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Study of Cadmium Electrochemical Deposition in Sulfate Medium

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The cadmium electrochemical deposition process from sulfate medium was studied by means of different electrochemical techniques in both stationary and nonstationary diffusion regimes. The kinetics of the electrochemical reduction of cadmium on solid cadmium electrodes was examined and the kinetic parameters are presented, as well as the diffusion coefficient derived from the different techniques. Temperature has an important effect on the cadmium reduction kinetics, and the activation energy of the process was evaluated. The electrochemical deposition of cadmium is a complex process due to the coexistence of adsorption and nucleation processes; the adsorbed electroactive species appears to be Cd^{+2}, and we propose a mechanism for cadmium electrodeposition on solid cadmium electrodes.

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Cadmium is a chemical element of great importance because of the wide variety of its applications such as in rechargeable batteries[1] and solar energy capture devices.[2] In the case of solar energy conversion devices, cadmium is combined with other elements to obtain semiconductor materials. These materials can be obtained from a broad variety of physical chemical, and electrochemical techniques.[3,4]

Electrochemical techniques to prepare cadmium-based semiconductor materials are principally of empirical character because of the lack of precise information concerning the individual electrochemical behavior of the components in the electrochemical solution of interest. Thus it is clear that a formal study about the alloy formation process must be, first, focused on the study of the individual deposition process for each one of the alloy components in the same chemical medium, just as it has been pointed out in Kroger's[5] and Landolt's[6] works.

Cadmium has been electrochemically studied for some time, and the literature about the matter is quite broad. Most of the research work has been accomplished by using either mercury or mercury amalgam working electrodes and applying different techniques such as ac polarography, potential step, current step, faradic impedance, and others.[7,8] In these kinds of electrodes the cadmium deposition process, starting from either perchlorate or sulfate baths, is a fast process ($k_o > 10^{-2}$ cm s^{-1}). It is considered that values for the reaction rate constant are abnormally high and, additionally, there is not a clear explanation concerning the broad variety of values for the charge-transfer coefficient. In some work[9,10] the effect of the electrode nature on the kinetic behavior of cadmium reduction has been investigated and it has been demonstrated that mercury not always behaves as an inert substrate, and in some cases reaction kinetics is favored by the presence of mercury. Therefore the high values obtained for k_o are due to the use of noninert working electrodes and consequently the polarographic results cannot be taken as a foundation when solid electrodes are employed. In works carried out on either mercury or mercury amalgam the cadmium reduction mechanism has been analyzed.[11-14] In this case, most of the authors assume a two-step reduction mechanism involving the existence of an absorbed monovalent intermediate[11.12]; however, results do not always support this assumption.

For the cathodic deposition of Cd on solid electrodes only few works are published.[8,15-19] In this case, the cadmium deposition process was studied by electrochemical techniques such as current step, faradic impedance, and others. It has been established that the reduction process is affected by selective adsorption of anions, which come from the electrolytic bath, and they cause that the deposition process be kinetically less favorable than on mercury electrodes.[15,17,20] Using this, k_o values in the range of 10^{-2} to 10^{-5} cm s^{-1} have been obtained. For cadmium reduction on solid cadmium electrodes, also a two-step mechanism involving the existence of Cd^{+} as an intermediate in the adsorbed state[21] has been assumed. However, a cadmium reduction mechanism involving one step has also been proposed.[22] On the other hand, Hedrich[23] suggests that the cadmium discharge mechanism depends on the applied current density, and he proposes that a one-step mechanism prevails at low current density while a two-step mechanism takes place at high current density. As is clear, there is no agreement about the cadmium reduction mechanism, and it remains an open question.

In this paper we report and discuss our results on cadmium deposition, with the notion that this information will be helpful toward baths for the preparation of CdTe. Specifically, the electrochemical deposition of Cd^{+2} on solid cadmium electrodes from aqueous solution using different electrochemical techniques in both stationary and nonstationary diffusional conditions is described. The investigation mainly focused on the kinetic and mechanistic aspects of the cadmium deposition process and the associated phenomena coupled to the charge-transfer reactions. In order to avoid electrode contamination and uncertainty in the electrochemical data, this study was carried out by using cadmium electrodes prepared *in situ*.

Experimental

Two solutions were prepared by using chemical reagents of analytic grade (Aldrich) and triply distilled/deionized water. A solution of 0.2 M $CdSO_4 \cdot 8H_2O$, in 0.5 M K_2SO_4 was used only for preparation of the working cadmium electrodes while for cadmium electrochemical reduction studies a solution of 0.01 M $CdSO_4 \cdot 8H_2O$ in 0.5 M K_2SO_4 was used. In both electrolytes H_2SO_4 was added until the pH was 2.2.

Two conventional (80 and 250 mL) three-electrode electrochemical glass (Pyrex) cells were used, the larger one being employed in the electrochemical quartz crystal microbalance (EQCM) experiments. The electrolytic solutions were purged with nitrogen for 30 min prior to each experimental series and then kept under flowing nitrogen during the experiments.

Two kinds of working electrodes were used: a platinum rotating disk electrode (RDE) (4 mm diam) embedded in a cylindrical Teflon holder (13 mm diam) and for the microbalance sensor, a thin crystal quartz disk (13.2 mm diam). Both electrodes were covered with a cadmium thin film for immediate use as a working electrode. The reference electrode was $Hg/Hg_2SO_4/K_2SO_4$ (saturated) (SSE, 0.64 V *vs.* NHE at 25°C) and all potentials are referred to this electrode. As the counter electrode a platinum gauze was employed. The working temperature was controlled at 25 ± 0.1°C. When cadmium reduction was studied at different temperatures, the reference electrode was placed out of the cell, maintained at constant temperature (25°C), and connected to the cell by means of a glass tube (fritted glass in one end) filled with supporting electrolyte.

