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Thermal and kinetic study of electrochemical deposition of lead on FTO substrate

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ABSTRACT

We report the electrochemical deposition of lead (Pb) onto fluorine-doped tin oxide (FTO) electrodes in a sodium nitrate bath (0.4M NaNO₃) at constant potential conditions. The kinetics electrodeposition processes have been *in situ* monitored for advanced nucleation stages by chronoamperometry for various temperature at fixed concentration of Pb²⁺, that is 0.1M. The microstructure and morphological characteristics of the deposit layers were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-Ray EDX techniques. The results show that the current density as well as the deposits density strongly depend on the temperature. The correlation between the experimental results and the theoretical process of the lead deposits was discussed and verified.

Keywords: kinetic electrodeposition, lead, theoretical process of the deposits, FTO

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I. Introduction

Lead (Pb), as an electrodeposit, is a low cost material and extremely attractive due to its distinguishable chemical and electronic properties mainly the high conductivity and the considerable overpotential for the evolution of the oxygen reaction in comparison to other metal's deposits [1,2]. The Pb also shows a long lifetime and a good resistance to corrosion factors. These properties provide ample opportunities for the application of lead deposits of different sizes in sensing platforms and in microelectronics application [3]. More specifically, the electronic properties of isolated Pb particles change considerably when their sizes are evolving from the nanometer to the micrometer scale or contrary. For these reasons, there is a large demand to develop the growth techniques used to produce Pb clusters with controlled size and morphology and to understand the related growth kinematics. In this regard, electrochemical deposition technique (ECDT) is an attractive approach that has been used to produce lead in nano as well as in micro clusters. The advantages of the ECDT is a simple and non-expensive technique which can be implemented under ambient conditions and easily scalable to industrial level [4]. It presents a high deposition rate and allows a precious control of the growing nanostructure properties (dimension and morphology) by adjusting the electrical parameters [5]. Nevertheless, a good knowledge of the growth parameters involved during the electrodeposition process is required to achieve a precise control of the Pb cluster's synthesis. In this regard, sodium nitrate solution (NaNO_3) have been the preferred systems to electrodeposit lead nanoclusters onto graphite substrate [6,7], indium-tin oxide [8], platinum [9], silver [10], and lead foil electrodes [11–13].

We consider that a good understanding of the kinetics of lead electrodeposition will provide a good control of size and morphology of Pb nanoparticles. Therefore, in this work, we investigate the advanced nucleation phases by ECDT, of lead onto FTO electrode in a NaNO_3 solution using cyclic voltammetry (CV) and chronoamperometry measurements. The electrodeposits were characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-Ray (EDX). The correlation between the experimental results and the theoretical process of the lead deposits was discussed as well.

II. Experiments:

II.1 Electrodeposition process

The electroplating of metals on a conductive substrate consists in reducing the metal ions of various possible electrolytes. The lowering of ions generally present as cation (positive charge) in the solution, to produce a neutral metal atom on the cathode as a deposit in the following way.

