Preparation and Characterization of Electrodeposited Cadmium and Lead thin Films from a Diluted Chloride Solution

Abbas Hamid Sulaymon¹, Sawsan A. M. Mohammed², and Ali Hussein Abbar^{3*}

¹Environmental Engineering Department, University of Baghdad, Iraq

²Chemical Engineering Department, University of Baghdad, Iraq

³Chemical Engineering Department, Al-Qadissya University, Iraq

ABSTRACT

Cd-Pb thin films were electrodeposited from a diluted chloride solution using stainless steel rotating disc electrode. The linear sweep voltammograms of the single metallic ions show that electrodeposition of these ions was mass transfer control due to the plateau observed for different rotations at concentration (50 and 200 ppm). The voltammograms of binary system elucidate that electrodeposition process always start at cathodic potential located between the potential of individual metals. Currents transients measurements, anodic linear sweep voltammetry (ALSV) and atomic force microscopy (AFM) were used to characterize the electrocrystallization process and morphology of thin films. ALSV profiles show a differentiation for the dissolution process of individual metals and binary system. Two peaks of dissolution Cd-Pb film were observed for the binary system with different metal ion concentration ratios. The model of Scharifker and Hills was used to analyze the current transients and it revealed that Cd-Pb electrocrystallization processes at low concentration is governed by three – dimensional progressive nucleation controlled by diffusion, while at higher concentration starts as a progressive nucleation then switch to instantaneous nucleation process. AFM images reveal that Cd-Pb film electrodeposited at low concentration is more roughness than Cd-Pb film electrodeposited at high concentrated solution.

Keywords: Electrodeposition, Anodic dissolution, Chronoamperometry, Cd-Pb thin film, Electrocrystallization.

Received July 19, 2014 : Revised August 4, 2014 : Accepted September 4, 2014

1. Introduction

Electrodeposition of metals is an attractive method for the recovery of metal ions from different industrial effluents such as plating, metal finishing and electronics [1,2]. Some of these toxic metals of particular concern in treatment of industrial wastewaters are cadmium, and lead. Cadmium has been classified by U.S. Environmental Protection Agency as a probable human carcinogen. Chronic exposure of cad-

mium results in kidney dysfunction and high levels of exposure will result in death. Lead can cause central nervous system, kidney and liver damage [3].

Various technologies such as precipitation, adsorption [4], biosorption [5], ion exchange [6], reverse osmosis [7], electrodialysis [8], ion exchange-assisted membrane separation [9-11] and electrochemical methods [12,13] have been employed to remove these metals from various effluents. However electrochemical methods have been receiving greater

*Corresponding author. Tel.: 009647806898052

E-mail address: aliabbar68@yahoo.com

Open Access DOI: <http://dx.doi.org/10.5229/JECST.2014.5.4.115>

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

attention in recent years due to the distinctive advantages of environmental compatibility, versatility and safety.

The literatures of the removal of cadmium or lead from aqueous electrolytes using electrochemical deposition method are extensive [14-19]. Cadmium and lead may be existed simultaneously at different concentrations in the effluents from different industrial activities. No information can be found about the basic aspect of the electrochemistry of co-deposition of these two heavy metals. The knowledge of the nucleation and subsequent growth of electrodeposits at the nanometer scale promotes understanding the process as accurately as possible to achieve desired properties and applications, therefore the characterization of the deposited films is essential for any electrochemical removal process to investigate the morphology and mechanism of formation of such deposits [20,21].

The characterization and mechanism of electrodeposition of single Pb or Cd had been investigated extensively for different electrolytes and cathode materials [21-26]. References may be found for the characterization of binary systems such as Cu-Pb [27,28], Cu-Cd [29-31], however no information are found about the characterization of Cd-Pb system. Most of the previous studies have been achieved for preparing alloys of Cd-Pb from flouborate solutions of special properties [32,33]. To the best of authors' knowledge, no previous work has been conducted to characterization the Pb-Cd films electrodeposited from diluted chloride medium using stainless steel as cathode material.

Based on the above consideration, the present work was carried out to prepare and characterize Pb-Cd thin films with different metal ion concentration ratios electrodeposited on stainless steel cathode from diluted chloride solution. Stainless steel is very effective as a cathode for metal removal from wastewaters, and is an inexpensive material compared to graphite felt or reticulated vitreous carbon [34-36].

