J. Braz. Chem. Soc., Vol. 9, No. 3, 211-218, 1998.
Printed in Brazil.

© 1998 Soc. Bras. Química
0103 – 5053 $6.00 + 0.00

Article

Electrochemical Deposition of the First Cd Monolayer on Polycrystalline Pt and Au Electrodes. An Upd Study

Mauro C. dos Santos, and Sergio A.S. Machado

Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780,
13560-970 São Carlos - SP, Brazil; email: sasmach@iqsc.sc.usp.br

Received: February 5, 1998

A deposição em subtensão de Cd sobre Pt e Au policristalinos foi estudada por voltametria nos eletrodos estacionário e de disco-anel rotatório. Sobre Pt, os picos de redissolução do Cd_{ads} se sobrepõem àqueles relacionados com a oxidação do H_{ads}, dificultando assim a avaliação precisa das cargas de dessorção. Um modelo proposto para se calcular estas cargas a partir de voltametria no eletrodo estacionário revelou um valor de 285 μC cm^{-2} para a monocamada completa, o que corresponde a um recobrimento de 90%, com os ad-átomos de Cd apresentando uma valência de eletrossorção de 0,5. Os resultados obtidos com a técnica de coleção do eletrodo rotatório confirmam plenamente estes valores. A diferença entre os tamanhos dos raios atômicos do Cd e da Pt justificam o recobrimento de menos de 100%.

Por outro lado, sobre Au, a ausência de Hads simplifica o procedimento para a determinação das cargas de redissolução da monocamada de Cd. Aqui, um valor de apenas 41 μC cm^{-2} foi calculado, o que corresponde a um recobrimento máximo de 15%, com valência de eletrossorção de 0,5. Os resultados obtidos com os experimentos de coleção estão em perfeita concordância com estes valores.

The underpotential deposition of Cd on polycrystalline Pt and Au was studied by voltammetry at stationary and rotating ring-disc electrodes. On Pt, the Cd_{ads} dissolution peaks overlap those related to the oxidation of H_{ads}, thus hindering the precise evaluation of desorption charges. A model proposed to calculate such charges from voltammetry at stationary electrodes revealed a value of 285 μC cm^{-2} for the monolayer dissolution, which corresponds to a coverage of 90% with Cd_{ads} presenting an electrosorption valence of 0.5. Rotating ring-disc experiments fully confirmed such values. The misfit between atomic radii of Cd and Pt justifies the less-than-100% coverage.

On the other hand, on Au, the absence of H_{ads} simplifies the procedure for determination of dissolution charges for the Cd monolayer. Here, a value of only 41 μC cm^{-2} was calculated, which corresponds to a maximum coverage of 15%, with the electrosorption valence of 0.5. The results obtained in the collecting experiments with the rotating electrode are in complete agreement with those values.

Keywords: *underpotential deposition, cadmium, ad-atoms, electrodeposition*

Introduction

The underpotential deposition (UPD) of metals onto a foreign substrate is a very useful electrochemical procedure, which provides orderly modified surfaces with special properties suitable for utilization in different fields like electrocatalysis[1,2,3], semiconductors[4,5], electrodepositon of alloys[6,7], etc.

In its broader sense, UPD is related to the electrodeposition of a metallic ion, Me^{z+}, in a potential range more positive than the reversible potential of the redox couple Me^{z+}/Me. The driving force of this apparent violation of the Nernst Law is the difference in work function between the substrate (S) and the ad-atom, which provides an extra energy and promotes the deposition of the first monolayer of the depositing metal, at more positive potentials. This can be represented by the Eq. 1[8]:

$$\Delta E_{ML} = \Delta^{0}_{ML} + \frac{RT}{\gamma_{UPD}\, F} \ln \frac{a_{M}{}^{z+}}{a_{ML}} \tag{1}$$

where ΔE_{ML} is the submonolayer equilibrium potential, $\Delta E_{ML}0$ the standard submonolayer potential, γ_{UPD} the electrosorption valence, $a_M z+$ the activity of the metal ions in the solution and a_{ML} the activity of the submonolayer while the other symbols retain their usual meaning. γ_{UPD} is defined by the difference between the valence of the ion in solution (z) and the charge transferred to it during the deposition process.

Reviews available in the literature include the classic work of Kolb and co-workers[9], an extensive paper by Szabó[10] analyzing the theoretical aspects of UPD, which are updated by the recent work of Leiva[11], and the papers of Adzic[12,13] and Kokkinidis[14] concerning mainly the influence of UPD processes in the oxidation of small organic molecules. These reviews cover a great amount of the theoretical development, applications and electrochemical techniques used in the study of surfaces modified by underpotential deposition of metals.

