysis of metal layers at solid electrodes is considerably influenced by strong interactions at the deposited monolayer level [1,2]. For various systems the underpotential deposition (UPD) of metals occurs within a potential range where another surface process such as O-electrosorption takes place simultaneously. In this case the interactions at the metal UPD level can be modified significantly. Some of these effects can be observed in voltammetric studies of UPD of Ag on Pt performed with Pt ring–disc electrodes [3], accompanied by the inhibition of hydrogen adsorption on Pt [4], the displacement of adsorbed hydrogen by UPD Ag and Cu [5,6], and UPD and overpotential deposition (OPD) of Ag on Pt [7].

In the present work results obtained for Ag deposition on polycrystalline Rh in $H_2SO_4 + Ag_2SO_4$ solutions are reported. This system offers a relatively wide potential range where both reactions, namely, the UPD of Ag and O-electrodesorption can be studied either simultaneously or independently.

EXPERIMENTAL

The working electrode was a polycrystalline (pc) Rh wire (Johnson Matthey Chemical Co, Spec-pure, 0.1 mm dia., 0.59 cm² apparent area). The electrode pretreatment was the same as described previously [8]. A Rh counterelectrode and a $Hg/Hg_2SO_4/1$ *M* H_2SO_4 reference electrode were employed, but potentials in the text are referred to the reversible hydrogen electrode in the same solution (RHE). The electrolyte solution was 1 *M* H_2SO_4 which was prepared from 98% H_2SO_4 (Merck AR) and purified distilled water (Milli Q®). Ag_2SO_4 (Mallinckrodt, p.a.) was added to the electrolyte in the 10^{-5} to 10^{-3} *M* range. The experiments were

made with nitrogen saturated solutions in the 0–65°C range by using triangular potential scanning combined with potential steps [8,9].

RESULTS AND DISCUSSION

A typical voltammogram of the pc Rh electrode in 1 M $H_2SO_4 + 2.5 \times 10^{-4}$ M Ag_2SO_4 in the $E_{s,c} = 0.03$ V to $E_{s,a} = 1.4$ V range at 0.1 V/s is shown in Fig. 1. The main anodic current contributions in the entire potential range are the remaining H-electrodesorption ($I_{H,a}$) at ca. 0.1 V, an asymmetric peak (II_a) at 0.75 V, preceded by a shoulder at 0.6 V (II_a') and followed by a hump at 0.85 V (II_a''), and the constant current region (III_a) due to Rh oxide formation extending from ca. 1.0 V upwards. The current peaks II_a, II_a' and II_a'' are related to the stripping of the different Ag layers competing with the Rh oxide formation in the low potential region (see Ag^+ ion-free voltammogram, dotted line in Fig. 1) [8,9].

The electroreduction scan exhibits a wide cathodic peak (III_c) at ca. 0.45 V and the H-electroadsorption peak ($I_{H,c}$) at 0.1 V. The sequential formation of the different Ag layers becomes evident as $E_{s,a}$ is decreased stepwise from 1.4 V downwards. Peak III_c shifts to more positive potentials and decreases gradually while the shoulder at 0.6 V (II_a') becomes an anodic current peak. Further on, two cathodic peaks (II_c and II_c'), which correlate with the corresponding anodic peaks, are progressively distinguished. The H-electrodesorption charge decreases systemati-
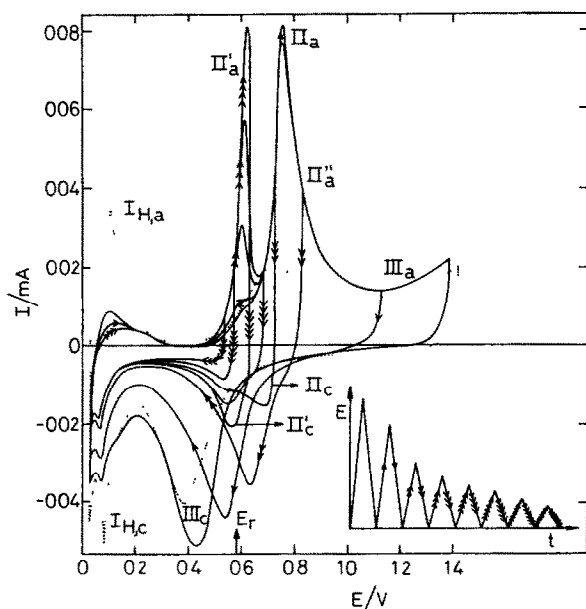