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Most measurements were performed using a standard electrochemical potentiostat (EG&G PAR, model 273 A) controlled by a computer and coupled to a rotating disk electrode system (Pine, model AFMSRX). For some experiments an EQCM (Maxtek Inc., model PM600) with crystals operating at 5 MHz was used. The potential at the microbalance sensor was controlled by a potentiostat (Voltalab model PGZ301).

Preparation of the working electrodes.—The platinum rotating disk electrode was mechanically polished using alumina of 0.1 μm, followed by cleaning with deionized water and ultrasound to remove the alumina traces and finally the electrode was rinsed with deionized water. The microbalance sensor was treated with 10% HCl solution for 10 min and then thoroughly rinsed with water. Both electrodes were covered with a cadmium deposit (500 nm thickness) prepared under the following galvanostatic conditions: cathodic current density 153 μA cm^{-2}, deposition time 81 min, temperature 25°C, and a rotation rate of the electrode of 1500 rpm. As rotation was not possible for the microbalance sensor, a magnetic stirrer was used to impose the necessary hydrodynamic regime. This procedure was used to obtain solid cadmium electrodes generated *in situ* and with this, contamination problems (such as oxide formation) are avoided. Once the working electrodes were prepared we proceeded to study the electrochemical system Cd^{+2}/Cd in the working solution by means of different electrochemical techniques.

In the case of electrochemical measurements performed at a slow potential scan rate or in the case of pulsing techniques with long periods, it was always necessary to use a new electrode to avoid the influence of the electrode surface roughening. In the case of pulse techniques with short periods, multiple experiments were performed with the same electrode, because roughening was not appreciable.

Results and Discussion

The basic electrochemical characteristics.—The cadmium electrochemical reduction process was first studied by using the linear potential scan voltammetry technique in a nonstationary diffusion regime. Potential scans in the cathodic direction were applied starting from the equilibrium potential in the working solution (−1.141 V); the study was made with potential scan rates (v) in the range of 5 to 1000 mV s^{-1}.

Figure 1 shows voltammograms obtained for some potential scan rates. In general, these curves show a quick growth of current at low overpotentials, which is indicative of favorable kinetics for the reduction process of Cd^{+2} to Cd^0. Because of this behavior several works in the literature[7,8] consider the cadmium reduction as a reversible process. The curves in Fig. 1 show a peak in the measured current density, which is normal in the voltammetric technique under nonstationary diffusion conditions. Such a peak is due to the electroactive species depletion on the electrode surface, and the magnitude of the cathodic peak current density (j_{pc}), was increased as v did too. Besides this, a gradual displacement of the peak potential toward more negative values was observed as v was increased. In this sort of *j-E* curves hydrogen evolution is only observable at potentials lower than −1.55 V.

The measured j_{pc} values showed a linear variation with regard to $v^{1/2}$, thus pointing out that the reduction process is under diffusion control and therefore meets the Randles-Sevcik[24] equation at 25°C

$$j_{pc} = 2.69 \times 10^5 n^{3/2} C_0^* D^{1/2} v^{1/2} \qquad [1]$$

where n is the number of electrons involved in the reduction process. Here $n = 2$, C_0^* is the bulk concentration of the electroactive specie, and D is the diffusion coefficient of the same species. From the slope of the j_{pc} *vs.* $v^{1/2}$ curve it was possible to estimate the apparent diffusion coefficient for the electroactive species $D = 5.3 \times 10^{-5}$ cm^2 s^{-1}. This value is larger than that reported in the literature (0.52×10^{-5} cm^2 s^{-1}) for Cd^{+2} in a similar electrolytic medium.[25]

When the absolute value of the difference between the cathodic peak potential and the cathodic half-peak potential, $|E_{pc} - E_{pc/2}|$, was represented against log v, only for v values lower than 40 mV s^{-1} such a difference was closer to that expected for a fast system (29.5 mV at 25°C and $n = 2$)[24] and only in this condition our results are in agreement with those normally observed in polarographic studies,[7,8] *i.e.*, the system is reversible. However, for v larger than 100 mV s^{-1} the difference $|E_{pc} - E_{pc/2}|$ was closer to the expected value for an irreversible system (47.7 mV at 25°C, $n = 2$ and $\alpha = 0.5$).[24] Then, in order to attain a better understanding about the electrochemical behavior of Cd^{+2} reduction, a more complete kinetic study was carried out.

The kinetics.—The cadmium electrochemical reduction in stationary diffusion regime was studied by using the RDE technique. A constant potential scan rate (2 mV s^{-1}) was imposed and the electrode rotation rate (ω) was varied from 100 to 1200 rpm. Some *j-E* curves obtained under these conditions are shown in Fig. 2. At low overpotentials the *j-E* curves show a slight dependence with respect to the electrode rotation rate, but such dependence is more evident at high

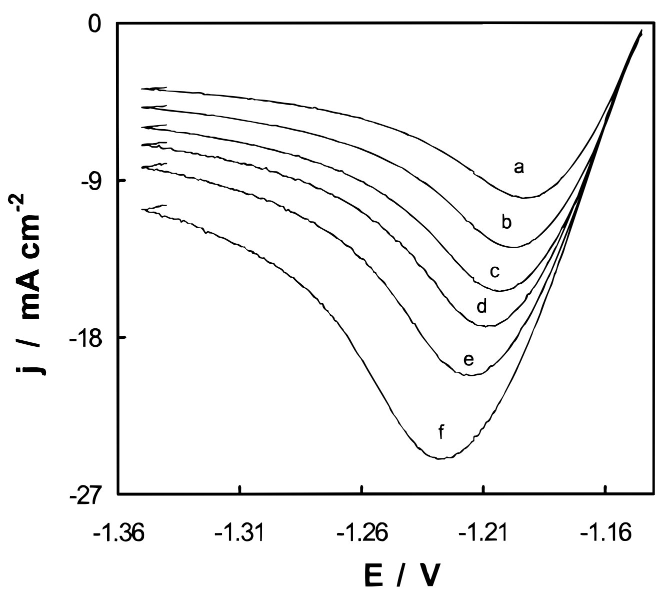

Figure 1. Linear sweep voltammograms for cadmium reduction in sulfate medium: a, 30; b, 50; c, 70; d, 90; c, 125; and f, 200 mV s^{-1}.