Among several Me/S systems which are usually studied in the underpotential region, cadmium on platinum or on gold seems to be a suitable subject. Jovicevic *et al.*[15] have analyzed the deposition of cadmium on foreign substrates. These authors have investigated the Cd deposition on Ni, Pb, Ag, Au and Cu by potential sweep and potentiostatic methods with the simultaneous observation of the surface by optical microscopy. They verified that substrates with an increased affinity for the ad-atom favour epitaxial growth. In this case are included Cu, Ag and Au. On the others surfaces, the deposition initiates with a nucleation and growth mechanism. Daujotis and Raudonis[16] have studied the Cd UPD on Pt from acid medium with a potential step relaxation technique, which led the authors to propose a deposition mechanism. This mechanism is composed by: (i) direct underpotential adsorption of Cd(II) from the solution onto certain sites of the surface, followed by one-electron transfer, (ii) rapid surface migration of Cd(I) between two types of adsorption sites, (iii) discharge of Cd(I) adsorbed onto the second specie of active site and (iv) slow underpotential adsorption of Cd(II) from the solution onto the second kind active site followed by a simultaneous two-electron transfer. Equilibrium constants for two adsorption states were determined via analysis of the transformed relaxation data in (real) Laplace space. Martins *et al.*[17] have discussed the surface alloying promoted by cadmium underpotential deposition on irregular silver electrodeposits by anodic stripping cycles. These authors studied the surface rearrangement processes involving the formation of Cd+Ag alloys at Cd coverage less than or close to unity. A place-exchange mechanism was proposed to account for the kinetics of alloy formation.

An important application of Cd UPD monolayers comes from the need for high quality thin film semiconductor devices. Compounds like cadmium telluride (CdTe) are very convenient for solar energy conversion since its bandgap is 1.47 eV, which provides optical match to the solar spectrum[18]. In this way, Gregory *et al.*[19] have investigated Cd and Te UPD together with their alternate deposition on polycrystalline Au, Pt and Cu substrates. They observed that, on Pt, the UPD process for Cd is ill defined, with the voltammetric peaks overlapping the hydrogen response. On the other hand, Au is a most suitable substrate, due to the large double-layer region and the lack of interference of adsorbed hydrogen. Results obtained from the alternate deposition studies on Au revealed that Te can displace UPD Cd from the surface at potentials slightly more negative than that for Cd UPD. This displaced Cd^{2+} can then be underpotentially deposited onto the surface-bonded Te[19]. In a further publication, Gregory and Stickney[20] discussed the formation of epitaxial layers by alternate deposition of Cd and Te. They referred to the technique as 'ECALE' for electrochemical atomic layer epitaxy. Another system analyzed by Colleti *et al.*[21] using the same technique was CdS.

In electrocatalysis, the modification of surfaces with UPD Cd has been applied in order to promote important effects in electrochemical reactions of interest. Huang *et al.*[22] studied the reduction of nitrate on gold surfaces mediated by Cd UPD. They concluded that in acid media, nitrite is the only detectable product, as analyzed by FTIR-RAS. Such reaction was found to be absent on smooth Au surfaces. These results confirmed the previous analysis of Xing and Scherson[23] who studied the same system with a rotating ring-disk technique. Ritzoulis[24] reported data concerning the effect of Pb, Cd and Tl ad-atoms on the reduction process of N_2O on polyoriented Pt electrodes. This surface reaction requires adsorbed H available to react with N_2O molecules. Ritzoulis proposed that the only effect of these three ad-atoms was to block the active sites for hydrogen adsorption, thus inhibiting the reaction under study. More favorable effects were observed in the oxidation of formic acid on Pt modified by Pb, Tl, Cd and Ge ad-atoms[25].

Modifications with any of the four metals produced a large enhancement in the currents of the voltammetric responses. The effect was attributed to the co-adsorption of O or OH on Ge or Cd at potentials more negative than on Pt. El-Shafei *et al.*[26] have also studied the catalytic influence of underpotentially deposited submonolayers of different metals in ethylene glycol oxidation on various noble metal electrodes in alkaline medium. The same conclusions about simultaneous adsorption of O or OH on the ad-atom has been inferred but with Cd UPD exerting only a slight effect in the organic molecule oxidation.

Another very interesting aspect that becomes evident in the discussions concerning the CD UPD mechanism is the electrosorption valence of the ad-atom. As stressed by Varga *et al.*[27], the total voltammetric charge measured in the UPD studies points to two possibilities. In the first one, assuming that a total discharge of Cd^{2+} takes place, the charge measured would indicate that no more than half a monolayer of cadmium is formed on Pt(111). On the other hand, if the discharge is incomplete and a full monolayer of cadmium is formed, the apparent electrosorption valence is 0.8. Those authors were not able to decide between the two possibilities mainly because they have used only voltammetric experiments at stationary electrodes to calculate the charges. A more complete investigation in this subject was performed by Machado *et al.*[28] using the rotating ring-disk electrode. In their experiments the authors were able to show that Cd ad-atoms present an electrosorption valence of 0.45 and that a complete monolayer corresponds to a Cd coverage close to 100%. In that work, those authors also analyzed the influence of Cd_{ads} on the oxygen reduction reaction. They found that a total coverage with Cd_{ads} promotes a modification in the reaction mechanism in order to produce H_2O_2 as the final product, instead of the H_2O detected on bare surfaces.

The objective of this paper is to analyze Cd UPD on polycrystalline Pt and Au surfaces, from acid medium, using either stationary and rotating ring-disc electrode voltammetry.