The charge is provided by an external current source and a layer of atoms is deposited at a permitted time. The higher the concentration of ions the greater the number of atoms deposited on the substrate is important and eventually to form a lattice. Deposition rates are proportional to the concentration of active ions in the solution for electron reduction provided by the cathode. When the ions reach the surface of the electrode, to minimize them, the surface nuclei can grow in one, two, or three dimensions depending on the electrical disassembly parameters and the nature of the solution. This can create single deposits, single layer or multiple layers. The crystalline structure, microscopic structure, and initial formation of sediments under certain conditions will determine the physical properties as well as the chemical properties of the deposits. Here, the electrolyte solution is the sodium nitrate (NaNO_3 , fisher scientific company, USA, 99.99 %) which was dissolved in distilled water. Commercial lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$, Honeywell FlukaTM, Chemische Fabrick, Germany, ≥ 99.0 %) was used. It was dissolved in distilled water until a transparent liquid was obtained. Sodium nitrate and lead (II) nitrate solutions were mixed in a molar ratio of 2:1 at 60°C. The pH of the solution is systematically checked before each measurement, it was found 5.4. Fluorine-doped tin oxide (FTO) conducting glass of resistance $13 \pm 0.2 \, \Omega/\text{square}$ and a thickness of 2.2 mm (purchased from Ossila Ltd.) were used as the substrates for electrodeposition. Before deposition, the FTO substrates were rinsed with detergent, distilled water, acetone, and isopropyl alcohol. Each rinsing step was carried out in an ultrasonic bath for 15 min, followed by drying at 80°C. After that, the electrochemical experiments were performed in a conventional three-electrode open cell connected to a water chiller to control the temperature inside the cell, (Figure 1). The FTO substrate was fixed in the working electrode (WE), a platinum wire (0.05 cm in diameter) was used as the counter electrode (CE). For the reference electrode (RE), we use an Ag/AgCl electrode (Thermo ScientificTM OrionTM) in contact with the solution through a Luggin capillary. All the electrodes in the electrochemical cell were polished and cleaned with deionized water after each measurement attempt. The voltammetry and amperometry experiments were carried out using a HEKA Potentiostat/Galvanostat PG510 controlled by a POTMASTER software (Serial No. 290157A). The minimum intensity which can be resolved by the potentiostat is 1 nA.

Figure 1: Electrodeposition scheme.

II.1.1 Static analysis

Figure 2 is a typical representation of the polarization curve (cyclic voltammogram) obtained by electrodeposition technique. These experiments were carried out at the scan rate of 60 mV/s. Recorded cyclic voltammogram (I-V) represents the static diagram of current I versus voltage V at different temperature in the interval of voltage [-1.5V and +1.5 V]. Figure 2 shows a comparison of the experimental I-V obtained from the solutions with and without Pb^{2+} . The reference (without Pb^{2+}) I-V (black line) has a symmetrical shape and does not show any current peak. However, in presence of lead, the current intensity measured through the voltage window seems somewhat sensitive to Pb^{2+} cations. The current density peaks appeared close to the potentials of -0.8 V for all the studied sample in different temperature. Cyclic voltammograms (green, blue and red lines) are characterized by the presence of a large current peak intensity. The presence of these peaks are associated with the presence of an electrochemical processes on the electrode surface. It is shown that the peak intensity increases by increasing the temperature. Reduction of Pb^{2+} cations to Pb occurred as described by Eq. 0. As it will be demonstrated later, the higher the temperature of the cell the greater the density of the deposit Pb [14].

Figure 2 Typical cyclic voltammograms measured for the FTO electrodes over the same voltage range and different temperature in a pure distilled water, the curves are obtained from aqueous solution of 0.1M $\text{Pb}(\text{NO}_3)_2$ in 0.4 M NaNO_3 . Scan speed is 60 mV/s

II.1.2 Kinetic analysis

The chronoamperograms recorded for electrolytes containing 0.1M lead nitrate in 0.4M sodium nitrate at the potential -0.8 V at different temperatures are shown in Figure. 3. These curves present an *in-situ* evolution of the current transient. They clearly show that the nucleation rate changes *versus* temperature. The chronoamperograms present three visibly different parts describing the whole process. Each current density reaches its threshold noted as j_m (maximum density of current) at time t_m . Then, they decrease slightly, practically they remain constant. The first portion is characterized by a relatively stable current intensity noted as silent part. The duration of this stability is strongly affected by the temperature. Indeed, it decreases as the temperature increases. The second portion corresponds to the nucleation process. It starts when the current intensity begins to have a significant increase. It is clearly shown that, the current density versus time slope increases when the temperature increases. The third portion is the part in which the density of current is practically stable. We may say that during this plateau like shape, the Pb

deposits across the FTO surface reaches its equilibrium state. As reported by González-García and his coworkers [15–17], the electrochemical-deposition is a very complex process and is strongly influenced by the experimental conditions. Hence, to understand this mechanism properly, these experimental results are computed and discussed.