The Cd-Pb films were electrodeposited and dissolved by a cathodic and anodic linear sweep of electrode potential in the solution containing ions of both metals and in the NaCl solution, respectively. Another procedure used here was based on potentiostatic transients of current where the dependence between current and experiment time for the formation and growth of Cd-Pb films at a constant negative

potential is recorded.

2. Experimental Work

The electrochemical experiments were carried out in a conventional three-electrode cell (Pyrex glass). A 0.0314 cm^2 stainless steel (316-AISI) rotating disc electrode (RDE) was used as a working electrode. Its surface was polished before each experiment with emery paper of grade 600 (3M). A platinum plate (0.35 cm^2) and a saturated calomel electrode were used as a counter and a reference electrode respectively. Electrochemical experiments were controlled with a potentiostat PGSTAT30 (Autolab), under a computerized control. Chemicals used were PbCl_2 , CdCl_2 , NaCl, and boric acid (reagent grade). The electrolytic solutions were freshly prepared with doubly distill water. The Cd-Pb ratios were 1:1, 1:4, 4:1 corresponding to concentration ratios as (50:50), (200:200), (50:200) and (200:50) ppm respectively. The supporting electrolyte was 0.5M NaCl and 0.1 M H_3BO_3 with final pH of 5 adjusted by using NaOH or HCl. It is important to point out that such solutions were prepared to resemble the concentration of metallic ions and pH of a typical composition of an effluent of plating industries [35]. All experiment were performed at $25 \pm 1^\circ\text{C}$. All cathodic linear sweep voltammetry experiments (LSV) were performed at 5 mV s^{-1} (scanning from positive to negative direction). The applied potentials for potentiostatic experiments were determined based on the results of voltammetric experiments. The ALSV experiments were performed in a cell of the same type. In this cell saturated calomel electrode (SCE) used as a reference electrode. The deposition on the RDE was washed with extra pure water and transferred into the cell for the ALSV analysis. ALSV analysis was performed in solution of 0.5M NaCl, 0.1 M H_3BO_3 , and pH = 5 with a sweep rate of 2 mV s^{-1} at 1200 rpm. In all cases after the dissolution no traces of the deposit left on the St.St surface were detected, indicating complete dissolution of the deposit. Before each experiment (in the case of deposition and ALSV), the electrolyte was purged with nitrogen (99.999%) for 30 min, while a nitrogen atmosphere was maintained over the solution during the experiment to prevent contact with oxygen. In the chronoamperometry experiments, series of potential step experiments at different increments were achieved in stationary

solution by stepping from an open circuit potential to the selected final potentials based on the result of linear sweep voltammograms. The AFM analysis was performed using SPM-AA3000 (Angstrom Advanced Inc., USA) in contact mode. AFM images were recorded over scan area ($2\ \mu\text{m} \times 2\ \mu\text{m}$). The XRD measurement was achieved by using XRD-6000 (Shimadzu co., Japan).

3. Results and Discussion

3.1 Voltammetric measurements

Fig. 1 (a,b,c,d). shows polarization curves corresponding to lead and cadmium electrodeposited on stainless steel rotating disc electrode for several rotation speeds (400, 800, 1200, 1600, and 2000 rpm) at concentration of 50 and 200 ppm respectively. The voltammograms show a limiting current zone in the potential range -725 to -900 mV vs. SCE for lead, and -900 to -1100 mV for cadmium. Under such conditions, the reaction rate is limited by the mass trans-

port rate and the limiting current at the smooth rotating disc in laminar flow can be predicted by the Levich equation [37]:

$$I_L = 0.62zFAD^{2/3}\omega^{1/2}\nu^{-1/6}c_b \quad (1)$$

Where I_L is the limiting current mA, A is the area of electrode cm^2 , z is the number of electron, F is Faraday constant, D is the diffusion coefficient $\text{cm}^2\ \text{s}^{-1}$, ω is the rotation rate $\text{rad}\ \text{s}^{-1}$, ν is the kinematic viscosity of the electrolyte $\text{cm}^2\ \text{s}^{-1}$ and c_b is the bulk concentration $\text{mol}\ \text{cm}^{-3}$.

To investigate whether the reduction of Cd and Pb occurred under mass transfer condition, the limiting currents were calculated from the polarization curves and plotted against $\omega^{1/2}$ Fig. 2. The limiting current was found at the middle point of a straight line that follows the plateau region and is limited by E_{max} and E_{min} [38]. These values are the points at which the straight line departs from I vs. E curve. The results indicate that the reduction of Cd and Pb is under mass transfer control.