Experimental

All the experiments were carried out in a single-compartment Pyrex® electrochemical cell with a Teflon® cover. The auxiliary electrode was a Pt foil with 2 cm^2 geometrical area and the reversible hydrogen electrode was used as the reference system. The rotating ring-disc electrodes were Pine Instruments products. The Pt/Pt and Pt/Au electrode presented geometric areas of 0.001 and 0.160 cm^2 for ring and disc, respectively, and with collection factors of 0.195 and 0.211, respectively, as determined in experiments with the Fe^{2+}/Fe^{3+} couple[29,30]. All glassware were boiled in a HNO_3/H_2SO_4 solution and thoroughly washed with purified water.

The electrodepositions of Cd on Pt and Au were conducted from solutions composed either by (1, 2, 4 and 5 x 10^{-5}) M $CdSO_4$ + 0.1 M H_2SO_4 or by (5 x 10^{-6} and 5 x 10^{-5}) M $CdSO_4$+ 0.1 M H_2SO_4, respectively. The $CdSO_4$ used was Merck PA, while the H_2SO_4 was Merck suprapur. The water was purified in a Milli-Q system from Millipore Inc.. Prior to the experiments the solutions were deaerated by bubbling N_2 SS White Martins.

The stationary electrode experiments were performed with an EG&G PARC model 273 potentiostat/galvanostat linked to an IBM compatible microcomputer, through a GPIB interface and controlled by the M270 software from EG&G PARC. The rotating ring/disc experiments were conducted with an EG&G PARC model 366A bipotentiostat and recorded in a Hewlett Packard model 7046B instrument.

Results and Discussion

Cyclic voltammetric experiments on polycrystalline Pt and Au electrodes

The stationary voltammetric responses of Pt and Au disc electrodes in 0.5 M H_2SO_4 solutions at 0.05 V s^{-1} are presented in Figs. 1A and 1B, respectively. The excellent definition of voltammetric peaks for H adsorption/desorption on the Pt and oxides formation/reduction on both surfaces attests the purity of the solution and the electrode surface[31,32].

From theses experiments it is possible to determine the active area of the electrodes. For Pt surfaces this determination involves the calculation of the charge under the hydrogen desorption peaks, between 0.05 and 0.4 V. As it already has been well established[33,34], for polycrystalline Pt surfaces, the occupation of all active sites of the surface with a complete monolayer of adsorbed hydrogen requires a charge of 210 μC cm^{-2}. As the corresponding area in Fig. 1A presented a charge of 58 μC, it should correspond to an

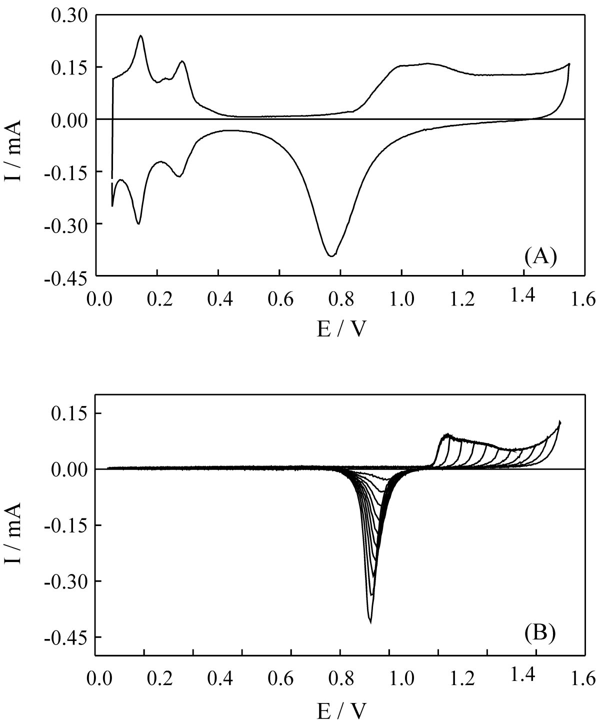

Figure 1. Steady-state voltammetric responses for Pt (A) and Au (B) electrodes in 0.5 M H_2SO_4 solutions at 0.05 V s^{-1}. In (B), the effect of expanding the potential window in the voltammetric profile is presented.

electrochemical area of 0.27 cm^2. In the case of Au surfaces, the methodology to obtain the electrochemical area involves repetitive potential scanning to increasingly positive values, followed by the measurement of several cathodic charges associated to the reduction of the oxide formed at each potential scan. A plot of charge against the inversion potentials should contain straight lines with, at least, three different slopes, as displayed in Fig. 2. The interception between the second and third straight lines should correspond to the charge required for the formation of an AuO complete monolayer, *i.e.*, 380 μC cm^{-2} [32,25]. In the present work, the second inflection point obtained from the plot of Q *vs.* E_{inv} was associated with a charge of 220 μC, indicating an electrochemical area of 0.55 cm^2. Such values of electrochemical area were used throughout this paper in order to normalize the different set of voltammetric data.