Fig. 1. Sequence of voltammograms on pc Rh in 1 M $H_2SO_4 + 2.5 \times 10^{-4}$ M Ag_2SO_4 by decreasing stepwise $E_{s,a}$. E_r indicates the Ag/Ag^+ reversible potential. 25°C.

cally since the stripping of the Ag layers is not fully accomplished for $E_{s,a} < 1.0$ V. Silver ion electrodeposition takes place continuously for $E_{s,c} < E_r$, E_r being the reversible potential.

Similar results are obtained by decreasing the Ag_2SO_4 concentration down to 10^{-5} M, but in this case peaks II_a' and II_c' are not evident unless a certain holding time, τ, at $E_{s,a}' \leqslant E_r$ is included. For 0.6 V $< E_{s,a}' <$ 0.8 V, peak III_c becomes wider and its charge smaller than that obtained in Ag^+ ion-free solution, while for 1.0 V $\leqslant E_{s,a}' \leqslant$ 1.3 V, the total charge of peak III_c is equivalent to that obtained in Ag^+ ion-free 1 M H_2SO_4 solution. Thus, the charge related to the stripping of Ag layers can be evaluated as the total positive charge (Q_a^T) for $E_{s,a} > 1.0$ V minus the negative charge (Q_c^T) related to the electroreduction of O-containing species independently of its electroformation potential.

The electrodeposition of Ag^+ ions is influenced by the presence of the O-containing surface species on the substrate. This can be studied through the stripping voltammogram including a holding potential E_s' during a certain time τ either in the positive ($E_{s,a}'$) or negative ($E_{s,c}'$) potential scan. For $E_{s,a}' > E_r$ (Fig. 2a), Ag UPD takes place on a surface free of O-containing surface species, and the stripping voltammogram shows first the increase in height of peak II_a'' and later the appearance of peak II_a. These changes occur simultaneously with the decrease of the anodic current around 0.6 V which is related to $(RhOH)_{ad}$ formation [8,9]. The electroreduction scan shows an increasing charge for peak III_c due to the electrodeposition of Ag and the electroreduction of O-containing species occurring simultaneously. The voltammograms depicted in Fig. 2b show the influence of the O-containing Rh surface on Ag UPD. The processes during the negative scan involve mainly the electroreduction of the fraction of O-species remaining at the surface after the potential hold and the H-electroadsorption. The diffusion-controlled electrodeposition of Ag^+ ion interferes with both processes. The stripping voltammogram depicted in Fig. 2c was obtained after applying a potential step during the electroreduction scan at an $E_{s,c}'$ value close to E_r. Under these circumstances the substrate is covered by only a fraction of the O-containing surface species. The characteristics of peak II_a as well as the rest of the voltammogram depend strongly on τ. The O-electroadsorption charge is considerably smaller than that observed in Fig. 2b for $\tau \leqslant 120$ s. Otherwise, the cathodic current contribution at the positive side of peak III_c increases according to the height of peak II_a for $\tau > 120$ s. Therefore, peak II_a results from the stripping UPD Ag and formation of the O-containing surface species on pc Rh, and its contribution becomes considerable for $\tau > 300$ s. In this case, when the first Ag monolayer has been completed, peak II_a'' turns into the hump of peak II_a.

Otherwise, the electroreduction charge of the O-containing surface species for $E_{s,a} > 1.0$ V remains practically independent of τ, whereas the charge of electrodeposited Ag increases regularly with τ in the 60 s $\leqslant \tau \leqslant$ 600 s range, attaining a maximum value estimated as 1.6 times the Ag monolayer charge (0.260 mC/cm^2).