Fig. 1. Linear voltammetric curves for reduction of lead and cadmium on stainless steel rotating disc electrode at different rotation speeds: a)Pb at 50 ppm,b)Pb at 200 ppm,c)Cd at 50 ppm,d)Cd at 200 ppm. Supporting electrolyte (0.5 M NaCl + 0.1 M H_3BO_3), pH = 5.

Fig. 3 (a,b,c,d). Shows polarization curves for electrodeposition of Cd-Pb binary and single systems from chloride solution at 1200 rpm. It can be seen that at low current densities (-0.3 mAcm^{-2}), the polar-

ization curve of Pb lies at considerably more positive potentials than Cd. Pb deposition begins earlier than Cd. This result indicates that Pb is the noble metal.

At higher current densities, a crossing of lead and

Fig. 2. Levich plots for the limiting currents taken at potentials of -790 mV vs. SCE for Pb (a) and -1025 mV for Cd (b) at two concentrations 50 and 200 ppm. Supporting electrolyte (0.5 M NaCl+0.1 M H_3BO_3), pH = 5.

Fig. 3. Linear voltammetric curves for reduction of cadmium-lead on stainless steel rotating disc electrode at (1200 rpm) in comparison with individual single metal curves: a) Cd, Pb at 50 ppm, b) Cd, Pb at 200 ppm, c) Cd at 200 ppm, Pb at 50 ppm, d) Cd at 50 ppm, Pb at 200 ppm, supporting electrolyte (0.5 M NaCl + 0.1 M H_3BO_3), pH = 5.

cadmium curves was observed for all concentration ratios except for Pb at concentration 200 ppm with Cd at concentration 50 ppm. This crossing may be ascribed to a large increase of hydrogen evolution on cadmium. It is cleared that the polarization curves of Cd-Pb system start at potential lies between the initial potentials of the individual metals. The codeposition enables the less noble metal (Cd) to deposit at more positive potentials and causes more noble metal (Pb) to deposit at more cathodic potentials than individual deposition case [39]. At more negative cathodic potential the polarization curve for Cd-Pb system is higher than the individual curves for all concentration ratios. All the polarization curves for Cd-Pb system exhibit two well defined regions with no plateau in all cases. The first region start at -550 mV vs. SCE referred to codeposition of Pb and Cd in which lead is controlled while the second region start at -850 mV vs. SCE in which the cadmium is the predominated. At

cathode potential more negative than -1100 mV vs. SCE hydrogen evaluation is increased more rapidly.

3.2. Anodic linear sweep voltammetry

ALSV has been developed as an appropriate in situ technique for electrochemical characterization of the phase composition of thin layers of electrodeposited alloys [40,41]. In the present work, this technique was adapted to characterize the Cd-Pb films electrodeposited under potentiostatic conditions. Therefore, the electrode potential was maintained at -1025 mV vs. SCE for 5 min to form the deposits of Cd-Pb and then anodic dissolution was carried out using a slow sweep rate (2 mV/s) in the positive direction. The deposition and dissolution steps were achieved at 1200 rpm. The ALSV curves of dissolution of single Pb, Cd, and Cd-Pb binary system are shown in Fig. 4 (a,b,c,d). The well separated two anodic peaks, coinciding with those obtained with corresponding single

Fig. 4. ALSV curves recorded at the sweep rate of 2 mVs^{-1} for dissolution of Pb, Cd and Cd-Pb binary system electrodeposited from electrolytes containing (a) Cd, Pb at 50 ppm, (b) Cd, Pb at 200 ppm, (c) Cd at 50 ppm, Pb at 200 ppm, (d) Cd at 200 ppm, Pb at 50 ppm, Supporting electrolyte (0.5 M NaCl + 0.1 M H_3BO_3), pH = 5, rotation = 1200 rpm, deposition time = 5 min.

metal deposits, clearly demonstrate the existence of two different phases. Fig. 5 shows the phase diagram of Cd-Pb alloy which is eutectic type with no miscibility between Pb and Cd in the solid phase [42]. Since the interaction between Pb and Cd in the solid phase is negligible therefore the free energy of each component should not be changed and the reversible potential of each component in the alloy should be similar to the reversible potential of pure components of the corresponding grain size leading to two separated peaks of dissolution of each component from the alloy. The peak of dissolution of Pb from binary system is shifted to the more negative potential than dissolution of single Pb while Cd is shifted to more positive potential than dissolution of single Cd. This shifting was not exceeded 50 mV in almost cases.