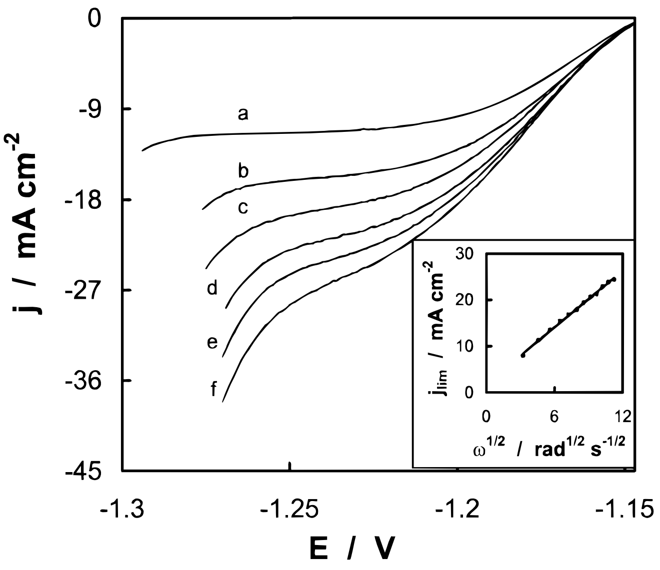

Figure 2. Potentiodynamical curves in stationary diffusion regime for cadmium reduction at 2 mV s^{-1}; a, 200; b, 400; c, 600; d, 800; e, 1000; and f, 1200 rpm. Inset: Variation of the cathodic limiting current density with agitation.

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overpotentials and different plateaus were observed which correspond to the limiting current densities (j_{lim}). The plateau width diminished as ω was increased. This is because the hydrogen evolution reaction is favored. This observation can be explained as a result of two effects: first, the H^+ reduction is favored to produce H_2 because H_2 is more rapidly displaced from the electrode surface when ω is increased and, second, at the end of the *j-E* curve the electrode surface has been modified by roughening (because of the slow potential scan rate) thus increasing the number of active sites for H^+ reduction. These two effects lead to an apparent displacement of the hydrogen reduction to less negative values of potential and, because of this, for $\omega > 1200$ rpm, the limiting current density was difficult to define.

The limiting current densities showed a linear variation with regards to $\omega^{1/2}$, as can be appreciated in the inset of Fig. 2, which means that the cadmium reduction process is limited by mass transport of the electroactive species. Under these conditions the Levich[26] equation is satisfied

$$j_{\mathrm{lim}} = 0.620nFD^{2/3}\nu^{-1/6}C_0^*\omega^{1/2} \qquad [2]$$

where F is the Faraday constant, ν is the kinematic viscosity (0.0094 $\mathrm{cm^2\ s^{-1}}$),[27] and the other parameters have the same meaning as defined in previous paragraphs. From the slope of the Levich-type plot (inset, Fig. 2) the apparent diffusion coefficient for the electroactive species was evaluated as $D = 2.19 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$. This value is a better estimation for the diffusion coefficient and agrees well with that reported in the literature from other techniques.[17,27] Extrapolating the curve j_{lim} *vs.* $\omega^{1/2}$ to $\omega^{1/2} = 0$ (Fig. 2, inset) leads to a nonzero current density value, revealing the existence of other phenomena coupled to the charge-transfer process which increase the current density.[26]

In order to evaluate the kinetic parameters, the current densities free from diffusional effects, j_{k}, were evaluated by plotting j^{-1} *vs.* $\omega^{-1/2}$ for several constant overpotentials and extrapolating to $\omega^{-1/2} = 0$, according to the equation[28]

$$\frac{1}{j} = \frac{1}{j_{\mathrm{k}}} + \frac{1.61\nu^{1/6}}{nFD^{2/3}C_0^*\omega^{1/2}} \qquad [3]$$

Some typical curves j^{-1} *vs.* $\omega^{-1/2}$ are shown in Fig. 3 for some fixed overpotentials and j_{k} was obtained from the intercepts. From the slope of each curve, the diffusion coefficient was evaluated, and it was almost the same as that obtained by using the Levich equation.

By using the pure kinetic current densities j_{k} for each overpotential, it was possible to estimate the kinetic parameters by using the rate equation related to a cathodic process under activation control, Tafel[28] equation

$$j_{\mathrm{k}} = j_0 \exp\left[-\frac{\alpha nF}{RT}\eta\right] \qquad [4]$$

which is a function of the charge-transfer coefficient α, the overpotential η, and the exchange current density defined[28] as $j_{\mathrm{o}} = nFk_{\mathrm{o}}C_{\mathrm{o}}^{(1-\alpha)}$, where k_{o} is the rate constant.

The Tafel plot is shown in Fig. 4 and, as can be seen, there is an overpotential range (−20 to −90 mV) where log j_{k} *vs.* η is linear, just as predicted by the Tafel equation. From the slope of this curve it was possible to obtain the charge-transfer coefficient $\alpha = 0.65$, and from the intercept the following values were estimated $j_{\mathrm{o}} = 3.41\ \mathrm{mA\ cm^{-2}}$ and $k_{\mathrm{o}} = 8.98 \times 10^{-5}\ \mathrm{cm\ s^{-1}}$. Therefore, the electrochemical reduction process of Cd^{+2} on solid cadmium electrode can be classified as quasi-reversible.[24,28]

As was expected, the cadmium electroreduction kinetics on solid cadmium electrodes is slower than the electrochemical reduction on a mercury drop or mercury amalgam electrode. In this work we have obtained a rate constant which is three orders of magnitude lower than in the case of mercury electrodes; however, the value for k_{o} we have obtained is similar to the ones reported from other electrochemical and nonelectrochemical experiments[15,17,18] performed on solid cadmium electrodes. As regards the charge-transfer coefficient, it is difficult to establish a comparison because in each of these works the values were different.

