Analysis of Nonlinear Galvanostatic Oscillations in Ag-Cd Alloys Electrodeposition

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Cathodic potential oscillations with low and high amplitudes were registered after induction periods during electrodeposition of Ag-Cd alloys from an acid cyanide electrolyte, below the limiting diffusion current and at very high current. In the range between the limiting current and the highest ones, mixed-mode oscillations appear, composed by periodical high amplitudes interrupted by smaller ones, having more positive potentials. A similar behavior was observed at twice the lower concentration of Cd in the electrolyte. The cathodic oscillations during Ag-Cd deposition maintained the upper value of potential between -1.3 V and -1.4 V, which coincides with that of electrodeposition of pure Cd from an acid cyanide electrolyte. This fact permits to conclude that the potential oscillations of both processes have the same nature. The FFT analysis shows that the lower amplitude oscillations have larger frequencies than those with higher amplitudes. Space phase projections (attractors) of the time series of cathodic potential oscillations at different current densities were constructed. When the potential started to oscillate below the limiting current density, the attractor was a simple limit cycle, period-1. At the limiting diffusion current of the metal ions, when the periodic intensive hydrogen bubble evolution was observed, the atractor structure was not well discernible. The presence of many peaks with almost no separation between them in the corresponding FFT, signals possible chaotic behaviour. At higher current densities the attractor had period-3 and the electrochemical system returned to a simple limit cycle (period-1) at the highest current. XRD analysis made possible the correlation of the oscillations with the composition of the surface layer of deposits

1. INTRODUCTION

Evidence of nonlinear chemical behaviour is all around us, most notably in periodic phenomena in living organisms, such as the changes in leaf colours or rhythms as the heartbeat, and in

pattern formation in biological and certain geological systems. The first systematic observations of periodic behaviour in an inorganic chemical system, the luminescence associated with the oxidation of white phosphorus, were made as early as the 17th century, and there are scattered notes in the literature for the next 250 years [1].

The first report on an oscillating electrochemical reaction appeared in print in 1828, where A. Th. Fechner described an electrochemical cell which produced an oscillating current during the anodic polarization of iron in nitric acid [2]. Since then, numerous other examples of electrochemical oscillators during anodic dissolution or cathodic deposition of metals have been investigated, and they display not only current or potential oscillations, but also pattern formation. They can exhibit interesting steady-state and dynamic behaviour, such as simple and complex periodic oscillations, quasiperiodicity, and chaos [1-17].

Oscillatory phenomena in nonlinear chemical and electrochemical reactions are often accompanied by a type of complex temporal behaviour known as mixed-mode oscillations which consist of a mixture of two distinctly different kinds of oscillations, usually small, fairly harmonic oscillations, and large amplitude relaxation spikes, with the intermediate amplitudes left unrealized [18]. Such behaviour has been observed in many different fields of chemical kinetics, such as homogeneous liquid-phase Belousov-Zhabotinskii (BZ) reaction. Experimental results obtained with the BZ reaction in a continuous stirred reactor have been analyzed in order to distinguish between periodic and chaotic behaviour [19, 20]. A review paper presents briefly the main concepts of nonlinear dynamics and their exemplary manifestations in selected systems, including those important from the point of view of materials science [21].

The dynamical behaviour during electrochemical experiments often depends not only on the surface concentration of electrochemically active species but also on the potential drop across the double-layer. When the electrode potential plays an essential role in the origin of current oscillations, the electrochemical system exhibits negative differential resistance (NDR) in a certain region of the overpotential; this NDR can sometimes be hidden (HN-NDR) by a slow charge transfer reaction [22]. Because of this general underlying mechanism, the parameter dependence of non-linear behaviour is similar for the NDR class of electrochemical systems; this notion serves as a basis for classification of electrochemical oscillations based on dependence of oscillations on external resistance [23] and double-layer capacitance [24].

During cadmium electrodeposition form cyanide electrolytes intensive cathodic potential changes with amplitude of more than 400-500 mV were observed by Vishomirskis [25]. The author suggested that the reason is the formation/destruction of some passive film formed on the surface of the electrode. During the electrodeposition of some metals from cyanide electrolytes the passivation is a result of the formation of a compound with general formula $Me_x(CN)_y(OH)_z$ on the cathode. The author stated that the hydrogen evolution does not play the main role in originating the cathodic potential oscillations in time.

Otherwise, cathodic potential oscillations were reported under galvanostatic conditions, observed during the electrodeposition of cadmium from alkaline cyanide solutions, when the electrolysis was carried out at current densities above the limiting one [26]. The authors suggested that the potential oscillations occur in the diffusion layer of cadmium ion (order of 1 μm) which is formed at

the vicinity of the cathode surface, and they concluded that the electrochemical system exhibits bistability.

Similar cathodic potential oscillations have been observed also in the course of electrocrystallization of tin in the presence of adsorbable species [27, 28], and the oscillations occur in the adsorption layer (order 0.1 nm) of the species.

It is suggested that the following conditions may be necessary in order for the emergence of potential oscillations related to hydrogen bubbles [29]: a) that the electrolyses be carried out at current densities above the limiting current, and b) that the potential difference between the deposition potential of the metal ion and that of hydrogen evolution on the metal be sufficiently large.

Using linear stability analysis, a simple model has been elaborated which extracts the basic dynamical properties of convection coupled with electrochemical process of Hg ions at the mercury electrode [30]. The authors derived the stability criteria and constructed the bifurcation diagram, showing bistability, in accordance with the experimental data. An atypical example of the effect of the self-induced convection on the morphology of current-potential responses was described, for the case of the parallel electroreduction of some metals cations (Cd^{2+}, Cu^{2+}, Zn^{2+} and Eu^{3+}) and H^+ ions at the Hg electrode [31].