It was found that ALSV can be used as a method of phase composition determination of alloys superior to the X-ray method [27,36, and 43]. The ALSV

Fig. 5. The phase diagram of Cd-Pb binary alloy. "Reprinted with permission from ref.42".

Fig. 6. XRD patterns of electrodeposited Cd-Pb film prepared from electrolyte containing Cd-Pb (200:200) as concentration ratio in ppm. Supporting electrolyte (0.5 M NaCl + 0.1 M H₃BO₃), pH = 5, 1200 rpm.

enables quantitative analysis of the phase composition in that the amount of charge under a given peak, contrasted with the total charge under the ALSV, can render the content of the phase whose dissolution is reflected in the peak. Therefore the wt% of cadmium is approximately 1.5 times that of lead for the films electrodeposited from solutions containing either Cd-Pb(50:50) or Cd-Pb(200:200) since the charge under the peak of cadmium is higher than that for lead, consequently the wt% Pb is five times that of Cd for film deposited from solution with Cd-Pb(50:200). Fig. 6 shows the XRD analysis for film electrodeposited from solution containing Cd-Pb(200:200) which is coincided with ALSV results.

3.3. Chronoamperometric measurements

Chronoamperometry (CP) was used as an electrochemical technique suitable for electrochemical nucleation mechanisms studies [44]. There are several published methods that utilize the coordinates of chronoamperometric peaks to determine nucleation mechanisms and parameters related to nucleation [45], among which the model developed by Scharifker and Hills [46] is the most widely used. This model allows simple and rapid classification of experimental transients into the two limiting nucleation mechanisms-instantaneous or progressive. Instantaneous nucleation, Eqs. (2 and 3), corresponds to a slow growth of nuclei on a small number of active sites, all activated at the same time, while progressive nucleation, Eqs. (4 and 5), corresponds to fast growth of nuclei on many active sites, activated during the course of electroreduction [47]:

For instantaneous nucleation

$$i = \frac{zF\pi(2Dc)^{3/2}M^{1/2}N_o t^{1/2}}{\rho^{1/2}} \quad (2)$$

$$\frac{t^2}{i_m^2} = \frac{1.9542}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_m} \right)^2 \right] \right\}^2 \quad (3)$$

For progressive nucleation

$$i = \frac{2zF\pi(2Dc)^{3/2}M^{1/2}AN_o t^{3/2}}{3\rho^{1/2}} \quad (4)$$

$$\frac{t^2}{i_m^2} = \frac{1.2254}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-2.3347 \left(\frac{t}{t_m} \right)^2 \right] \right\}^2 \quad (5)$$

Where i is the current density (A cm^{-2}), A is the nucleation rate constant (s^{-1}), N_0 is the number density of nuclei (cm^{-2}), z , F , M , ρ , D , c and t are the number of electron, Faraday constant, the atomic weight, density of the depositing metal (g cm^{-3}), the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), the concentration of the electrodepositing species (mol cm^{-3}) and the time of nucleation (s) respectively. i_m and t_m are the current density and the time, as respective peak coordinates. The plots of experimental current transients $(i/i_m)^2$ versus (t/t_m) coordinates fall at either of these two limiting cases.

The first twenty seconds of current transients recorded at three potential steps for all single and binary system are presented in Figs. 7(a,c), 8(a,c), 9(a,c), and 10(a,c). Each of the chronoamperograms in these figures were characterized by the initial current increase as a response to the applied potential, formation of a peak characteristic for nucleation, and final convergence to the limiting current corresponding to linear diffusion to a planar electrode.

Initial current increase is due to the increase of sur-

face area whenever the nucleation is involved. As nucleation progresses, the nuclei will begin overlapping. Each nucleus will define its own diffusion zone through which metal has to diffuse, representing the mass-supplying mechanism for continuation of growth. Since the diffusion zones are much larger than the underlying nuclei, the overlapping zones would eventually include the entire electrode area. Further reaction is strictly controlled by the rate of mass transfer through the control area of the diffusion zone. Within the diffusion zone, growth of already-established metal nuclei can continue, or additional nucleation can be initiated on various sites, both governed by the steady state conditions [44].

The experimental current transients plotted in reduced current–time coordinates, along with the lines for instantaneous and progressive nucleation (solid and dashed lines, for Eqs. 3 and 5) are shown in Figs. 7(b,d), 8(b,d), 9(b,d), and 10(b,d). The reduced current transients of lead at concentration 50 ppm follow the instantaneous nucleation model for potential steps equal or higher than -790 mV Fig.