It is known that temperature plays an important role in the kinetics of electrochemical reactions. Therefore, the temperature effect on the cadmium electrochemical reduction process was investigated by using the RDE technique. Potentiodynamic curves in stationary diffusion regime were obtained for a well-defined hydrodynamic condition $\omega = 300$ rpm and a slow potential scan rate (2 $\mathrm{mV\ s^{-1}}$). These *j-E* curves are shown in Fig. 5. In these curves the equilibrium potential of the working electrode is displaced toward less negative values when the temperature is increased. The direct comparison of the curves shows that at low temperatures (curves a and b) an applied overpotential of −30 mV, with respect to the start of each curve, leads to a cathodic current of 2-3 $\mathrm{mA\ cm^{-2}}$, while the same applied overpotential when the temperature is high (curves g and h) produces a reduction current approximately five times higher, thus revealing that kinetics is enhanced with temperature increase.

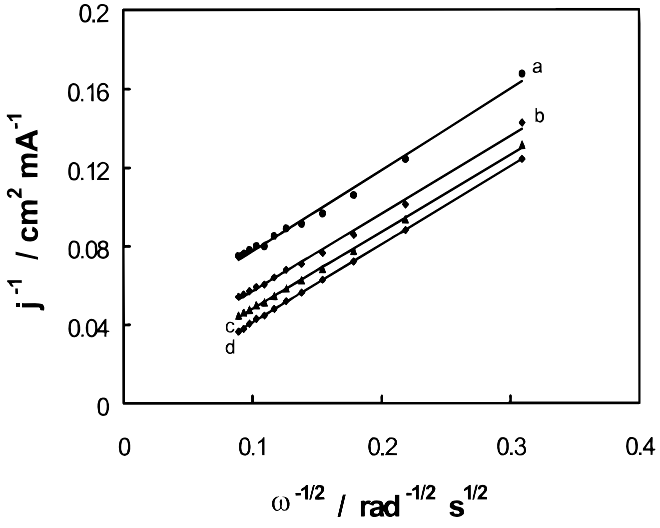

Figure 3. Plot of j^{-1} *vs.* $\omega^{-1/2}$ for some overpotentials: a, −40; b, −55; c, −70; and d, −100 mV.

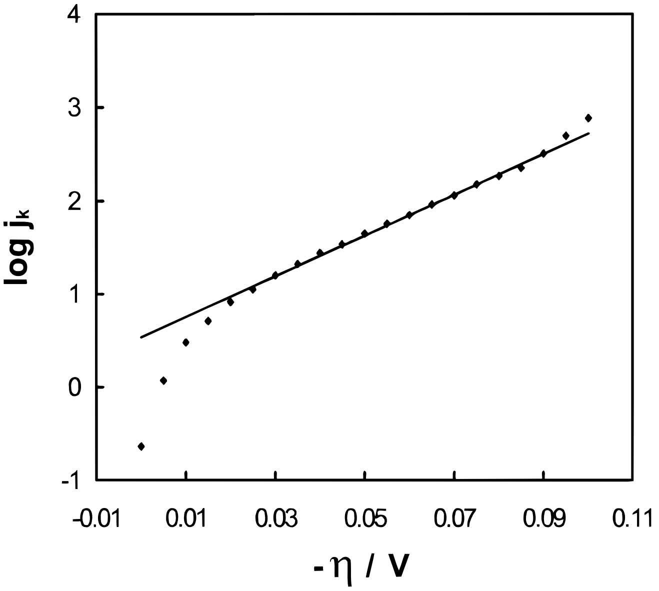

Figure 4. Tafel plot for cadmium reduction at 25°C, j_{k} in mA $\mathrm{cm^{-2}}$.

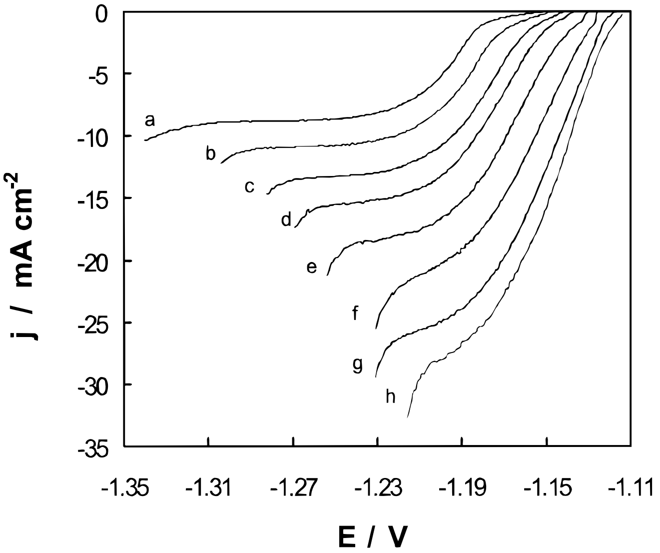

Figure 5. Effect of temperature on cadmium reduction at 2 mV s^{-1} and ω = 300 rpm: a, 5; b, 15; c, 25; d, 35; e, 45; f, 55; g, 65; and h, 75°C.