In our previous work galvanostatic oscillations were registered during cadmium electrodeposition from cyanide electrolyte and for the first time potentiostatic oscillations were also observed [32]. Experiments on stationary and rotating electrodes showed the possibility of formation of passive layers of $Cd(OH)_2$ on the electrode surface, which, besides the simultaneous hydrogen evolution under limiting current density conditions, could be and additional promoter of the oscillatory behaviour of the electrochemical system. Potential oscillations were observed also during the electrodeposition of Ag-Cd alloys at high current densities. They appeared when the cadmium content in the deposit was more than 45 wt.% and probably the oscillations had the same origin as those observed during the cadmium electrodeposition process. Their periods and frequencies depend on the current density of the electrodeposition process, as do the deposited Cd fraction and total amount. Formation of periodical patterns was registered on the deposited surface and XDR analysis revealed that they consist of different phases of the Ag-Cd alloy.

This new study gives a detailed investigation of the cathodic potential oscillations observed during the electrodeposition of silver-cadmium alloys at different current densities. The data were processed with the Fast Fourier Transform (FFT) to determine the frequencies of the oscillations and their behavior as a function of the current density. The values of potentials, registered in the chronopotentiometric curves, were used for the reconstruction of their attractors (space phase projections). XRD analysis was carried out to correlate the cathodic oscillations with the composition of the surface layer of deposits.

2. EXPERIMENTAL

The cadmium, silver and silver-cadmium alloys were deposited from cyanides electrolytes. Pure cadmium was deposited from a solution containing 0.14 M Cd as $CdSO_4 \cdot 8/3\ H_2O$ + 0.035 M

KCN, pure silver from a solution containing 0.035 M Ag as $KAg(CN)_2$ + 0.035 M KCN and Ag-Cd alloys from a solution containing 0.035 M Ag as $KAg(CN)_2$ + 0.14 M Cd as $CdSO_4$ · 8/3 H_2O + 0.035 M KCN. The electrolytes were prepared using chemicals of *pro analysis* purity and distilled water. The electrochemical experiments were performed in a 100 cm^3 three-electrode glass cell at room temperature. A reference electrode of calomel ($E_{Hg/Hg2Cl2}$ = 0.2444 V vs SHE) and two platinum counter electrodes (about 4 cm^2 each) were used. Alloy coatings were deposited onto vertical copper cathodes with an area of 2 x 1 cm^2 in the cell for electrochemical experiments. The preliminary preparation of the copper cathodes includes a standard procedure of electrochemical degreasing, followed by pickling in a 20% solution of sulphuric acid. The chronopotentiometric curves were recorded at a sample period of 0.001 s and because of this fact the time of register was limited to 260 s. The experiments were carried out by means of a computerized potentiostat/galvanostat Series G 750 (Gamry Instruments Inc.) using the software PHE 200. XRD analysis (Siemens-5000) was performed to identify the crystalline phases of the Ag-Cd alloys.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry curves

Figure 1 compares the cyclic voltammetry curves of Ag, Cd and Ag-Cd electrodeposition obtained in cyanide electrolytes. Silver deposition (dashed curve) starts at -0.95 V (*vs* SCE) and the limiting current density is reached at a potential of -1.02 V (The dissolution of silver is shown by the anodic peak with a maxima at -0.30 V). Cadmium deposition (black curve) occurs at a relatively more positive potential (-0.93 V) and the limiting current density is reached at -1.05 V. Cadmium current oscillations were observed at potentials higher than -1.5 V, accompanied with an intensive hydrogen bubble evolution. Those oscillations during cadmium deposition in cyanide solutions have been previously reported [25-28, 32, 33].
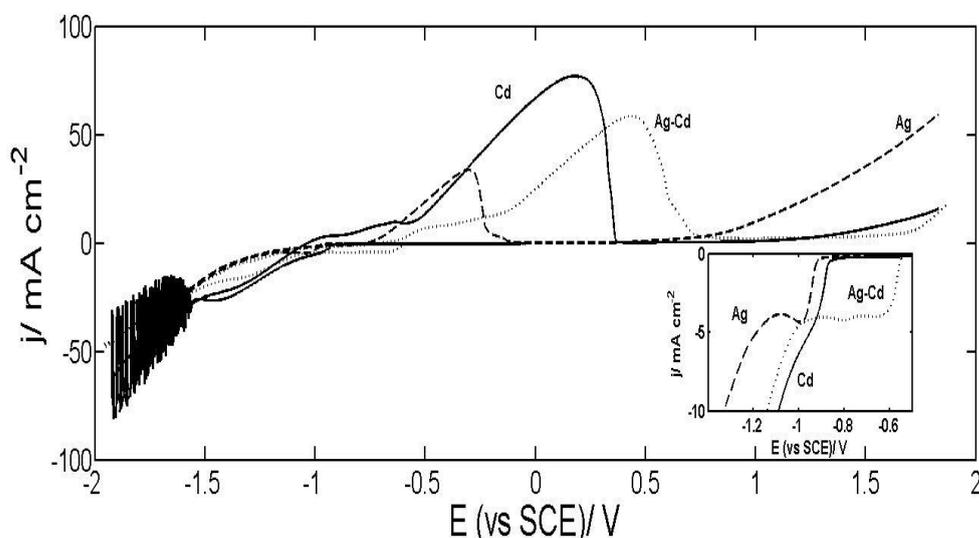
Figure 1. Cyclic voltammetry curves of Ag, Cd and the alloys electrodeposition (scan rate 25 mV s^{-1}).