Cd UPD on polycrystalline Pt

Figure 3 shows the voltammetric responses, obtained at stationary electrode, for Cd UPD from 0.1 M H_2SO_4 + 5 x 10^{-5} M $CdSO_4$. The potential variation includes different delays at 0.05 V in order to allow the progressive metal deposition followed by a potential excursion at 0.2 V s^{-1}. The occupation of the surface by the ad-atoms is shown to inhibit the adsorption of hydrogen, mainly the weakly adsorbed H ad-atoms. This behaviour is in complete agreement with previous results published by Machado *et al.*[28] and by Gregory *et al.*[19]. In the line related to the dissolution of Cd monolayer deposited during 600 s, it is possible to observe three distinct anodic peaks denoted by A, B and C where peak A occurs at *ca.* 0.65 V, B at 0.45 V and C at 0.3 V. Here, one of the major problems found in using stationary electrode voltammetry for such a study becomes evident. As one can see in the voltammograms of Fig. 3, Peak C completely overlaps the dissolution peak of adsorbed hydrogen. The difficulty in the separation of charges due to Peak C and H_{ads} brings, as a consequence, a deviation from linearity in the Q_{Cd} *vs.* Q_H plot. Such plots are decisive in order to determine the number of electrons transferred by active site on the surface, which can be calculated from its slope. This can be seen in Fig. 4, where the relationship between both charges is presented. For deposition times up to 90 s, when only peaks A and B develop and no overlapping occurs, the linear relationship stands. After that time, with the beginning of peak C and overlapping, the points deviate from the straight line, which can be associated to an underestimation of the Q_{Cd}, due to the interference of Q_H. An important feature in Fig. 4 is that, if the deposition is carried out during a sufficiently long time to allow the complete monolayer to be formed (point i, 600 s), the measured point returns to the straight line. This seems to confirm that a full monolayer of Cd was deposited and only small amounts of H_{ads} remain on the surface. The slope of

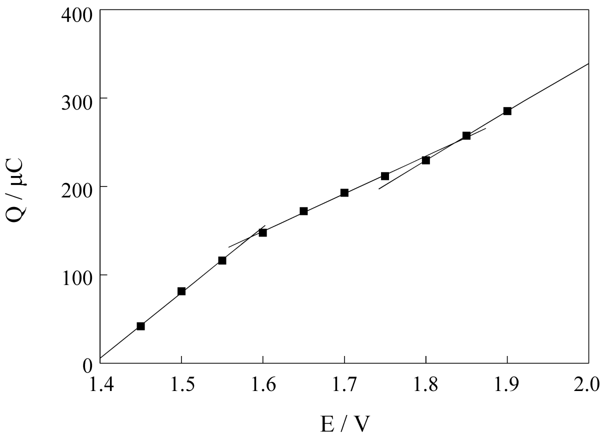

Figure 2. Linear relationships between reduction charges and inversion potentials for the voltammograms displayed in Fig. 1(B).

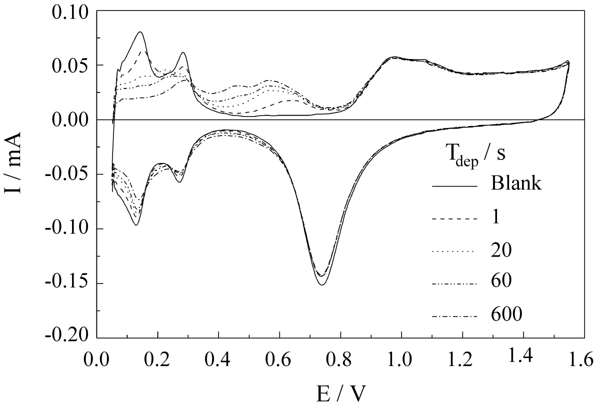

Figure 3. Steady-state voltammogram for the stationary Pt electrode in 0.5 M H_2SO_4 electrolyte (—) and first-cycle responses after the addition of 5 x 10^{-5} M $CdSO_4$ for different deposition times at 0.05 V: (- - -) 1, () 20, (- -) 60, and (- - -) 600 s.

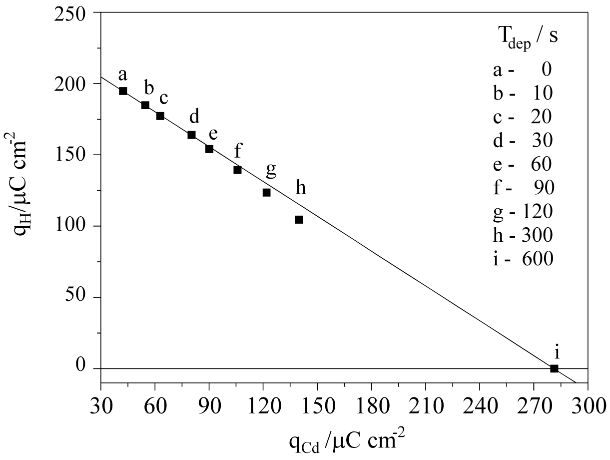

Figure 4. Linear dependence of the dissolution charges for H and Cd ad-atoms on Pt in the conditions of Fig. 3. Deposition times at 0.05 V are: (a) 0, (b) 10, (c) 20, (d) 30, (e) 60, (f) 90, (g) 120, (h) 300, and (i) 600 s.

the straight line can be described by the following relationship:

$$\text{slope} = N\,\frac{n_{H_{Ads}}}{n_{Cd_{Ads}}} \qquad (2)$$

where N is the number of H ad-atom displaced by each Cd_{ads} and n the number of electrons transferred to each kind of ad-atom. In this case, considering that the slope value is 0.74, N is equal to 1.1, as obtained from the relationship between the atomic radii of Cd and Pt (1.54 and 1.39 Å, respectively), and that $n_{H_{ads}}$ is 1, the number of electrons transferred to each Cd ad-atom can be calculated as 1.5. This means that each Cd ad-atom on Pt retains a partial charge of 0.5 in a unique feature in UPD studies. Moreover, the maximum amount of charge related to the desorption peaks of Cd_{ads} is 285 μC cm^{-2}, which means that 90% of the Pt surface is covered with Cd in a full monolayer.