From the curves in Fig. 5 it was possible to evaluate the activation energy E_a for the reduction process by using the limiting currents[29] and the Arrhenius equation in the form[30]

$$j_{\text{lim}} = A \exp^{(-E_a/RT)} \quad [5]$$

where A is the frequency factor, R is the universal gas constant, and T is the absolute temperature. The activation energy of the diffusional process was evaluated from the slope of the plot ln j_{lim} *vs.* T^{-1} (Fig. 6) as $E_a = 11.86$ kJ mol^{-1}, which is a reasonable value for a process under mass-transport control.[31]

Nucleation and adsorption processes.—Coupled phenomena to the charge transfer were studied by using other electrochemical techniques in nonstationary diffusional regime. The chronamperometric behavior of the cadmium electrochemical reduction was studied by imposing different overpotentials (−5 to −348 mV) to the working electrode during different time intervals t (300-3000 ms). Figure 7 shows some j-t responses, and at low overpotentials (curves a and b) a current response similar to that obtained in the stationary diffusion regime is observed. However, at long times (not shown in the figure) a slight increment of the current was obtained which is caused by the nucleation phenomenon, as discussed below.

As potential steps are more negative (curves c and d, Fig. 7), a slight mass-transfer dependence of the current is expected, that is to say, a decay of the cathodic current density with time should be observed. However, during the first 300 ms the current response in Fig. 7 (curves c and d) shows that this is not the case. On the contrary, after 300 ms the cathodic current shows an increment characteristic of a nucleation phenomena.[25,32] At higher overpotentials a maximum in the j-t response appears (curves e to j, Fig. 7) and such a maximum increases and moves toward shorter times. In these curves only after a certain time the measured current falls down with t; this behavior being characteristic of systems with nucleation under diffusional control as observed for other metallic systems.[33-35] Consequently, the shape of this set of curves indicates that the electrochemical cadmium reduction is initially (curves a-b in Fig. 7) sustained at defects already present at the Cd surface. But at high overpotentials new defects are needed to sustain the high rate of deposit growth, and these are generated through nucleation, indicating a transition from Stranski-Kossel to Erdey-Gruz and Volmer growth modes as overpotential (or current density) is increased.[36]

In order to investigate if the nucleation phenomenon was under diffusional control we applied the Scharifker's nondimensional $(j/j_m)^2$ *vs.* t/t_m analysis[33] on our j-t transients (with j_m and t_m as defined in Ref. 33). Figure 8 shows this type of plot for an applied overpotential of −75 mV, and from this figure it is clear that the cadmium nucleation process does not fit to a diffusionally controlled 3D nucleation and growth model (neither progressive nor instantaneous) thus confirming that cadmium reduction is a complex process. In Fig. 8, the experimental points are over the corresponding curves for the nucleation models thus revealing the existence of a coupled phenomenon which contributes to the measured current. The presence of adsorbed species on the electrode surface gives rise to measured currents higher than those expected (for a given nucleation model) in the rising part of the plots $(j/j_m)^2$ *vs.* t/t_m, as has been discussed in some papers.[33,37] Therefore, in our case, a phenomenon like this might be possible, and this possibility was analyzed by means of other techniques.

For applied overpotentials larger than −285 mV the j-t response does not any longer depend on the applied overpotential (curve k in Fig. 7). Then, the typical decay of the current with time is observed, and in this condition the Cottrell[38] equation should be satisfied

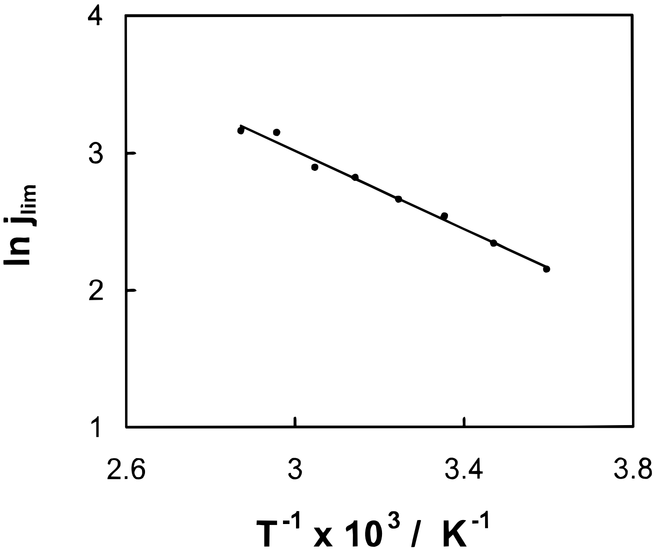

Figure 6. Arrhenius plot for cadmium reduction, j_{lim} in mA cm^{-2}.

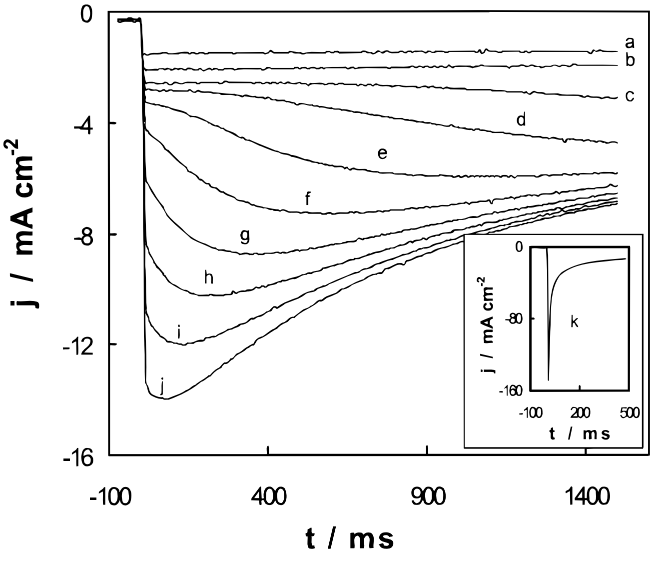

Figure 7. Chronoamperometric curves for cadmium reduction after application of several cathodic overpotentials: a, 19; b, 31; c, 35; d, 39; e, 43; f, 47; g, 51; h, 55; i, 59; j, 63; and k, 285 mV.