Figure 1 (dotted curve) shows the cyclic voltammetry curve of Ag-Cd alloy, whose deposition is considered of a regular type, because the more noble metal (Ag) deposits preferentially and the process is under diffusion-controlled [34]. XRD-spectra analysis revealed that silver initiated its deposition as a part of the alloy at -0.59 V, which is about 0.36 V a more positive potential than that of pure Ag (Fig. 1, dashed curve). At -0.62 V a shoulder appeared indicating diffusion-controlled deposition of Ag. The codeposition of Ag-Cd alloy started at potentials more negative than -1.0 V and a shoulder of limiting current density (15 mA cm^{-2}, maximum rate of codeposition) was reached at -1.31 V. At more negative potentials than -1.5 V an intensive hydrogen evolution (bubbles) was observed, however current oscillations were not registered. The electrode processes that occur during the deposition of Ag-Cd alloys from cyanide complexes have been recently discussed using anodic linear sweep voltammetry [35]. It has been shown that from the solution containing both metal ions, Ag starts to deposit at more positive potential, as a result of the reduction of the dominant complex $[Ag(CN)_3]^{2-}$, which equilibrium potential is -0.737 V. In the presence of Cd ions most of the CN^- anions are consumed in several Cd-CN complexes ($[Cd(CN)]^+$, $[Cd(CN)_2]$, $[Cd(CN)_3]^-$ and $[Cd(CN)_4]^{2-}$), and the dominant Ag-CN complex becomes $[Ag(CN)_2]^-$, with the equilibrium potential of -0.479 V. Due to those facts, is it obvious the appearance of the first shoulder in Figure 1 (solid curve, presenting Ag-Cd alloy deposition), corresponds to the deposition of pure Ag from $[Ag(CN)_2]^-$ complex, which is the dominant cyanide complex in the Ag-Cd-CN electrolytes.

It should be considered that the CV curve for Ag deposition (dashed curved) shows a small NDR region between -1.0 and -1.1 V. The CV curve for Ag-Cd alloy does not show this behavior. The hidden NDR region (HN-NDR) could be a result of the superposition of the Cd deposition. Such systems are known to produce oscillations under galvanostatic conditions; therefore, there is no upper limit for resistance at which oscillations can develop [36].

3.2. Chronopotentiometric curves of Ag-Cd electrodeposition and their Fast Fourier Transform characterization

It should be noted that current oscillations during potentiostatic electrodeposition of the Ag-Cd alloys were not observed. The registered cathodic potential oscillations observed during electrodeposition of Ag-Cd alloys at different current densities were processed with the Fast Fourier Transform (FFT) to determine the frequencies of the oscillations and their behavior as a function of the current density.

Chronopotentiometric curves of the cathodic potential oscillations during Ag-Cd electrodeposition at different current densities (from 12.5 to 25.0 mA cm^{-2}) are shown in Figure 2, values which are below and above the limiting diffusion current (15 mA cm^{-2}). At current densities lower than 12.5 mA cm^{-2} potential oscillations were not registered. The data indicate (Fig.2) the appearance of different induction periods of several seconds in the mentioned interval of current densities, before the start of the oscillatory phase, when the potential falls to more negative values. The increase of current density causes a reduction in the induction and oscillatory periods. These facts are a consequence of the higher rate of silver and cadmium metal ions reduction (consumption) and their

rapid depletion at the electrode surface. It should be noted that Ag-Cd electrodeposition is always accompanied by hydrogen evolution.