Figure 3: Current density versus time recorded during the electrodeposition of Pb^{2+} on a FTO electrode. Black, blue, and green lines are the experimental results for $T=5$, 20, and 35°C , respectively. Red line corresponds their best fit.

III. Theory of nucleation and crystal growth

The elaboration of the crystalline materials involves phenomena of nucleation and growth. Electro-crystallization is the study of these two phenomena under the influence of an electric field. According to Amblard [18], these two phenomena are in competition with each other. They influence on kinetics, structure, and properties of the deposits. For example, the faster the nucleation speed, the finer the grains that form the deposit.

Theoretical electro-crystallization models have been proposed to demonstrate the nucleation and growth mode during the electrodeposition process. The nucleation process is generally described by two types: instantaneous and progressive process. The growth process is typically divided into three categories [19]:

- Two-dimensional (2D) growth mode or Frank-Van der Merve mechanism which is generally found in the case where the metal and the substrate are of the same chemical nature.
- 3D growth mode or Volmer-Weber mechanism, it can be exploited to produce nanostructures.
- Stranski-Krastanov mechanism which begin by 2D growth mode followed by 3D growth.

According to the ref[20]:

- In 2D growth process the current density can be expressed by Eq.1 and Eq.2 for instantaneous and progressive nucleation, respectively.

$$j_{2D}^{inst} = \frac{zF\pi hMN_0k_{2D}^2t}{\rho} \exp\left(-\frac{\pi M^2N_0k_{2D}^2t^2}{\rho^2}\right) \quad (1)$$

$$j_{2D}^{prog} = \frac{zF\pi hMA_{2D}k_{2D}^2t^2}{\rho} \exp\left(-\frac{\pi M^2A_{2D}k_{2D}^2t^3}{3\rho^2}\right) \quad (2)$$

where k_{2D} is the lateral growth rate constants ($\text{mol cm}^{-2} \text{s}^{-1}$), h the layer height (cm), N_0 the total number of active centers (cm^{-2}), A_{2D} the nucleation rate ($\text{nuclei cm}^{-2} \text{s}^{-1}$), M the atomic weight (gmol^{-1}) and ρ the density (g cm^{-3}) of the deposit.

- In 3D growth process, the current density can be expressed by Eq.3 and Eq.4 for instantaneous and progressive nucleation, respectively.

$$j_{3D}^{inst} = zFk' \left[1 - \exp\left(-\frac{\pi M^2k^2N_0t^2}{\rho^2}\right) \right] \quad (3)$$

$$j_{3D}^{prog} = zFk' \left[1 - \exp\left(-\frac{\pi M^2k^2A_{3D}t^3}{3\rho^2}\right) \right] \quad (4)$$

where k and k' are, respectively, the lateral and vertical growth rate constants and A_{3D} the nucleation rate.

- In Stranski-Krastanov mechanism, the current density can be expressed by a combination of Eq.1 or Eq.2 and Eq.3 or Eq.4.

Furthermore, in Harrison and Thirsk [21] studies, the current density is divided in two parts: the first one is due to 3D crystal growth which can be given from Eq.3 or Eq.4. The second part is the

current caused by an outward growth on a substrate base plane at a free surface uncovered by growing nuclei, if. Their equations in the case of an instantaneous or progressive nucleation are given by Eq.5. or Eq.6, respectively.

$$j_f^{inst} = zFk_0 \exp\left(-\frac{\pi M^2 k^2 N_0 t^2}{\rho^2}\right) \quad (5)$$

$$j_f^{prog} = zFk_0 \exp\left(-\frac{\pi M^2 k^2 A_{3D} t^3}{3\rho^2}\right) \quad (6)$$

where k_0 is the growth rate constant on the base plane of the substrate.