Fig. 7. Chronoamperometry of Pb electrodeposition on stainless steel electrode with the corresponding Scharifker-Hills' model: a,b) Pb at 50 ppm, c,d) Pb at 200 ppm, supporting electrolyte (0.5 M NaCl+0.1M H_3BO_3), pH=5.

7(b). At potential step -750 mV, a small deviation from instantaneous model has been observed due to the mixed control of diffusion and charge transfer in this region. For lead at concentration 200 ppm, the reduced current transients follow the progressive at ($t/t_m < 2$) then switched to the instantaneous nucleation models at higher values of ($t/t_m > 2$) for all three potential steps Fig. 7(d). However the general behavior is in agreement with previous work using chloride medium at higher concentration of lead [48].

The nucleation mechanism of cadmium at concentration 50 ppm is progressive for all three potential steps Fig. 8(b). At higher concentration (200 ppm), the situation is different, the reduced current transients follow the progressive at ($t/t_m < 3$) then switched to the instantaneous nucleation models at higher values of ($t/t_m > 3$) for all three potential steps Fig. 8(d). The mechanism of Cd electrodeposition has been studied on different metal substrates such as: Cd, Ni, Cu, Se, Pt, glassy carbon, and SnO_2 [49-51]. The cited studies reveal that the growth of Cd crystals has been catalogued as complex due to existence of

adsorption and nucleation processes. Gunawardena et al. [49] found that cadmium electrodeposition onto glassy carbon is progressive in perchlorate and sulfate media while no nucleation occurred in nitrate solution. Edgar et al. [25] studied the electrocrystallization of cadmium on anodically formed titanium oxide using diluted sulfate medium and found that the nucleation process is fitted to progressive model. Therefore it is cleared that the nucleation mechanism tend to instantaneous model as the concentration increased.

The reduced current transients of Cd-Pb electrodeposition for three potential steps at concentration ratio Cd-Pb (50:50) is shown in Fig. 9(b). It is cleared that the transients follow the progressive model. Accordingly it may be concluded that the mechanism of nucleation in the codeposition of lead with cadmium is controlled by cadmium which is progressive when cadmium is alone or mixed with lead.

For Cd-Pb system at higher concentration Cd-Pb (200:200), the reduced current transients follow the progressive at ($t/t_m < 2.5$) then switched to the instan-

Fig. 8. Chronoamperometry of Cd electrodeposition on stainless steel electrode with the corresponding Scharifker-Hills' model: a,b)Cd at 50ppm, c,d)Cd at 200 ppm, supporting electrolyte (0.5 M NaCl + 0.1 M H_3BO_3), pH = 5.

Fig. 9. Chronoamperometry of Cd-Pb electrodeposition on stainless steel electrode with the corresponding SCHARIFKER-Hills' model: a,b)Cd and Pb at 50 ppm, c,d)Cd and Pb at 200 ppm , supporting electrolyte(0.5 M NaCl + 0.1 M H_3BO_3), pH = 5.

taneous nucleation model at higher values of ($t/t_m > 2.5$) for all three potential steps Fig. 9(d). The most interesting behavior occurred in Cd-Pb system of concentration ratios (50:200) and (200:50) are shown in Fig. 10 (b, d). The reduced current transients exhibit progressive nucleation at ($t/t_m < 3$) switching to instantaneous nucleation after that is approximately similar to the nucleation mechanism of Cd-Pb system with higher concentration Cd-Pb(200:200). Hence the mechanism of nucleation in the codeposition of lead with cadmium is controlled by instantaneous nucleation when the concentration of either ions is increased.

4. Characterization of the deposits

Atomic force microscopy is an excellent tool to study morphology and texture of diverse surfaces. The versatility of this technique allows meticulous observations and evaluations of the textural and morphological characteristics of the films, showing better

facilities than other microscopic methods [52]. Table 1.shows the results of AFM measurements while Figs. 11 and 12 show the AFM images for the cathode substrate (St.St) before using, Pb films electrodeposited at electrode potential -790 mV vs. SCE at concentrations 50 and 200ppm, Cd films electrodeposited at electrode potential -1025 mV at concentrations 50 and 200ppm, and Cd-Pb films electrodeposited at electrode potential -1025 mV from different concentration ratios.