At 12.5 mA cm^{-2} (Fig. 2 a) periodic potential oscillations appear for a period of more than two hours. Increasing the current density up to 17.5 mA cm^{-2} (Figs. 2 b, c), the dynamic behavior of the process changes, showing mixed potential oscillations, characterized by cycles of abrupt shifts of the potential to more negative values (when hydrogen bubbles detach from the surface), and their immediate return to less negative (noble) values when the smaller amplitude oscillations start. At the highest current densities (Fig. 2 e), the potential oscillations become similar to those observed at the lowest current density (Fig. 2 a) and it was possible to observe very intensive hydrogen evolution.
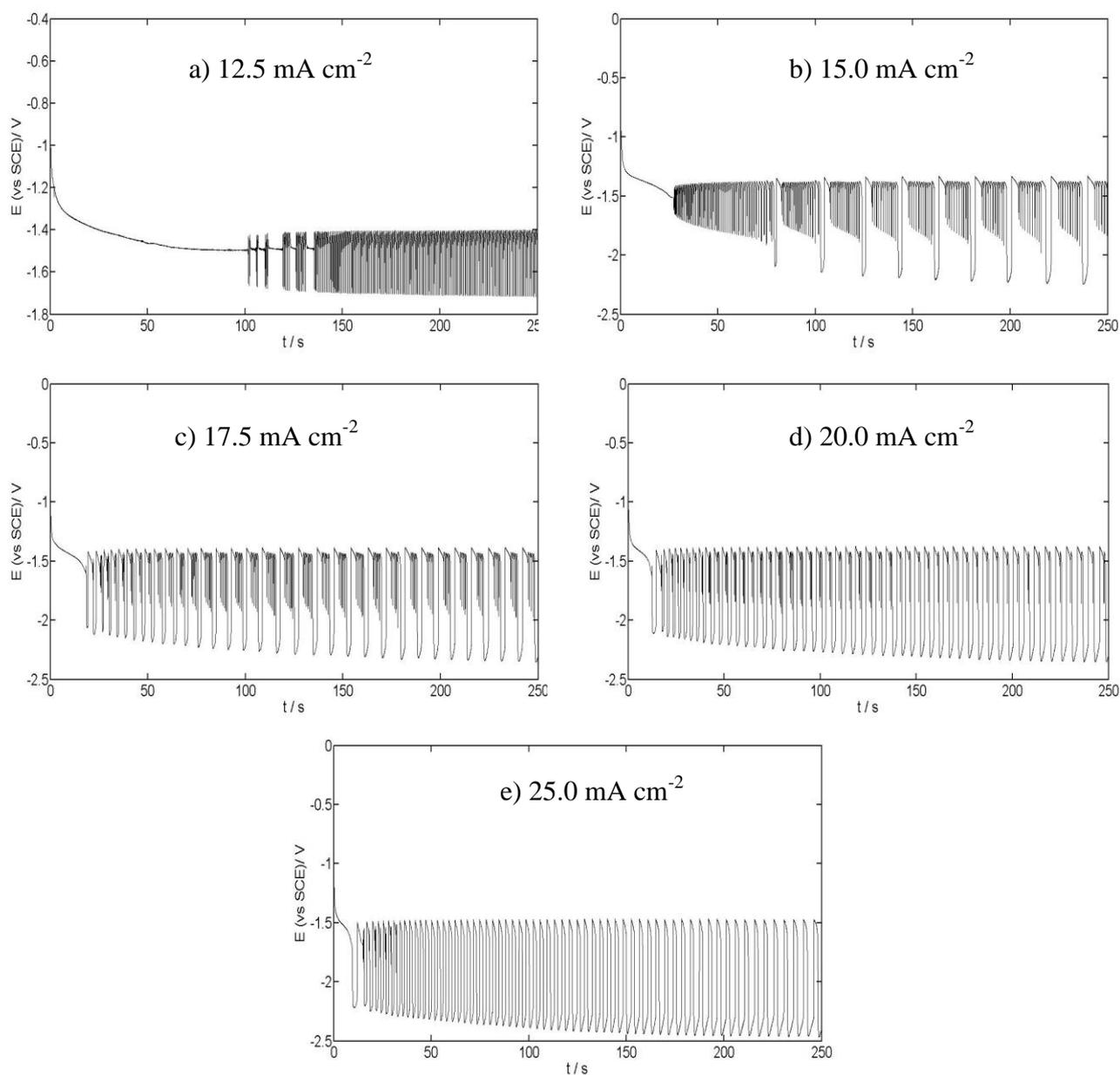
Figure 2. Cathodic potential oscillations registered during Ag-Cd electrodeposition from cyanide electrolytes at different current densities.
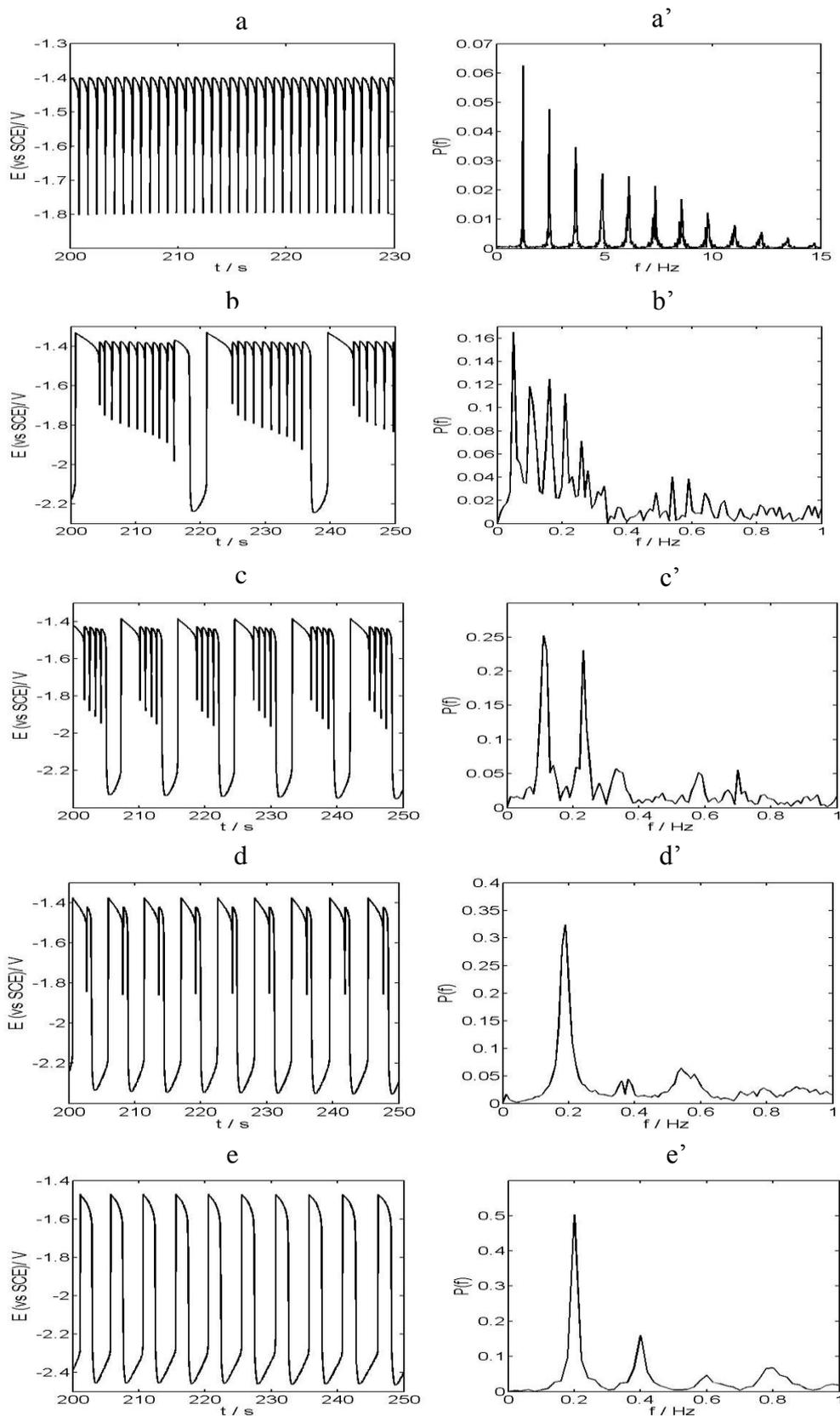
Figure 3. Dynamic behavior of the potential oscillations during the eletrodeposition of Ag-Cd from cyanide electrolyte (a-e) and their Fast Fourier Transform spectra (a'-e'): (a-a') 12.5 mA cm^{-2}; (b-b') 15.0 mA cm^{-2}; (c-c') 17.5 mA cm^{-2}; (d-d') 20.0 mA cm^{-2}; (e-e') 25.0 mA cm^{-2}.