III.1 Approximations of current-time transients: nucleation and crystal growth models

As shown in Figure 3, the current-time transients are different in shapes at different temperatures. This indicates that the temperature strongly affects the nucleation and growth mechanism. The behavior of current-time characteristics for three temperature, 5°C, 20°C and 35°C is analyze theoretically. Experimental results have been simulated and tested by 2D and 3D models from Eq. 1 to Eq. 6.

In figure 3a, the current fit is described by combination of three parts, Eq.7:

$$J(t) = i_0 \exp(-P_1 t^3) + P_2 t^2 \exp(-P_1 t^3) + P_3 [1 - \exp(-P_4 (t - t_0)^3)] \quad (7)$$

Where:

$$\begin{aligned} i_0 &= zFk_0 \\ P_1 &= \frac{\pi M^2 A_{2D} k_{2D}^2 t^3}{3\rho^2} \\ P_2 &= \frac{zF\pi h M A_{2D} k_{2D}^2}{\rho} \\ P_3 &= zFk' \\ P_4 &= \frac{\pi M^2 k^2 A_{3D}}{3\rho^2} \end{aligned}$$

t_0 is the induction time.

The best fit confirms that the nucleation and crystal growth at 5°C starts by a progressive nucleation and 2D crystal growth. Then, at an induction time t_0 , a second process progressive nucleation and 3D crystal growth as describe by Stranski-Krastanov mechanism.

The chronoamperometric curve of the electrodeposition of lead, obtained at 20°C, (Figure 3b) shows that two quasi-plateaus appear at shorter and longer times which follows the model of 3D growth [22]. To obtain further information regarding this process, different equations (from Eq.1 to Eq.6) were tested. The best fit of the experimental results is obtained by Eq.8 which is a combination of Eq.5, Eq.3 and Eq.4. This global process begins by an instantaneous nucleation and 3D growth followed by a progressive nucleation and 3D growth after the induction time t_{ind} .

$$J(t) = i_0 \exp(-P'_1 t^2) + P_3 [1 - \exp(-P'_1 t^2)] + P'_3 [1 - \exp(-P'_4 (t - t_{ind})^3)] \quad (8)$$

Where:

$$P'_1 = \frac{\pi M^2 k^2 N_0}{\rho^2}$$

$$i_0 = z F k_0$$

$$P'_1 = \frac{\pi M^2 k^2 N_0}{\rho^2}$$

$$P_3 = z F k'$$

$$P'_3 = z F k'_s$$

$$P'_4 = \frac{\pi M^2 k_s^2 A_{3D}}{3 \rho^2}$$

t_{ind} is the induction time, k_s and k'_s are respectively the lateral and vertical growth rate constants for secondary growth process.

At 35°C, the current-time transient curve is characterized by higher slope (Figure 3c). This mechanism can be described by progressive nucleation and 3D growth or Volmer-Weber model [19]. The modelling resumed on Eq.9, which is the combination of Eq.6 and Eq.4 leads to the best fit.

$$J(t) = i_0 \exp(-P_4 t^3) + P_3 [1 - \exp(-P_4 t^3)] \quad (9)$$

Figure 4 shows the values of $\log(k_0)$, $\log(k')$ and A_{3D} as functions of temperature which are extracted from the best fits. For the rate constant, k_0 , the dependence was linear and increasing by varying the temperature from 5°C to 35°C (black curve). Concerning the vertical growth rate constant, k' , it is found to be nonlinear for the first 3D growth process (red curve). Indeed, k' increases as temperature increases from 5°C to 20°C and then becomes, practically, stable from

20°C to 35°C. We also investigated the nucleation rate, A_{3D} assuming that the growth rates in two different directions are same. It decreases as temperature increases, as shown in blue curve.

Figure 4: Dependence of $\log(k_0)$, $\log(k')$ and A_{3D} on temperature for lead (II) on FTO.