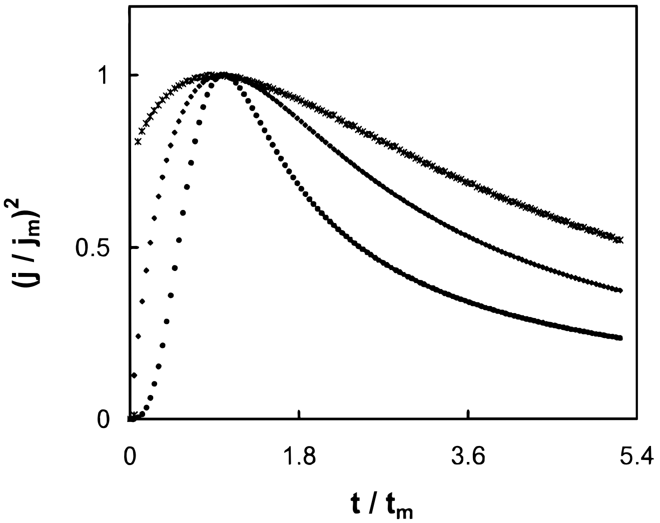

Figure 8. Comparison between experimental points for cadmium deposition on Cd (*) and the theoretical nondimensional plots for instantaneous (◆) and progressive (●) nucleation models.

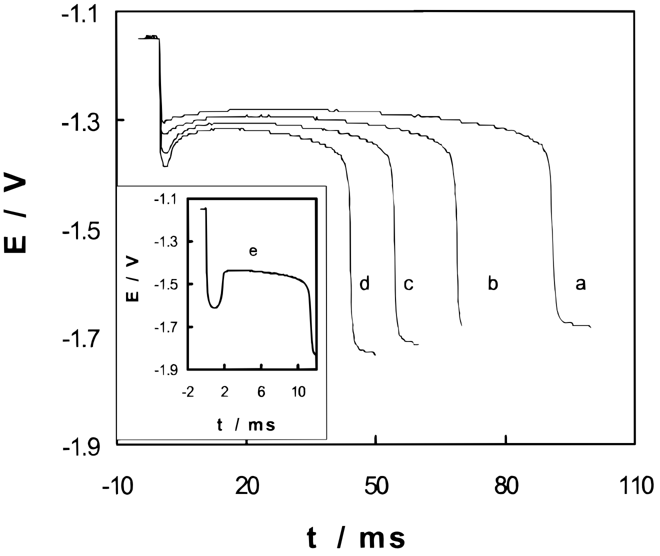

Figure 9. Chronopotentiometric curves for different cathodic current pulses: a, 39; b, 45; c, 51; d, 58; and e, 128 mA cm^{-2}.

$$j = \frac{nFD^{1/2}C_0^*}{\pi^{1/2}t^{1/2}} \qquad [6]$$

where all the parameters have been defined.

When j values were plotted against $t^{-1/2}$ for $t > 40$ ms, most of the experimental points followed a linear behavior. But for $t < 40$ ms the experimental points deviated from this trend, and deviation increased as t was smaller. In this region ($t < 40$ ms) the measured current was larger than that expected according to the Cottrell equation. As deviation is large, such behavior cannot only be attributed to double-layer charging effects because these are not too high. Consequently, nucleation can be viewed as the most important phenomenon causing the observed deviation. Once this takes place, the reduction process is favored at short times thus abnormally increasing the measured current. After this, the deposition rate is only limited by the diffusional process, and the Cottrell behavior is observed. Then, from the slope of the linear part of the j-$t^{-1/2}$ plot, it was possible to estimate the apparent diffusion coefficient as $D = 5.68 \times 10^{-5}$ cm^2 s^{-1}, which is slightly larger than the value previously obtained from voltammetry in nonstationary diffusion regime.

In order to clarify and obtain a better understanding of the processes coupled to the charge-transfer reaction we continued the study of the cadmium reduction process by the chronopotentiometric technique. In this case cathodic current steps (4 to 128 mA cm^{-2}) were imposed to the working electrode during several time intervals. Some E-t responses are shown in Fig. 9. In all cases the E-t response has a minimum in the potential immediately after the current pulse. This minimum grows and becomes narrow as the imposed current density is increased. It has been suggested that such kind of minimum in the E *vs.* t response may be caused by impurities in either the working solution or on the working electrode surface,[39] however, this is not the case because in this work special care was taken about this. On the other hand, there are some papers[40-42] in which that behavior is associated with the discharge mechanism of metallic divalent ions in two steps, that is to say, from M^{+2} to M^{+1} and finally to M^0. But in this study we found no evidence of such a sequence. According to our results, the minimum in the E-t curves is then clearly due to a nucleation process because nuclei generation requires additional energy, but once these nuclei have been generated less energy is required to continue the reduction process and the electrode potential goes toward less negative values. Milchev and Montenegro[43] have previously discussed this situation.

To reinforce this interpretation, the working electrode was subjected to a pulsed current train without stirring. A 10.5 mA cm^{-2} cathodic current was applied during 1.5 s followed by a zero current during 1 s; in these conditions, the electroactive species consumed during the pulse are regenerated during the zero current condition. Repeating this sequence produces the E-t response shown in Fig. 10. The start of the experiment is at $t = 1$ s; before this time the working electrode is only stabilized. When current is applied, the E-t response shows transition times (τ) with the first one larger than the second one and so on. This means that regeneration of the electroactive species at surface level is not complete, even though the electrode potential is completely recovered during $j = 0$. On the other hand, this behavior could be indicative of the existence of electroactive species in the adsorbed state on the working electrode. These adsorbed species are formed during the stabilization time of the electrode at open circuit. Nevertheless, the most important point in Fig. 10 is the observation of a minimum in the E-t curve (point A) only the first transition time, such as that observed in the curve series in Fig. 9. This means that the nucleation process certainly occurs but once it takes place subsequent pulses simply result in deposition on the previously formed nuclei. This behavior eliminates the possibil-