The most important parameters of AFM measurements are average roughness, root mean square roughness (Sq), surface skewness, and surface kurtosis [53]. The AFM analysis of cathode substrate shows that Sq is 0.0589 nm, i.e. the surface of St.St is smooth confirming the mechanical polishing is well. The Sq values are 1.9 and 1.52 nm for Pb electrodeposited at concentrations 50 and 200 ppm respectively and 1.65 and 1.18 nm for Cd electrodeposited at concentrations 50 and 200 ppm respectively. The results indicated that lead was rougher than cadmium

Fig. 10. Chronoamperometry of Cd-Pb electrodeposition on stainless steel electrode with the corresponding SCHARIFKER-Hills' model: a,b) Cd at 50 ppm, Pb at 200 ppm, c,d) Cd at 200 ppm, Pb at 50 ppm, supporting electrolyte (0.5 M NaCl + 0.1 M H_3BO_3), pH = 5.

Table 1. AFM measurements for cathode substrate, single, and binary films electrodeposited potentiostatically at -790 mV, -1025 mV vs. SCE from chloride solution respectively.

CSPM Imager surface roughness analysis	Roughness average [nm]	Root mean square [nm]	Surface skewness [nm]	Surface kurtosis [nm]	Peak-peak [nm]	Ten point height [nm]
St.St substrate	0.047	0.0589	-0.666	3.15	0.318	0.194
Pb (50)	1.9	2.32	-0.564	2.68	11.2	6.61
Cd(50)	1.65	2.06	-0.669	3.15	10.6	6.33
Pb (200)	1.52	1.87	-0.468	2.63	9.09	4.53
Cd(200)	1.18	1.44	-0.491	2.51	6.36	3.56
Cd-Pb(50:50)	2.88	3.53	-0.517	2.57	15.9	8.94
Cd-Pb(200:200)	1.97	2.4	-0.505	2.51	11.7	6.59
Cd-Pb(50:200)	2.73	3.39	-0.534	2.81	17.5	9.43
Cd-Pb(200:50)	2.49	3.04	-0.562	2.57	13.7	7.11

and the roughness was decreased as the concentration of either metals increased. For the binary systems, Sq values are 2.88, 1.97, 2.73 and 2.49 nm for Cd-Pb binary system with concentration ratios (50:50),

(200:200), (50:200), (200:50) respectively. It can be seen that increasing the concentration of either ions with fixing the other lead to decrease the roughness, also increasing the concentration of these ions

Fig. 11. AFM images of st.st substrate, Pb and Cd films electrodeposited potentiostatically at -790 mV, -1025 mV vs. SCE: a)St.St, b)Pb at 50 ppm, c)Pb at 200 ppm, d)Cd at 50 ppm, e)Cd at 200 ppm, supporting electrolyte (0.5 M NaCl + 0.1 M H_3BO_3), pH = 5.

Fig. 12. AFM images of Cd-Pb films electrodeposited potentiostatically at -1025 mV vs. SCE: a)Cd,Pb at 50 ppm, b)Cd,Pb at 200 ppm, c) Cd at 50 ppm ,Pb at 200 ppm, d)Cd at 200 ppm, Pb at 50 ppm, supporting electrolyte(0.5 M NaCl + 0.1 M H_3BO_3), pH = 5.

together lead to decrease the roughness. An important point to be mentioned is the influence of nucleation mechanism on the surface roughness of the deposits. It was observed that the roughness was much higher when the deposition process was denominated by progressive formation of nuclei. Therefore cadmium deposited at concentration 50ppm was rougher than cadmium obtained at concentration 200 ppm because the mechanism of nucle-

ation was progressive at low concentration, this observation had been confirm by Minford et al. [53]. The roughness of cadmium was less than lead in spite of the nucleation process is a progressive type. This may be interrupted as the growth of Cd crystals is controlled by adsorption in combination with nucleation process [50]. The results refer that all films have negative surface skewness which means that surface has more valleys than peaks. Surface kurtosis

sis for Cd film deposited at 50 ppm was higher than 3 while the others were lower than 3 indicating a flat surface (Platykurtic).