When the potential hold is set at 0.03 V, close to the hydrogen electrode potential (Fig. 3), the voltammograms show that the H-electrodesorption charge firstly
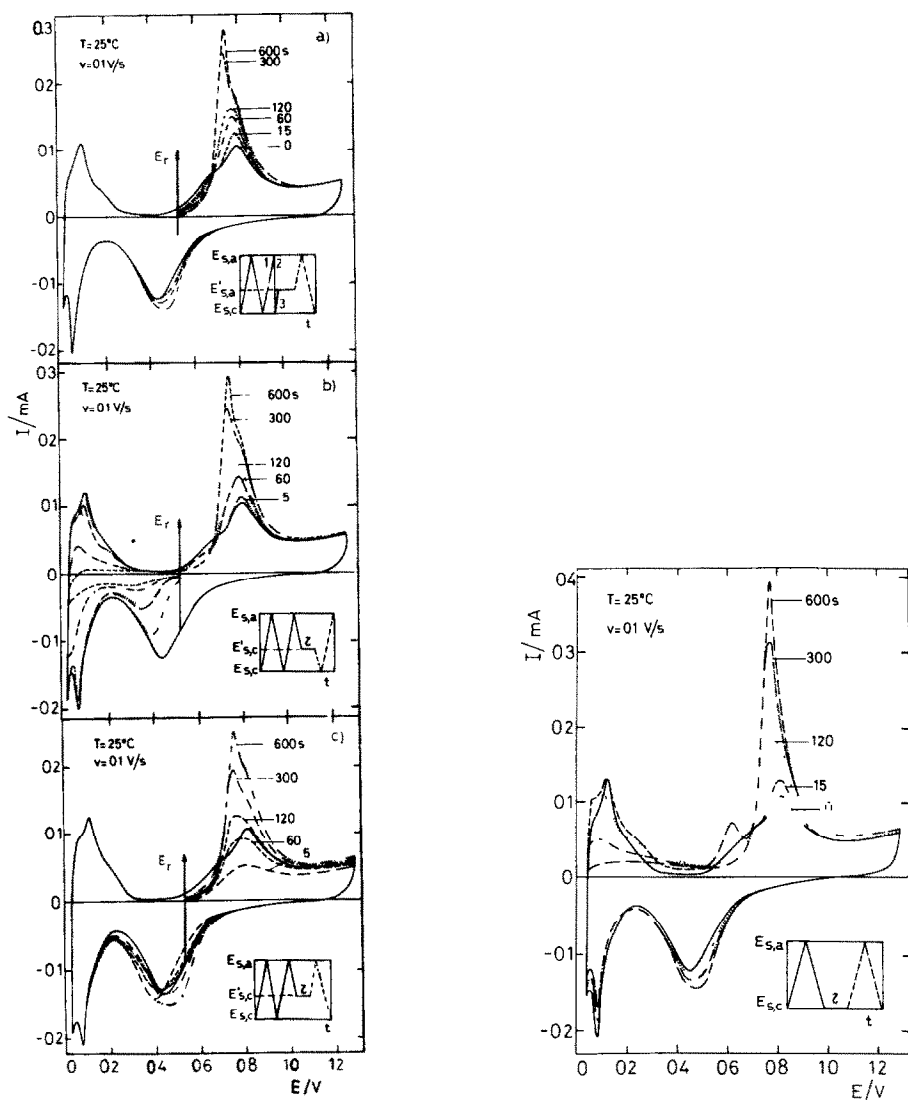
Fig. 2. Voltammograms on pc Rh run after including a potential hold at E_s' during a time τ $(0 \leqslant \tau \leqslant 600$ s). 1 M $H_2SO_4 + 10^{-5}$ M Ag_2SO_4. (a) Potential hold $E_s' = E_{s,a}' = E_r$ applied during the electrooxidation sweep which continues after τ. The potential scans preceding the potential hold were run at: $v = (1)$ 0.1, (2) 1.0 and (3) 1.0 V/s. (b) $E_s' = E_{s,c}' \cong E_r$. The potential hold is applied during the electroreduction sweep which continues after τ. (c) $E_s' = E_{s,c}' \cong E_r$. The potential hold is applied during the electroreduction sweep, and after time τ the electrooxidation scan starts from $E_{s,a}'$ upwards.