Extensions of the chronopotentiometric curves of electrodeposition of Ag-Cd alloys at different current densities, previously presented (Fig. 2), are shown in Figure 3 (a-e) and their Fast Fourier Transforms (FFT) in Figure 3 (a'-e'). FFT is known to be a useful tool for determining the fundamental frequencies and behavior of signals. It can be seen that at the lowest current density (12.5 mA cm^{-2}, Fig. 3 a), the FFT graph (Fig. 3 a') shows a fundamental frequency f_1 of 1.26 Hz, confirming the periodicity of the phenomena. The lower magnitude peaks (f = 2f_1, 3f_1, 4f_1…) correspond to the harmonic components of the Fourier series. The presence of harmonics is because of the non-sinusoidal nature of the signal. Our major interest was the potential oscillatory component; therefore, the base line of each signal was subtracted to remove the constant component whose transform generates a zero Hz frequency peak.

At higher current density (Fig. 3 b), potential oscillations appear periodically with higher amplitude and they are interrupted by smaller ones, located in a range of more positive potentials. The FFT (Fig. 3 b') revealed that the last ones possess a bigger frequency (0.71 Hz) than the oscillations with higher amplitude (0.05 Hz). Later, the increase of the cathodic current (Figs. 3 c, d) diminishes the residence time of the smaller amplitude oscillations and reduces gradually their number until only one remains (Fig. 3 d). At the highest current (25 mA cm^{-2}) the potential oscillations were represented only by high amplitude components, showing a frequency of 0.2 Hz (Fig. 3 e') and massive hydrogen evolution was observed. Generally, there is a tendency for the lower amplitude oscillations to have higher frequencies. A resume of the frequency values of potential oscillations, having higher and lower amplitudes, corresponding to different current densities, is presented in Table 1.

Table 1. Frequencies (*f*) of the potential oscillations during Ag-Cd electrodeposition at different current densities.

Current density j / mA cm^{-2}	Frequency of the potential oscillations, *f* / Hz	
	With the lowest amplitude	With the highest amplitude
12.5	1.26	-----
15.0	0.71	0.05
17.5	1.11	0.11
20.0	-----	0.18
25.0	-----	0.2

We would like to stress that even at different current densities, the cathodic oscillations presented in the Figure 2 a-e maintained the upper value of potential between -1.3 V and -1.4 V (vs SCE). According to our previously reported results [32], during the electrodeposition of pure Cd from a cyanide electrolyte the observed cathodic oscillations showed the same range of the upper value of potential. This coincidence permits us to conclude that the potential oscillations during Ag-Cd alloys deposition have the same nature as those observed during pure Cd deposition. In both electrochemical processes the metal ion reduction occurs with simultaneous hydrogen evolution. The detachment of H$_2$ bubbles from the electrode surface occurs when the cathodic potential shifts abruptly to more negative values, because of the depletion (almost zero concentration) of Cd ions in the inner interface electrode-

electrolyte, when the limiting diffusion rate of the supply of metal ions is reached. The surface concentration of the metal ions is restored as a consequence of the forced convective mass transport created by the hydrogen bubble detachment and the cathodic potential shifts abruptly to less negative (noble) values, at which the metal deposition restarts and the cycles repeat.

A recent report [37], based on a density functional theoretical study of photocatalytic hydrogen evolution reaction, revealed that a Ag-H stretching band was not observed even at very negative potentials, suggesting that hydrogen (molecules or atoms) was not adsorbed on the silver surface. The authors suggested that the proton discharge took place at the interface close to the electrode, separated by solvent water layers, instead of directly on silver surface. Those results support our conclusion that during the electrodeposition of Ag-Cd, the adsorption of hydrogen atoms and their recombination (evolution) can occur directly only on the alloy multiphase sites where cadmium is present.

At current densities higher than 25.0 mA cm^{-2}, the electrochemical system enters in other, stable state when the potential oscillations show tendency to disappear. This fact could be a consequence of the massive nucleation, growth and a violent evolution of hydrogen bubbles, producing a forced convection, which replenishes the electrode surface concentration of metal ions. The hydrogen evolution becomes the predominant reaction, which process cannot be repressed by those replenished metal ions and the system enters into the other stable state (without potential oscillations).

3.3. XRD analysis of phases in Ag-Cd alloys

As was reported above, the potential oscillations with low amplitudes appeared when Ag-Cd alloy was electrodeposited at a current density (12.5 mA cm^{-2}) below the limiting one for the alloy (15 mA cm^{-2}). XRD analysis (Fig. 4) revealed that in this range of currents the relative intensity of the peak of Ag diminishes gradually, while Cd appears as a part of two crystalline multiphases in the Ag-Cd alloy deposit: Ag_5Cd_8 and Cd_3Ag. This tendency is maintained even at currents higher than the limiting one.