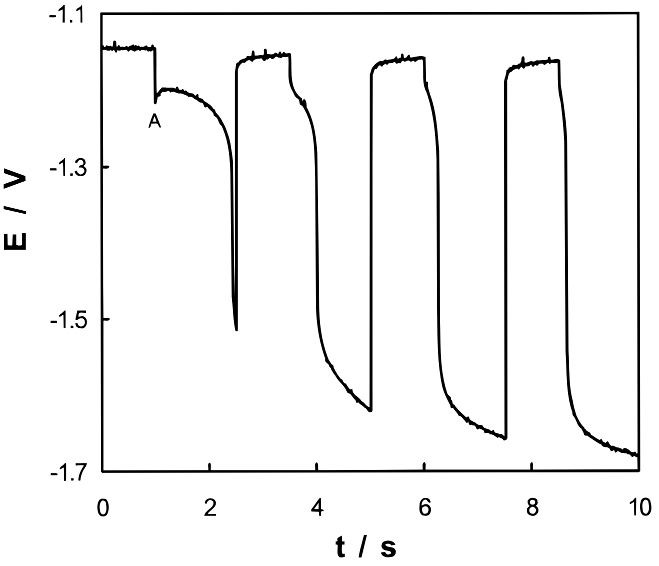

Figure 10. Potential-time response after application of a cathodic pulsed current: 10.5 mA cm^{-2} during 1.5 s and 0 mA cm^{-2} during 1 s.

ity of impurities in solution as a cause for the observed effect and besides this, the possible existence of M^+ species as intermediates in the reduction mechanism can be rejected because in such cases the minimum in the *E-t* response should be observed in all the patterns of successive galvanostatic pulses.

After these considerations, transition times showed in Fig. 9 were corrected by subtracting the time associated to the nucleation step. If the cadmium reduction process is limited by diffusion, the Sand[38] equation must be satisfied

$$j = \frac{nFD^{1/2}\pi^{1/2}C_0^*}{2\tau^{1/2}} \qquad [7]$$

and this means that the plot *j vs.* $\tau^{-1/2}$ must be linear. Figure 11 shows this kind of representation where a certain linear behavior is obtained but only for relatively larger τ values (left side in the graph), that is to say, at low *j* values. The deviation observed in the experimental data (curve a, Fig. 11) at small τ is because of the high contribution from the nucleation step and even though the τ values were corrected (curve b, Fig. 11), it was not possible to get good agreement with the Sand equation in such a region (curve c, Fig. 11).

From the corrected data (curve b, Fig. 11) at $j < 70$ mA cm^{-2} it was possible to obtain the apparent diffusion coefficient of the cadmium species in the working solution, $D = 4.53 \times 10^{-5}$ cm^2 s^{-1}, which is similar to those obtained from the other nonstationary techniques, and this is closer to the RDE value.

Our chronopotentiometric results allowed us to analyze the possible existence of adsorbed electroactive species on the electrode surface. This was done by plotting $j\tau$ *vs.* j^{-1} (Fig. 12) according to the equation[44]

$$j\tau = \frac{n^2F^2\pi DC_0^{*2}}{4j} + nF\Gamma_o \qquad [8]$$

where Γ_o is the amount of adsorbed species. Figure 12 shows a linear dependence between $j\tau$ and j^{-1} which means that both dissolved and adsorbed electroactive species are reduced; however, the adsorbed electroactive species are not totally reduced to Cd before reduction of the dissolved (Cd^{+2}) species starts.[28,44] From the intercept in Fig. 12 the amount of adsorbed electroactive species was evaluated as $\Gamma_o = 1.31 \times 10^{-9}$ mol cm^{-2}, which is less than the necessary quantity to form a monolayer. This value is small, and we decided to apply another technique in order to confirm such a result.

Another evidence for the existence of absorbed electroactive species on the electrode surface was obtained by simultaneously using two electrochemical techniques in nonstationary diffusion regime: the linear potential scan voltammetry and the electrochemical quartz crystal microbalance.[45,46] By coupling these two techniques it was possible to obtain, simultaneously, both the electrical response (voltammogram) and the corresponding deposit growth as a function of time. The potential scan rates were varied from 2 to 50 mV s^{-1}, and Fig. 13 shows the result for 2 mV s^{-1}.

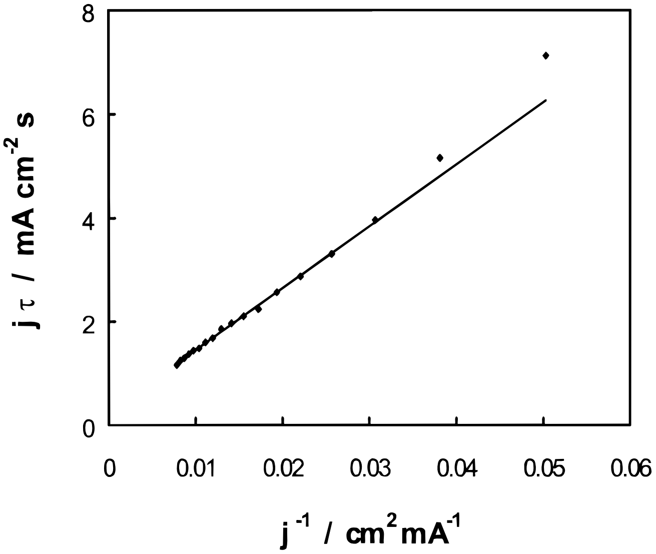

Figure 12. Plot of $j\tau$ *vs.* j^{-1} for cadmium reduction.

Curve 1 in Fig. 13 shows a fast current increasing at the beginning of the potential scan but, in spite of the high current density, the deposit thickness (δ) is not modified (zone A, curve 2). This behavior is due to the electrochemical reduction of the adsorbed species,[47] already quantified by the quartz crystal microbalance sensor. The B region in curve 2 corresponds to reduction of the electroactive species existing in the electrode vicinity, and, once the process is limited by diffusion, a peak appears in curve 1. The C region in curve 2 corresponds to the diffusion-limiting step, which implies a slightly lower deposition rate. For potential scan rates up to 30 mV s^{-1}, it is still possible to observe the three zones in the thickness-time curve but at higher potential scan rates the A region is shortened and the B and C regions are superimposed.