Fig. 3. Voltammograms on pc Rh run after including a potential hold at $E_{s,c}$ during a time τ $(0 \leqslant \tau \leqslant 600$ s) between each sweep. 1 M $H_2SO_4 + 10^{-5}$ M Ag_2SO_4.

increases up to a maximum as τ increases and later decreases to the baseline current, whereas the H-electroadsorption peak remains practically unaltered after Ag stripping. Likewise, the charge of peak II_a–II_a'' increases to reach a limiting value and immediately afterwards, the height of peak II_a' begins to increase. As peaks II_a–II_a'' and II_a' can be assigned to UPD and OPD. Ag on an O-free pc Rh surface, respectively, one concludes that at 0.03 V, the H-adatom layer is displaced progressively by electrodeposited Ag atoms. The anodic current contribution found in the 0.55–0.65 V range, which depends on both the concentration of Ag^+ ion in solution and the characteristics of the potential programme, can be related to two simultaneous reactions, namely, the formation of $Rh(OH)_{ad}$, and the stripping of OPD Ag. However, the formation of $Rh(OH)_{ad}$ is inhibited progressively due to the accumulation of Ag at $E_{s,c}'$ as τ increases. The stripping voltammograms show definitely that the formation of bulk Ag starts only after electrodeposition of the amount of Ag related to peak II_a. Furthermore, as the amount of stripped Ag increases, the negative potential scan shows an increasing negative charge due to Ag electrodeposition overlapping the O-electroreduction charge. Therefore, from these results one concludes that bulk Ag electrodeposition can apparently occur only after the surface coverage by Ag adatoms (θ_{Ag}) is slightly lower than two juxtaposed Ag layers ($\theta_{Ag} \cong 1.6$).

The electrodeposition of Ag increases the threshold potential for the reaction yielding $(RhOH)_{ad}$, whereas the presence of the O-containing surface species produces a substantial delay on the formation of Ag electrodeposits at UPD level (Figs. 2c and 3). For pc Rh partially covered by O-containing species, the growth of bulk Ag can occur without an appreciable amount of UPD Ag (Figs. 4a,b). The absence of stripping current peaks due to Ag UPD for certain values of $E_{s,c}$ is accompanied by the appearance of a hysteresis loop in the electroreduction scan which has been related to a nucleation and growth process [1,10,11].

No dramatic changes in the voltammograms are observed by changing the temperature. The voltammograms run under conditions comparable to those of Figs. 2a and 2c but at $0\,°C$ either for clean or O-containing Rh surfaces show that peaks II_a and II_a'' largely overlap at $0\,°C$ on a prereduced pc Rh. Conversely, current peaks II_a and II_a'' remain distinguishable and of the same order of magnitude after holding the potential at $E_{s,c}' = 0.53$ V for $\tau = 180$ s at $65\,°C$.

The competitive electroformation of Ag and O-containing surface layers on Rh can be explained in terms of the relative position of the potential window determined by the threshold potential for $Rh(OH)_{ad}$ formation, i.e. 0.6 V (vs. RHE) in $1\ M\ H_2SO_4$ [8,9], and the value of E_r. Thus, when E_r is lower than the threshold potential for $Rh(OH)_{ad}$ electroformation, Ag electrodeposition takes place on a Rh electrode free of O-containing surface species. Then the overall reaction can be interpreted as the initial formation of the Ag submonolayer, followed by the completion of the Ag UPD layer, and finally bulk Ag growth.