Although the results obtained in this work, using the stationary electrode voltammetry, are in complete agreement with previously published results, it is necessary to compare these data with those obtained with another experimental technique, in order to confirm the assumptions made above. Here, the second experimental technique was chosen to be the collecting experiment with a rotating ring-disc electrode system. To do so, the same experimental conditions used in stationary electrode experiments were preserved. The ring-disc system was rotated at 2,000 rpm. The ring potential was polarized at a value of -0.5 V during 15 min, in order to promote the deposition of massive Cd. In this situation, the Nernstian deposition current on the ring becomes constant and dependent only on the rotation rate and ion concentration in solution. After the ring current stabilizes, the disc was polarized at 0.05 V during 0, 1, 10, 20, 30, 60 and 120 s, followed by an anodic potential scanning at 0.2 V s^{-1} up to 1.55 V, after which both ring and disc responses were collected.

The results of the experiments described above are represented in Fig. 5. The first observation that can be made is the similarity between the voltammetric responses obtained here at the rotating disc electrode and those at the stationary one. Again three desorption peaks can be obtained at higher deposition times. The total voltammetric charge calculated for the three peaks reaches 285 μC cm^{-2}, a value identical to the previous one. On the other hand, for the ring response one can also distinguish three separated peaks, in a similar potential region to that for the disc. It must be noted that, for $t_{dep} = 0$, the ring current is always constant and equals 0.1 mA, its Nernstian value. In this way, the ring response does not include any hydrogen desorption or oxide formation contributions. The maximum charge calculated for the ring response is 74.1 μC cm^{-2}. Considering the collection factor of the rotating system, 0.195, the charge value obtained can be transposed for the disc as 380 μC cm^{-2}, which correspond to a maximum coverage of 90% for a two-electrons process, in close agreement with the value found in the stationary electrode experiments. This charge value is not affected by the electrosorption valence, since on the ring the deposition occurs towards Cd(0). In this way, the relationship observed be-

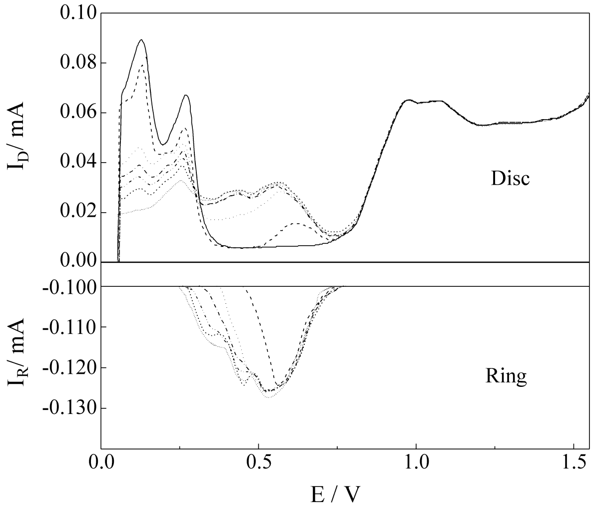

Figure 5. Rotating ring-disc responses to potential sweeps at 0.20 V s^{-1} on the Pt disc electrode at 2,000 rpm in 0.5 M H_2SO_4 + 5 x 10^{-5} M $CdSO_4$ solutions. The ring potential was kept constant at -0.5 V throughout the experiment. Prior to the potential sweep, the disc electrode was kept polarized at 0.05 V during: (—) 0, (- - -) 1, () 10, (- - -) 20, (- -) 30, (- - -) 60, and (...) 120 s.

Table 1. Charge values for the Cd UPD on polycrystalline Pt rotating ring-disk electrode.

T_{dep} /S	Q_{ring} / μC cm^{-2}	Q_{anodic} / (μC cm^{-2})	Q_{disk} / (μC cm^{-2})	Q_H / (μC cm^{-2})
0	0	210	0	210
1	164	295	120	175
10	284	307	213	94
20	312	315	234	81
30	342	309	257	52
60	368	304	275	29
120	380	285	285	0

tween the ring and the disc charge values at Cd_{ads} maximum coverage can be associated with the electrosorption valence of Cd on Pt. This relationship represents a value of 0.5, also in agreement with the value observed in stationary voltammetric experiments. In order to correlate the ring and disk responses, the complete set of charge values for different deposition times is collected in Table 1. The ring charges (column two) were obtained directly by integration of the ring curves. The total anodic charges (column three) are generated by the integration of the anodic branch of disc voltammograms, from 0.05 to 0.80 V. These values include both the hydrogen and Cd_{ads} oxidation contributions. The Cd_{ads} charge values on the disc (column four) are obtained from the ring values corrected by the collection coefficient and considering that, on the disc, the deposition is a 1.5 electrons reaction while on the ring it involves 2 electrons. Finally, in column five, the hydrogen contribution is calculated by subtraction of columns three and four. It can be noted that the hydrogen desorption contribution to the total anodic charge values diminishes correspondingly to the increasing coverage with Cd ad-atoms, approaching close to zero.