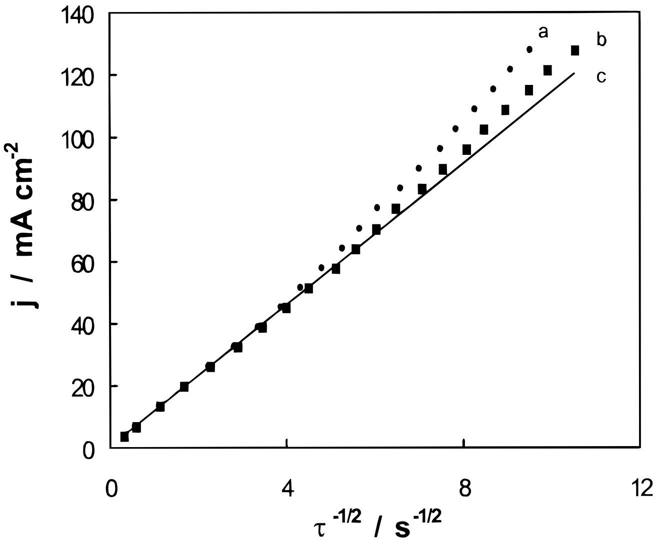

Figure 11. Sand plot for cadmium reduction: a, experimental transition times; b, nucleation-corrected transition times; c, Sand equation.

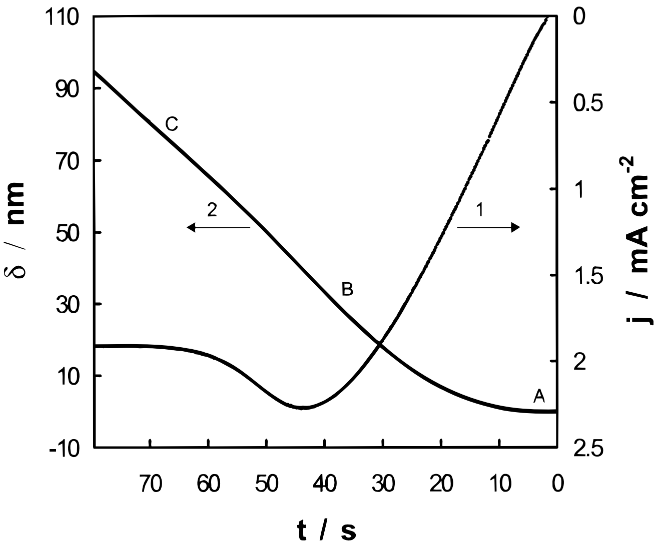

Figure 13. Linear sweep voltammetry for cadmium reduction at 2 mV s^{-1} (curve 1) and the corresponding growth of the deposit thickness, δ (curve 2).

The necessary time to observe a variation in the deposit thickness in Fig. 13 (curve 2) is approximately 5 s. For this time interval, integration under curve 1 (same figure) gives the charge associated to the adsorbed species reduction (0.37 mC cm^{-2}), and with this value it was possible to obtain the amount of adsorbed species, $\Gamma_o = 1.92 \times 10^{-9}$ mol cm^{-2} (coverage degree $\theta = 0.87$). This value is close to that obtained in chronopotentiometry and also corresponds to an amount of adsorbed species less than that necessary to form a monolayer, which confirms our previous result. As a reference, the quantity of adsorbed Cd^{+2} has been reported as 10^{-12} mol cm^{-2} in a perchlorate medium with this value being almost independent of the Cd^{+2} concentration.[16]

The existence of adsorbed electroactive species on the working electrode gives rise to an apparent higher concentration of Cd^{+2} in the vicinity of the electrode surface. This fact might be an explanation for the relatively high *D* values obtained from electrochemical techniques in nonstationary diffusion regime. Consequently, our *D* values are called here "apparent" and only when Cd^{+2} reduction takes place on electrodes of different nature and the process is simpler (without adsorption) is it possible to evaluate *D* in the order of 10^{-6} cm s^{-1}, as reported in some papers.[25,27]

In this work the presence of small quantities of adsorbed electroactive species on the electrode surface has been shown by using different electrochemical techniques. None of these techniques support the presence of a monovalent intermediate as was proposed in some papers. Therefore the Cd^{+2} seems to be the only adsorbed electroactive species, then leading to a reduction mechanism of the way

$$Cd^{+2} \rightarrow Cd^{+2}_{ads}$$

$$Cd^{+2}_{ads} + 2e^- \rightarrow Cd$$

This reaction sequence is taking place principally at temperatures below 35°C but the reduction process is complicated by a nucleation step, and at high temperatures cadmium reduction is kinetically more favorable.

Conclusions

The cadmium electrochemical reduction in sulfate medium was studied by means of different electrochemical techniques in both stationary and nonstationary diffusion regimes on solid cadmium electrodes generated *in situ*. Our experiments led to the following kinetic parameters: $\alpha = 0.65$, $j_o = 3.41$ mA cm^{-2}, and $k_o = 8.98 \times 10^{-5}$ cm s^{-1}, so demonstrating that the electrochemical process is quasi-reversible at 25°C. The diffusion coefficient of the electroactive species was almost the same for all the applied techniques, being the value from RDE closer to the literature's value. The diffusional step of the reduction process is characterized by an apparent activation energy of 11.86 kJ mol^{-1}, and temperature increase favors the deposition rate. The reduction process is preceded by an adsorption step of electroactive species, whose amount is less than the corresponding to form a monolayer on the working electrode surface. Besides, the deposition process is complicated by a nucleation step detected by impulsional techniques. The mechanism seems to be a two-step mechanism involving Cd^{+2} species in adsorbed state.

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