The analysis of XRD spectra of samples of Ag-Cd deposits, obtained at higher current densities (17.5 and 20.0 mA cm^{-2}), Figs. 4 b and c, showed the presence of $Cd(OH)_2$ as an additional phase, besides of the predominant ones of Ag_5Cd_8 and Cd_3Ag. This fact probably is due to the increase of pH (excess of OH^- ions) in the inner electrode interface, as a consequence of the intensive evolution of H_2 bubbles. We suppose that the formation of $Cd(OH)_2$ (consumption of OH^- ions) helps also to establish the initial acid pH at the electrode interface, needed to proceed with the Ag-Cd electrodeposition, even when some active sites of the surface are inhabited by the formed $Cd(OH)_2$.

Reported results on the removal of Cd^{2+} from wastewater by Fe-sponge (electrode), revealed that during the Cd deposition (removal) the initial pH values of the electrolyte(2.03 and/or 1.55) increased, reaching in 30 min pH=9.8 [38]. As a consequence, $Fe(OH)_2$ was formed on the electrode.
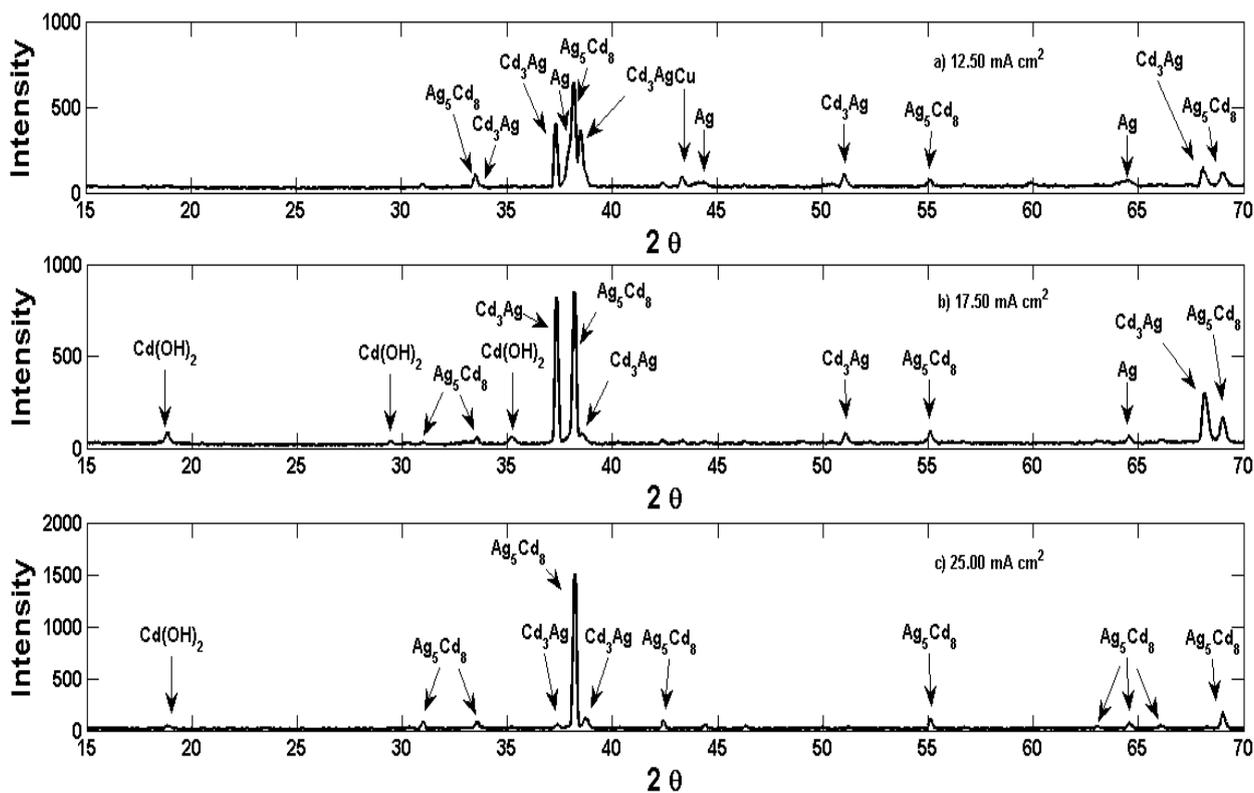
Figure 4. XRD patterns of crystalline phases formed in Ag-Cd alloys electrodeposited at different current densities: a) 12.50 mA cm^{-2}; b) 17.50 mA cm^{-2}; c) 25.00 mA cm^{-2}.

3.4. Space phase projection of the time series at different current densities

Figure 5 shows the graphs of the two-dimensional space phase projections (attractors) of the time series of the cathodic potential oscillations at different current densities (Fig. 2), during the electrodeposition of Ag-Cd alloys.