At this point, it is important to highlight that such charge value found for the ring electrode is absolutely free from any interference of hydrogen desorption or partial electron transference. Moreover, this value is concerned only with the reversible deposition of the Cd(II)/Cd(0) redox couple. The transposition for disc value through the collection factor also does not include any contribution other than the amount of Cd(II) ions coming from the disc during the monolayer dissolution.

Cd UPD on polycrystalline Au

The Cd UPD was also studied on polycrystalline Au surfaces in 0.1 M H_2SO_4 + 5 x 10^{-6} M $CdSO_4$ solutions by cyclic voltammetry at 0.2 V s^{-1}, using the stationary electrode. The results obtained by holding the potential scanning at 0.05 V for several deposition times are presented in Fig. 6.

An important feature displayed in Fig. 6 is the small amount of Cd_{ads} obtained in the conditions of such experiments. The maximum desorption charge measured under the unique peak at approximately 0.2 V reaches 41 μC cm^{-2}. A calculation involving the maximum charge for an AuO monolayer, *i.e.*, 380 μC cm^{-2} for a two electron reaction, allows one to postulate the formation of only 15% of the full monolayer, if it is considered a transference of 1.5 electrons[36], in a similar manner to that discussed for Cd UPD on Pt. Such low values for Cd coverage have already been observed[19], but those authors did not propose any interpretation for such phenomenon. An explanation for the low coverage with Cd_{ads} could involve the co-adsorption of anions (in this case sulphate), which inhibits the full monolayer formation. This is a currently controversial subject, though many authors have used this idea to justify incomplete monolayer formation by several metal ad-atoms[37,38].

In order to evaluate the participation of adsorbed sulphate anions in the low coverage value of the full Cd monolayer, voltammetric experiments at stationary Au electrode were also conducted in 0.1 M $HClO_4$ + 1 x 10^{-5} M $CdClO_4$, thus avoiding the presence of sulphate. The voltammetric profile, obtained in the same conditions as before, is presented in Fig. 7, for a deposition time of 600 s. The maximum coverage was assured by the absence of any further increase in peak-current after that time. The charge value calculated for the anodic peak at 0.23 V was 47 μC cm^{-2}, which is very close to that one observed in sulphate medium. It is already well-established that perchlorate anions adsorb very weakly on Au surfaces[32]. In this way, the agreement between the maximum charge

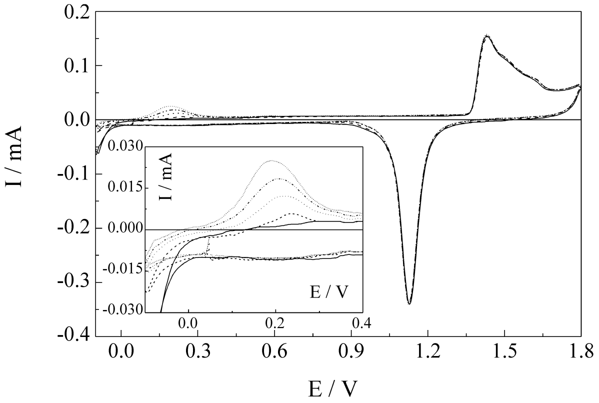

Figure 6. Steady-state voltammograms for the stationary Au electrode in 0.5 M H_2SO_4 electrolyte (—) and first-cycle responses after the addition of 5 x 10^{-5} M $CdSO_4$ for different deposition times at 0.05 V: (- - -) 1, () 20, (- -), 60 and (- - -) 600 s. The insert displays a magnification of the current response in the potential range of -0.1 to 0.4 V, where the UPD Cd peak is evident.

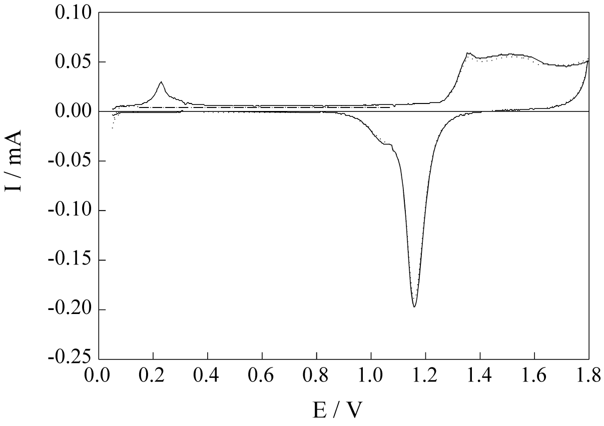

Figure 7. Steady-state voltammograms for the stationary Au electrode in 0.5 M $HClO_4$ electrolyte (–• –) and first-cycle responses after the addition of 5 x 10^{-5} M $Cd(ClO_4)_2$ and holding the potential at 0.05 V for 600 s (—).