IV. Micro-structure study

To correlate the chronoamperometry analysis, the morphologies of Pb deposit particles obtained at different temperature are characterized by SEM technique. The imaging analyses were performed by a FEI Quanta 600 microscope (Figure 5). The density of the individual crystals changes considerably with temperature which enables the correlation of the lead (Pb) deposits morphology, to their chronoamperograms. At 5°C, it is clearly seen that randomly distributed individual crystals with size in the order of 5 μm were formed on the substrate (Figure 5a). Their morphologies are characterized by flat faces and sharp edges and corners. At 35°C (Figure 5c), the agglomeration of the individual crystals is observed. The distancing between the crystallites is lowered one observes sand-rose-like morphology starts to begin at $T=20^\circ\text{C}$ (Figure 5b). This can be explained by the 3D crystal growth as describe by Stranski-Krastanov mechanism, mentioned above. The obtained surface morphologies are in line with data obtained by the chronoamperometry analysis. These morphologies are similar to many reports in the literature [19,23–25].

Figure. 5. SEM micrographs of Pb deposits on FTO substrate at different temperature.
a) T=5 °C, b) T=20 °C and c) T=35 °C.

Quantitative analysis of the obtained film is carried out using Energy Dispersive X-Ray Analysis (EDX). Results presented in Figure 6 show the presence of Lead (Pb), Oxygen (O), Silicon (Si), and Tin (Sn). Their percentage is given in the table inset. The results obtained from Figure 6 indicate that Pb (23.52%), O (20.58%), Si (2.35%), and Sn (53.54%). Sn is the major constituent of the sample since it is the principal element of the substrate Fluorine (F) doped SnO₂. F is missed maybe due to its low doped percentage. Si is present with low percentage because is totally covered by FTO substrate. The presence of Pb is the result of the electrodeposition process.

Figure. 6. Energy dispersive X-ray analysis (EDX) spectrum of lead deposit on FTO substrate at 20°C.

V. X-Ray diffraction Analysis

The powder X-ray diffraction (XRD) of the obtained electrodeposits samples was performed on a PanAlytical MPDPRO diffractometer (Bragg–Brentano geometry) equipped with a linear X'celerator detector using copper anticathode ($\lambda K\alpha_1/\alpha_2 = 1.540560/1.544330\text{\AA}$). X-ray diffraction patterns are obtained in 2θ range 20–70 °, the step size is 0.02 and the time per step is 30s. The X-ray patterns of the obtained samples at 5, 20, and 35°C are compared to Pb(NO₃)₂ as starting materials and FTO as substrate on which Pb is deposited (Figure 7). This figure shows disappearance of lead nitrate in the three samples: T5, T20, and T35. Their patterns show peaks corresponding to FTO (SnO₂: reference code 01-077-0452) in addition to extra lines observed at 22.5°, 29.5°, and 39.7°. No overlapping of the measured extra lines with those reported in the literature was found.

Since the Pb (II) cations were electrochemically reduced at the potential of -0.8 V, the obtained deposit should be lead (lead oxide is excluded). Deep X-ray diffraction study is in progress to determine the structure of this new phase.

Figure. 7. The XRD pattern of the lead deposited on FTO substrate (with a potential pulse at -0.8 V. at different temperature. The patterns of $\text{Pb}(\text{NO}_3)_2$ and FTO are given for comparison.

VI. Conclusion

Pb (II) cations were electrochemically reduced at the potential of -0.8 V on FTO substrate at different temperature. The kinetic parameters of electrodeposition processes were determined from the analysis of chronoamperometry data. The good agreement of the values of diffusion coefficients determined applying Cottrell equation and non-linear fitting method was observed. The density number of active sites and the nucleation rate constant have been discussed. A correlation between the morphology of the deposit particles and the chronoamperometry curves exist. After comparison with was reported in the literature, X-ray diffraction and energy dispersive X-ray analysis suggest the formation of new lead phase.

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