At 12.5 mA cm^{-2} (Fig. 5 a), when the potential started to oscillate, the attractor is a simple limit cycle, period-1, while the structure of the second one (Fig. 5 b), which corresponds to a current density of 15.0 mA cm^{-2}, shows a wide band, which is usually assumed to be a signature of chaotic behaviour. At this stage of electrodeposition of Ag-Cd, it was observed that the hydrogen bubbles detached periodically from the electrode surface (with the same period of the larger amplitude oscillations), producing forced convective mass transport of the metal ions, when the potential shifted abruptly to more negative values. At higher current densities (Fig. 2 c, d) the structure of the attractor is period-3 (Fig. 5 c, d). The electrochemical system returns to a simple limit cycle (period-1) at the highest current density (25 mA cm^{-2}). In this stage the potential oscillations were represented only by their high amplitude components (Fig. 2 e), showing a frequency of 0.2 Hz, displaying massive hydrogen evolution.
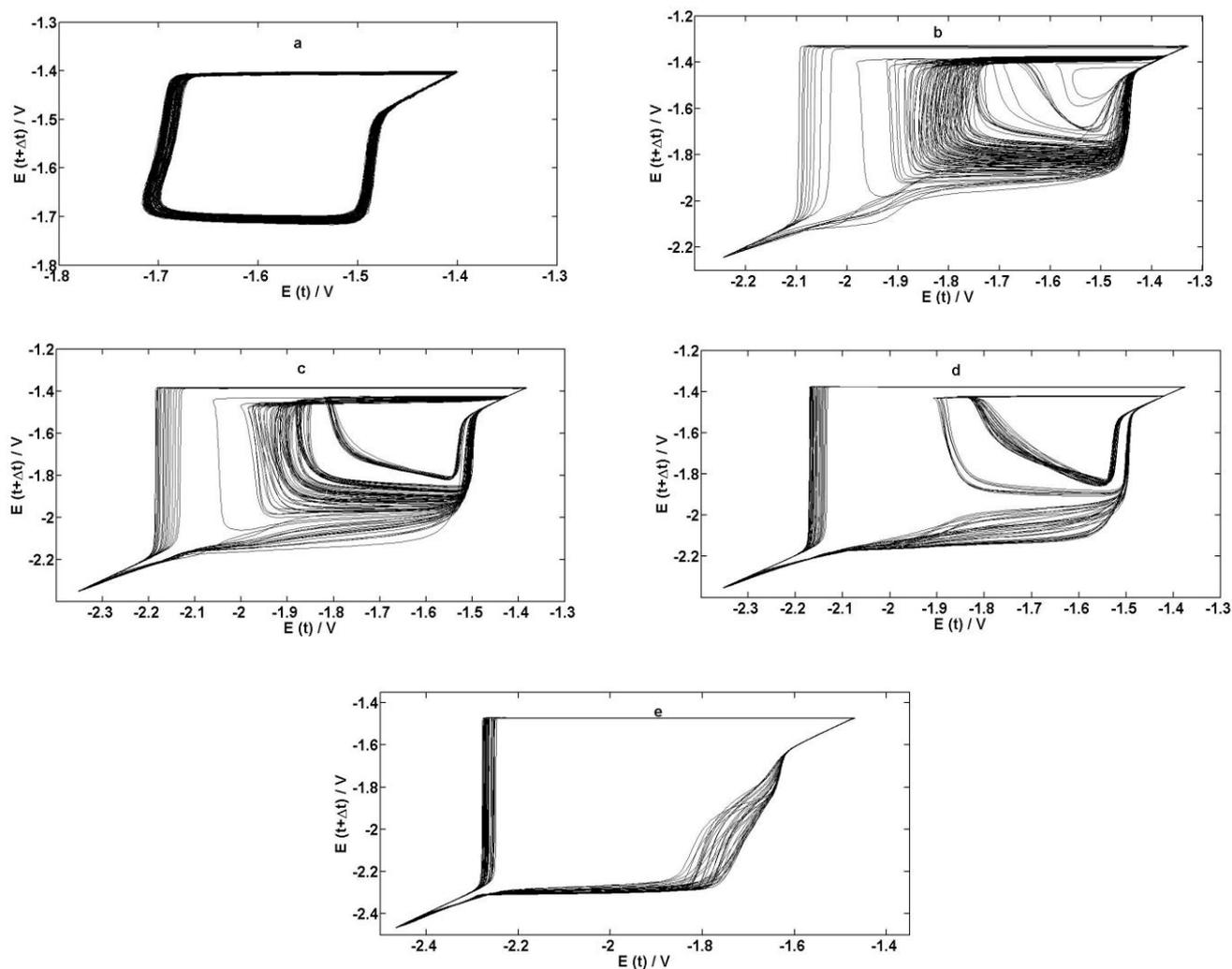
Figure 5. Two-dimensional phase space projections (attractors) of the time series of Ag-Cd electrodeposition at different current densities from Figure 2 ($\Delta t=0.03$ s).

3.5. Effect of the cadmium ion concentration on the cathodic potential oscillations during Ag-Cd electrodeposition

The process of electrodepositon of Ag-Cd was carried out using the same cyanide electrolyte, but with half the concentration of Cd ions (0.07 M Cd as $CdSO_4 \cdot 8/3$ H_2O). Figure 6 presents the time series of cathodic potentials registered at different current densities. Because of the lower cadmium content in the electrolyte, the potential oscillations started at the current density of 7.5 mA cm^{-2} (Fig. 6 a), lower than in the previous case (Fig. 2 a), when they initiated at 12.5 mA cm^{-2}. However, in both cases the amplitudes have similar values ($\Delta E \approx 0.4$ V).

Increasing the current density to 9.25 mA cm^{-2} (Fig. 6 b), it can be observed that mixed potential oscillations appeared, characterized by cycles of abrupt shifts of the potential to more negative values (when hydrogen bubbles detach from the surface), and its immediately return to less negative (noble) values, when the smaller amplitude ($\Delta E \approx 0.4$ V) oscillations start. A similar behaviour was observed for the higher concentration of Cd ions (Figs. 2 b-d). However, it should be