Otherwise, when E_r is greater than the threshold potential for $Rh(OH)_{ad}$ formation, Ag electrodeposition occurs on a Rh surface completely covered by an O-containing surface species electroadsorbed monolayer. In this case, Ag elec-
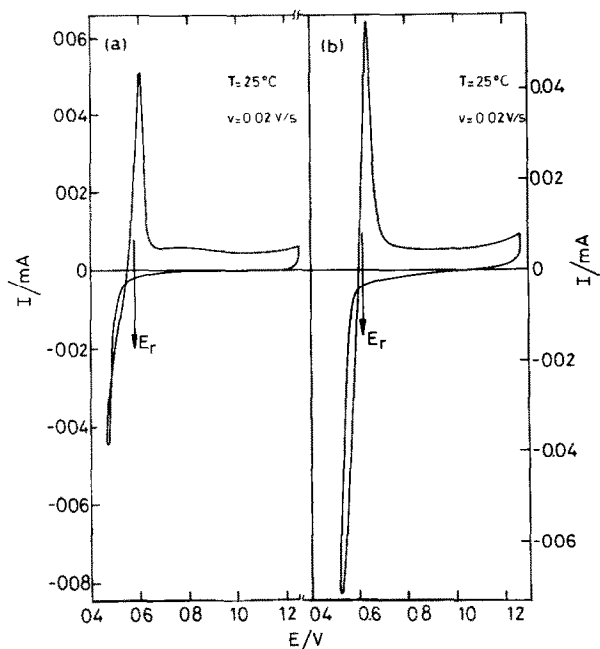
Fig. 4. Voltammograms on pc Rh exhibiting a loop in the lower potential region. (a) 1 M H_2SO_4 + 2.5 × 10^{-4} M Ag_2SO_4. (b) 1 M H_2SO_4 + 10^{-3} M Ag_2SO_4.
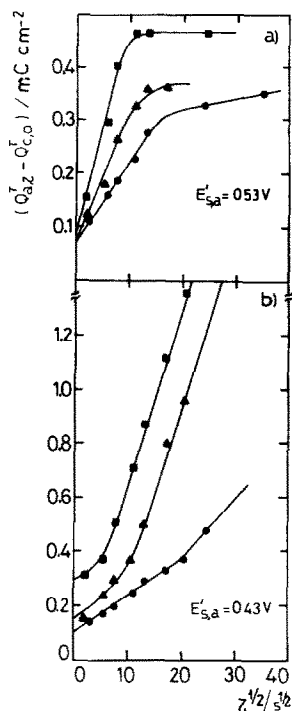
Fig. 5. Dependence of $(Q_{a,\tau}^T - Q_{c,0}^T)$ on holding time τ at two different E_s' and temperatures. 1 M H_2SO_4 + 10^{-5} M Ag_2SO_4. $v = 0.05$ V/s; (●) 15, (▲) 45, (■) 65°C.

trodeposition can proceed only immediately after free sites have been created at the Rh substrate through the electrodesorption of O-containing species. This implies two successive electron-transfer reactions at the same potential, that is O-electrodesorption and Ag electrodepostion. This explains the increase in voltammetric electroreduction charge, as seen in Fig. 2c.

The prevalence of each one of these situations results from a compromise between the Ag^+ ion concentration in solution, since this determines E_r, and the voltammetry parameters, namely, $E_{s,c}$, $E_{s,a}$ and v, which in turn settle the amount of O-species on the Rh electrode surface.

Finally, one can envisage the possible rate determining step of Ag electrodeposition through the dependence of voltammetric charges on τ at different potentials and temperatures. In this case, only the overall positive charge $(Q_{a,\tau}^T)$ resulting after the holding time τ, and the negative $(Q_{c,0}^T)$ charge without holding time are considered. The voltammetric data can be plotted as $(Q_{a,\tau}^T - Q_{c,0}^T)$ vs. $\tau^{1/2}$ for different $E_{s,a}'$ values (Figs. 5a,b). This charge difference can be related directly to

the charge involved in Ag electrodeposition plus the charge required for creating bare Rh sites through O-electrodesorption. These plots for $\tau < 100$ s and $E'_{s,a} = 0.53$ V (Fig. 5a) approach linear relationships. The slope of these lines as well as the $(Q^T_{a,\tau} - Q^T_{c,0})_{\tau=0}$ value, that is the charge difference for $\tau = 0$, both increase with temperature. For $\tau > 100$ s, and $E'_{s,c} \cong E_r$, limiting charge values related to Ag UPD can be observed. Otherwise, for $E'_{s,c} = 0.43$ V, that is, $E'_{s,c} < E_r$, bulk elec-trodeposited Ag prevails and in this case the linear relationship holds over the whole time window of the experiments. The slope of the line changes with temperature according to an Arrhenius plot, which yields an experimental activation energy equal to 20 ± 5 kJ/mol. The linear plots depicted in Fig. 5 and the activation energy value are consistent with a diffusion controlled process for any stage of Ag^+ ion electrodeposition. This is consistent with the fact that the value of the exchange current density for that reaction is about 1 A cm^{-2} [12].

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