values calculated for both media seems to minimize the influence of anion co-adsorption in the deposition of the first Cd_{ads} monolayer. Other authors proposed a formation of a Cd-Au alloy, in order to account for the low values of desorption charges[21,36]. Nevertheless, no evidence of such alloy formation was found in this work. Specifically, a cyclic voltammetric experiment performed after Cd monolayer deposition and moving the electrode to a Cd^{2+} free solution revealed only a smooth Au profile, with an active area similar to that obtained prior to Cd deposition. Another interpretation for the low coverage with deposited Cd is related to the vertical interactions between ad-atoms and substrate. This kind of interaction is very particular for each substrate, with the individual characteristics being revealed by the specific adsorption isotherm. Studies aiming to determine the adsorption isotherms for Cd on Pt and Au are now under progress in this laboratory.

The rotating ring-disc experiments for Cd UPD on Au were conducted in a similar manner to those already described for Pt. The electrolyte was composed by 0.1 m H_2SO_4 + 5 x 10^{-5} M $CdSO_4$. The scan rate value used here was 0.05 V s^{-1} and the rotation rate was 2,000 rpm. The ring was kept polarized at -0.5 V throughout the experiment and the deposition potential value for the disc was 0.05 V. At such conditions, depositions were carried out for several times and the voltammetric ring-disc response is presented in Fig. 8. By increasing the deposition time a gradually larger dissolution charge was obtained up to 60 s when it stabilized. Using the same methodology previously detailed for the Pt disc electrode, a total charge of 40 μC cm^{-2} was calculated for the Au rotating disc electrode. This corresponds to an occupancy of approximately 15% of the active sites on the Au surface, in complete agreement with the results found for the stationary experiments.

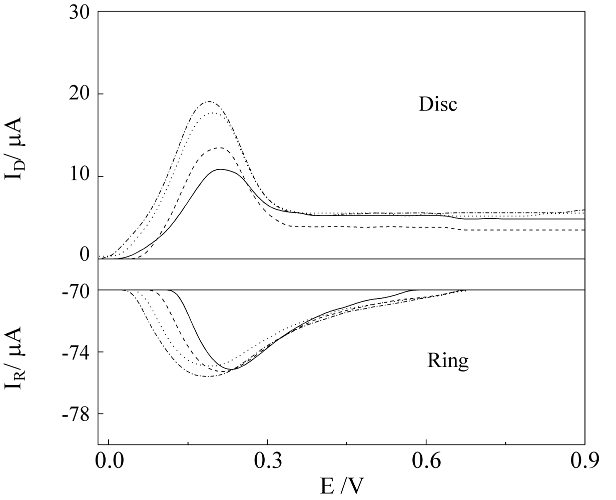

Figure 8. Rotating ring-disc responses to potential sweeps at 0.20 V s^{-1} on the Au disc electrode at 2,000 rpm in 0.5 M H_2SO_4 + 5 x 10^{-5} M $CdSO_4$ solutions. The ring potential was kept constant at -0.5 V throughout the experiment. Prior to the potential sweep, the disc electrode was kept polarized at 0.05 V during: (—) 5, (- - -) 10, () 20, and (- -) 60 s.

Conclusions

This work shows, in a very convincing way, the suitability of the rotating ring-disc technique to study the underpotential deposition of metals onto foreign substrates. The information obtained about electrosorption valences and maximum coverage is frequently beyond the limits of stationary voltammetric experiments.

The Cd UPD on Pt was characterized by the occupation of only 90% of the total available active sites on the surface and by an electrosorption value of 0.5 for the Cd ad-atom. The first characteristic can be associated to the small misfit observed for the atomic radii of Cd and Pt, while the second one is a very special character, only observed for the Cd ad-atoms. The dependence of the surface coverage by adsorbed hydrogen was found to be inversely proportional to the amount of UPD Cd and that the total coverage with Cd ad-atoms completely inhibits the hydrogen adsorption.

On the other hand, on Au surfaces, the maximum coverage found for Cd ad-atoms was about 15%. This low coverage was firstly associated with sulphate co-adsorption, which could block the active sites on the surface. However, experiments using free-sulphate electrolyte resulted in Cd coverage as low as before, thus indicating only a minor participation of sulphate in the adsorption process of Cd on Au. Another and more interesting proposition concerns the vertical interaction between adsorbate and substrate atoms. Such interactions are revealed in the isotherms for the Cd adsorption on Au and will be the subject of further work.

The ring-disc experiments, for both substrates, fully confirmed the stationary voltammetric charge data and, moreover, in the case of Pt as substrate, eliminated any influence of adsorbed hydrogen in the determination of the ad-atom monolayer charge.

Acknowledgments

The authors wish to thank CNPq and FAPESP (processes No. 97/02723-5 and 94/5863-4) for the financial support.

References

1. Frelink, F.; Visscher, W.; Cox, A.P.; van Veen, J.A.R. *Electrochim. Acta* **1995**, *40*, 1537.
2. Paul Wilde, C.; Zhang, M. *Electrochim. Acta* **1993**, *38*, 2725.
3. Xia, X.H.; Iwasita, T. *J. Electrochem. Soc.* **1993**, *140*, 2559.
4. Gregory, B.W.; Stickney, J.L. *J. Electroanal. Chem.* **1991**, *300*, 543.
5. Cachet, H.; Cortes, R.; Froment, M.; Maurin, G. *J. Solid State Electrochem.* **1997**, *1*, 100.