noted that the number of the low-amplitude oscillations was limited to two when the electrodeposition of Ag-Cd was carried out at half the concentration of Cd ions in the electrolyte. This fact could be attributed to the faster depletion of Cd ions at the interface electrode-electrolyte, inducing more frequent abrupt shifts of the cathodic potential to negative values, which then facilitate the reduction of H^+ ions and hydrogen bubble evolution.
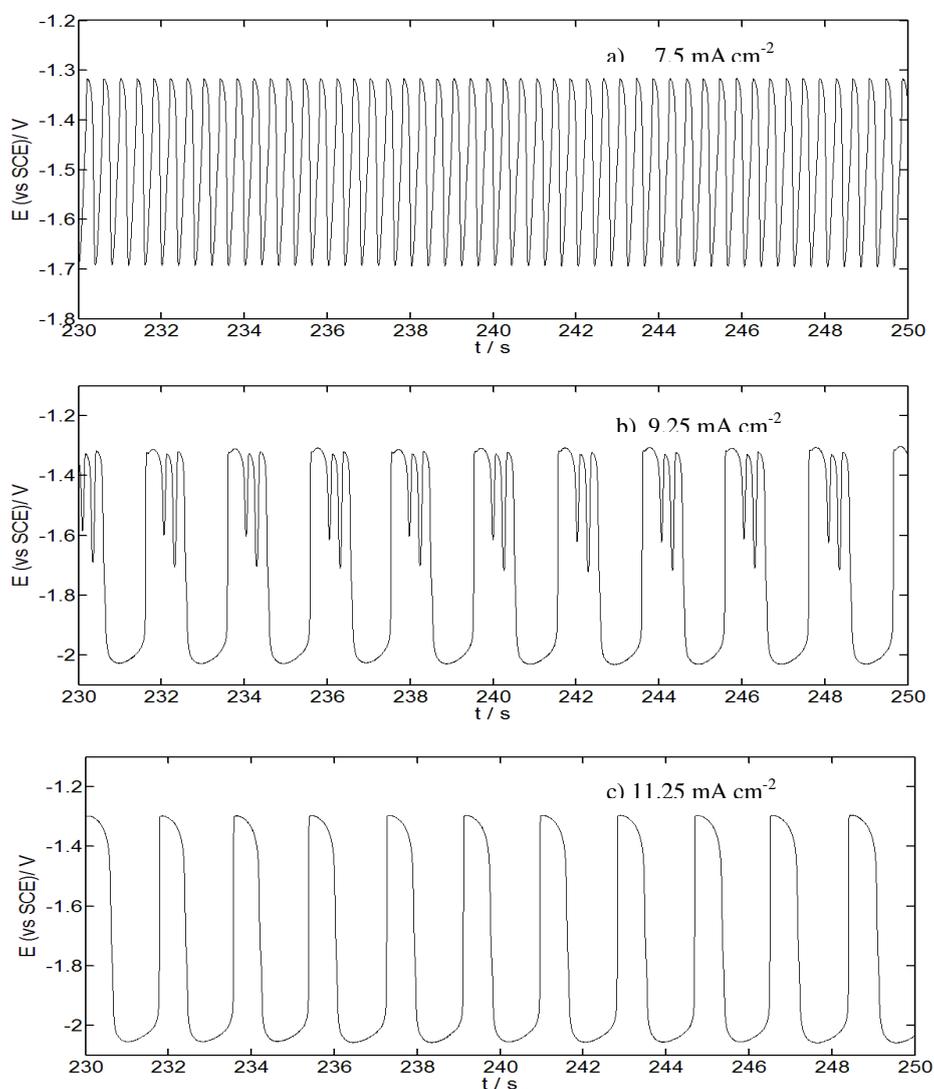
Figure 6. Cathodic potential oscillations registered during Ag-Cd electrodeposition form cyanide electrolytes at different current densities in the present of half the Cd ion concentration.

At the highest current density (11.25 mA cm^{-2}, Fig. 6 c) the potential oscillations presented only high amplitude components, and massive hydrogen evolution was observed. This behaviour is similar to that registered in Fig. 2 e, at the highest current. Besides, it should be noted that the high amplitudes of the cathodic potential oscillations are $\approx$ 0.95 V (Figs. 2 b-e), when the Cd ion concentration is twice that of the lower Cd content electrodeposition experiment, whose amplitudes are $\approx$ 0.75 V.

Table 2 compares different types of cathodic potential oscillations and the current densities when they start, as a function of Cd content in the electrolyte for Ag-Cd electrodeposition. An interesting fact is that the ratio between the current densities, corresponding to each type of oscillation is $\approx$ 1.7 (Table 2). For example, for the mixed potential oscillations the ratio of 15.00 mA cm^{-2} : 8.75 mA cm^{-2} = 1.71.

Table 2. Current density of Ag-Cd electrodeposition, when the different types of potential oscillations start, as a function of the Cd content in the electrolyte.

Type of potential oscillation	Current density (mA cm^{-2})	
	0.14 M Cd as CdSO$_4$. 8/3 H$_2$O	0.07 M Cd as CdSO$_4$. 8/3 H$_2$O
Only low amplitude oscillations	12.50	7.50
Mixed potential oscillations	15.00	8.75
Only high amplitude oscillations	25.00	15.00

4. CONCLUSIONS

1. Dynamic instabilities of the cathodic potential were observed during electrodeposition of Ag-Cd alloys from an acid cyanide electrolyte at different current densities. Potential oscillations with low amplitude were registered below the limiting diffusion current density and at higher currents the system oscillated in a mixed mode, with periodic high amplitude pulses, separated by trains of smaller ones, located in a range of more positive potentials. A similar behavior of the oscillations was observed at half the concentration of Cd in the electrolyte.

2. The cathodic oscillations during Ag-Cd deposition maintained the upper value of potential between -1.3 V and -1.4 V, which coincides with that of electrodeposition of pure Cd from an acid cyanide electrolyte. This fact allowed concluding that the potential oscillations of both processes have the same nature.

3. The oscillations were analyzed in terms of the FFT and it was identified that the lower amplitude oscillations have major frequencies than those with higher amplitudes.

4. XRD analysis made possible the correlation of the oscillations with the composition of the surface layer of deposits.

5. Space phase projections (attractors) of the time series of cathodic potential oscillations were constructed at different current densities, revealing periodic simple limit cycle characteristic below the limiting diffusion current density and a wide spread structure at the limiting current one, indicating possible chaotic behaviour. At the highest current densities the electrochemical system returned to a simple limit cycle.

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