5. Conclusions

Cd-Pb films have been successively electrodeposited from diluted chloride solution using St.St cathode under different metal ion concentration ratios. The electrodeposition of the single metals is mass transfer controlled process when the ion concentration is 50 ppm or 200 ppm as revealed by RDE voltammetry. Linear sweep voltammetry curves of electrodeposition of binary metals show that electrodeposition start at cathodic potential lies between the potentials of the two single metal ions and a crossing could be occurred between the single curves depending on the concentration ratios of these metals. The ALSV curves elucidate two well-defined of dissolution peaks for lead and cadmium at different concentration ratio. Based on ALSV measurements, it is possible to anticipate the phases present in the binary metal films. The peaks of these phases are situated between the dissolution potentials of single metals, their height depends on the potential under which the cathodic co-deposition of the binary system is proceeded. The relative heights of these peaks represent the weight percent ratio of these metals in deposited film as revealed by XRD results.

The experimental results indicate that the nucleation process in the codeposition of two metal ions depends on the interaction between ions and which is controlled the nucleation process, therefore it may be similar or not to the nucleation process of individual ions. Also increasing ion concentration lead to shifting the nucleation from progressive to instantaneous model. The Chronoamperometry combined with AFM is a successful experimental approach for characterizing the films deposited electrochemically. Based on the results of CP and AFM, the progressive nucleation always leads to higher roughness of the surface than instantaneous nucleation process, also increasing the concentration will give smooth surfaces.

Acknowledgment

The authors express their gratitude to Engineering Consulting Bureau/ Al-Qadissya University for

financial support of this work under the contract no.28-2. Special thanks is extended to Dr. A. Kareem ALSamaraee for his scientific helpful guidance in AFM analysis.

References

- [1] D. Pletcher and F.C. Walsh, *Industrial Electrochemistry*, Chapman and Hall (1990).
- [2] R.D. Armstrong, M. Todd, J.W. Atkinson, and K. Scott, *J. Appl. Electrochem.*, **26**, 379 (1996).
- [3] R. Naseem and S.S. Tahir, *Water Res.*, **35**, 3982 (2001).
- [4] J.P. Chen and X. Wang, *Sep. Purif. Technol.*, **19**, 157 (2000).
- [5] A.H. Hawari and C.N. Mulligan, *Bioresour. Technol.*, **97**, 692 (2006).
- [6] S. Kocaoba and G. Akcin, *Desalination*, **180**, 151 (2005).
- [7] M. Mohsen-Nia, P. Montazeri and H. Modarress, *Desalination*, **217**, 276 (2007).
- [8] T. Mohammadi, A. Razmi, and M. Sadrzadeh, *Desalination*, **167**, 379 (2004).
- [9] A. Smara, R. Delimi, C. Poinsignon, and J. Sandeaux, *Sep. Purif. Technol.*, **44**, 271 (2005).
- [10] S.L. Vasilyuk, T.V. Maltseva, and V.N. Belyakov, *Desalination*, **162**, 249 (2004).
- [11] C. Ahmed Basha, S. Josephine Selvi, E. Ramasamy, and S. Chellammal, *Chem. Eng. J.*, **141**, 89 (2008).
- [12] J.C. Bazan and J.M. Bisang, *J. Appl. Electrochem.*, **34**, 501 (2004).
- [13] C. Ahmed Basha, K. Ramanathan, R. Rajkumar, M. Mahalakshmi, and P. Senthil Kumar, *Ind. Eng. Chem. Res.*, **47**, 2279 (2008).
- [14] C.A.R. Ragnini, R.A. Di Iglia, W. Bizzo, and R. Bertazzoli, *Water Res.*, **34**, 3269 (2000).
- [15] C.Y. Cheng, G.H. Kelsall and D. Pilone, *J. Appl. Electrochem.*, **35**, 1191 (2005).
- [16] A.H. Sulaymon, A.O. Sharif, T.K. Al-Shalchi and A.H. Abbar, *Journal of Chemical Science and Technology*, **2**, 175A (2013).
- [17] E. Elshierief, *Electrochim. Acta*, **48**, 2667 (2003).
- [18] L.H. S Gasparotto, N. Bocchi, R.C. Rocha-Filho and S.R. Biaggio, *J. Appl. Electrochem.*, **36**, 677 (2006).
- [19] L.A.M. Ruotolo and J.C. Gubulin, *Chem. Eng. J.*, **149**, 334 (2009).
- [20] E. Budevski, G. Staikov and W.J. Lorenz, *Electrochim. Acta.*, **45**, 2559 (2000).
- [21] A. Milchev and L. Heerman, *Electrochim. Acta.*, **48**, 2903 (2003).
- [22] M. Gu and Q. Zhong, *J. Appl. Electrochem.*, **41**, 765 (2011).
- [23] D. Grujicic and B. Pesic, *Electrochim. Acta*, **50**, 4426 (2005).
- [24] F. Nasirpour, *ionics*, **17**, 331 (2011).
- [25] J. Edgar. Carrera-Crespo, P. Acevedo-Pena, M. Miranda-