6. Quiroz, M.A.; Salgado, L.; González, I.; Meas, Y.; Rojas-Hernández, A.; Vela, A. *J. Electroanal. Chem.* **1989**, *261*, 409.
7. Swathirajan, S. *J. Electrochem. Soc.* **1986**, *133*, 671.
8. Swathirajan, S.; Brunckenstein, S. *Electrochim. Acta* **1983**, *28*, 865.
9. Kolb, D.M.; Przasnyski, M.; Gerischer, H. *J. Electroanal. Chem.* **1974**, *54*, 25.
10. Szabó, S. *Int. Reviews in Phys. Chem*. **1991**, *10*, 207.
11. Leive, E. *Electrochim. Acta* **1996**, *41*, 2185.
12. Adzic, R.R. *Israel J. of Chem*. **1979**, *18*, 166.
13. Adzic, R.R. In *Advances in Electrochemistry and Electrochemical Engineering*, Gerischer, H. Ed., vol. 13, John Wiley, New York, p. 159, 1984.
14. Kokkinidis, G. *J. Electroanal. Chem*. **1986**, *201*, 217.
15. Jovicevic, J.N.; Despic, A.R.; Drazic, D.M. *Electrochim. Acta* **1977**, *22*, 577.
16. Daujotis, V.; Raudonis, R. *J. Electroanal. Chem.* **1992**, *326*, 253.
17. Martins, M.E.; Hernández-Creus, A.; Salvarezza, R.C.; Arvia, A.J. *J. Electroanal. Chem*. **1994**, *375*, 141.
18. Loferski, J.J. *J. Appl. Phys.* **1956**, *27*, 777.
19. Gregory, B.W.; Norton, M.L.; Stickney, J.L. *J. Electroanal. Chem.* **1990**, *293*, 85.
20. Gregory, B.W.; Stickney, J.L. *J. Electroanal. Chem.* **1991**, *300*, 543.
21. Colleti, L.P.; Teklay, D.; Stickney, J.L. *J. Electroanal. Chem.* **1994**, *369*, 145.
22. Huang, H.; Zhao, M.; Xing, X.; Bae, I.T.; Scherson, D. *J. Electroanal. Chem.* **1990**, *293*, 279.
23. Xing, X.K. and Scherson, D.A. *J. Electroanal. Chem.* **1986**, *199*, 485.
24. Ritzoulis, G. *J. Electroanal. Chem.* **1992**, *327*, 209.
25. El-Shafei, A.A.; Shabanah, H.M.; Moussa, M.N.H. *J. Electroanal. Chem.* **1993**, *362*, 159.
26. El-Shafei, A.A.; Shabanah, H.M.; Moussa, M.N.H. *J. Power Sources* **1993**, *46*, 1993.
27. Varga, K.; Zelenay, P.; Horány, G.; Wieckowski, A. *J. Electroanal. Chem.* **1992**, *327*, 291.
28. Machado, S.A.S.; Tanaka, A.A.; Gonzalez, E.R. *Electrochim. Acta* **1992**, *37*, 2559.
29. Machado, S.A.S. In *Deposição em Subtensão de Cobre, Cádmio e Chumbo Sobre Platina e Sua Influência na Reação de Redução de Oxigênio*, PhD Thesis, IQSC - USP, São Carlos, 1989.
30. Santos, M.C. In *Estudos da Deposição em Regime de Subtensão de Ag, Cd, Zn e Sn Sobre Diferentes Substratos em Meio Ácido*, Dissertation, IQSC - USP, São Carlos, 1997.
31. Conway, B.E.; Angerstein-Kozlowska, H.; Sharp, W.B.A. *J. Electroanal. Chem.* **1973**, *43*, 9.
32. Angerstein-Kozlowska, H.; Conway, B.E.; Hamelin, A.; Stoicoviciu, L. *Electrochim. Acta* **1986**, *31*, 1051.
33. Woods, R.A. In *Chemisorption at Electrodes*, Bard, A.J. Ed., Electroanal. Chem., v. 9, Marcell Deker, New York, 1976.
34. Trassati, S.; Petrii, O.A. *Pure & Appl. Chem.* **1991**, *63*, 719.
35. H. Angerstein-Kozlowska, H.; Conway, B.E.; Barnett, B.; Mozota, J. *J. Electroanal. Chem.* **1979**, *100*, 417.
36. Deakin, M. R. And Melroy, O., *J. Electroanal. Chem*. **1988**, *239*, 321.
37. Horanyi, G.; Wieckowski, A. *J. Electroanal. Chem*. **1990**, *294*, 267.
38. Zhang, J.; Sung, Y.E.; Rikvold, P.A.; Wieckowski, A. *J. Chem. Phys.* **1996**, *104*, 5699.
39. Deakin, M.R.; Melroy, O. *J. Electroanal. Chem.* **1988**, *239*, 321.

FAPESP helped in meeting the publication costs of this article