- Herandez, and I. Gonzalez, *J. Solid State Electrochem*, **17**, 445 (2013).
- [26] Q. Zhang and Y. Hua, *J. Appl. Electrochem*, **41**, 705 (2011).
- [27] V.D. Jovic, R.M. Zejnilovic, A.R. Despic, and J.S. Stevonic, *J. Appl. Electrochem.*, **18**, 511 (1988).
- [28] J.S. Stevonic, A.R. Despic, and V.D. Jovic, *Electrochim. Acta*, **42**, 873 (1997).
- [29] V.D. Jovic, A.R. Despic, J.S. Stevonic, and S. Spaic, *Electrochim. Acta*, **34**, 1093 (1989).
- [30] J.S. Stevonic, V.D. Jovic, and A.R. Despic, *J. Electroanal. Chem.*, **349**, 365 (1993).
- [31] M.R.H. deAlmeida, E.P. Barbano, M.F. deCarvalho, I.A. Carlos, J.L.P. Siqueira, and L.L. Barbosa, *Surface & coatings Technology*, **206**, 95 (2011).
- [32] D. Eyre, D. R. Gabet, D.R. Eastham, *Plating and surface finishing*, **72**, 113 (1985).
- [33] B. Campillo, J. Genesca, J. Avila, *et al.*, *Surface Engineering*, **14**, 320 (1998).
- [34] E.C. Weakly and H. Dicamillo, *Patent US 99-248064(RRT 10 Box 480, Glenwood, NM 88039, (2001).*
- [35] M. Paidar, K. Bouzek, M. Laurich, and J. Thonstad, *Water Environ. Res.*, **72**, 618 (2000).
- [36] C.P. De Leon and D. Pletcher, *Electrochim. Acta*, **41**, 533 (1996).
- [37] A.J. Bard and L.R. Faulkner, *Electrochemical methods: fundamentals and applications*, Wiley, New York (2001).
- [38] D.R. Gabe and P.A. Mekanjuola, In: *Electrochemical engineering. IChemE symposium series*, **98**, 309 (1986).
- [39] A. Bernner, *Electrodeposition of alloys*, vol.1 (Academic, New York) 1963.
- [40] A.R. Despic, V.d. Jovic, in P.R.E. White, J.O.M. Bockreis, and B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, Plenum Press., New York, 143 (1995).
- [41] B.M. Jovic, Ts. Dobrovolska, U. Lacnjevac, I. Krastev, and V.D. Jovic, *Electrochim. Acta*, **54**, 7565 (2009).
- [42] Boker, Hugh, Okamoto, Hiroaki, *ASM Handbook Volume 03-Alloy phase diagrams*, ASM International, USA (1992).
- [43] L. Skibina, J.S. Stevanovic, and A.R. Despic, *Electrochim Acta*, **310**, 391 (1991).
- [44] D. Grujicic and B. Pesic, *Electrochim. Acta*, **47**, 2901 (2002).
- [45] M.E. Hyde and R.G. Compton, *J. Electronal. Chem.*, **549**, 1 (2003).
- [46] B. Scharifker and G. Hills, *Electrochim. Acta*, **28**, 879 (1983).
- [47] M.P. Pardave, M.T. Ramirez, I. Gonzales, A. Serruya and B.R. Scharifker, *J. Electrochem. Soc.*, **143**, 1551 (1996).
- [48] M. Gircis and E. Ghali, *J. Appl. Electrochem*, **17**, 1234 (1987).
- [49] G. Gunawardena, G. Hills and I. Montenegro, *J. Electronal. Chem.*, **184**, 371 (1985).
- [50] A.M. Abed El-Halim, *J. Appl. Electrochem*, **14**, 587 (1984).
- [51] T. Montiel, O. Solorza and H. Sanchez, *J. Electrochem. Soc.*, **147**, 1031 (2000).
- [52] B.R. Kumar and T.S. Rao, *digest, Journal of nanomaterials and biostructures*, **7**, 1881 (2012).
- [53] M.L. Mnford, M.L. Sartorelli, L. Seligman, and A.A. Pasa, *J. Electrochem. Soc.*, **149**, C274 (2002).