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Movement of the deposit segment in thin layer electrochemical cell – a conjugate dissolution/deposition behavior

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Abstract

In this paper we report a novel phenomenon taking place in the thin layer electrodeposition of Pb. A segment of dendrite deposit, which was segregated from the cathode, moved and shortened spontaneously in the electrochemical cell. We find that this behavior arises from the concurrent electrodissolution and electrodeposition reactions taking place at two ends of the isolated segment of the deposits. A mechanism inducing this phenomenon is suggested.

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Keywords: Pb; Electrodeposition; Electrodissolution; Thin layer cell; Kinetics

1. Introduction

Investigation on the electrochemical behavior in a thin layer electrochemical cell is interested from fundamental and practical points of view [1-3]. During the past decades, a large number of theories and experiments have been directed to study the transport mechanisms and reaction kinetics in thin layer electrochemical cells [4-12].

Generally, when the electrolyte is confined to the quasitwo-dimensional space with the thickness from a few μ m to 100 μ m, the convection effect is eliminate, and the diffusion and electromigration of ion possess the different characteristics from that in bulk electrolyte cell [6,8]. For instance, the resistance of solution becomes extremely high when the thickness of the electrolyte layer is very thin. In such a condition, a very high ohmic drop and nonuniform current distribution over the working electrode cause many novel phenomena such as nonlinear effect, etc. Wang et al. [13] had studied the electrodeposition of copper in the ultrathin electrolyte layer. It was indicated that the nanostructure copper filaments with the periodic chemical composition formed due to spontaneous alternate accumulation of Cu and Cu²⁺ on the growing interface. The reason was that in the thin electrolyte layer the concentration of ions before the reaction interface may oscillate periodically, since the diffusion of ions was limited and the rate of electrode reaction is a mismatch for the velocity of ion transport. In addition, lots of models and equations have been formulated to describe the electrochemical process occurring in the thin layer electrochemical system, such as thin film electrodeposition, atmospheric corrosion, polymer electrolyte fuel cell and so on [14–17].

In this paper, we investigated a novel phenomenon taking place in the thin layer electrodeposition of lead. A segment of dendrite deposit, which was segregated from the cathode, could move and shorten spontaneously in the electrochemical cell. We suggested the mechanism resulting in these phenomena.

2. Experimental

2.1. Electrodeposition setup

The electrochemical deposition of Pb was carried out in the electrolyte layer sandwiched by two glass plates made

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Fig. 1. Schematic diagrams of the experiment setup: (a) side view, (b) top view.

of microscope slide. The experimental device is shown in Fig. 1. The size of the upper glass plate was 7 cm in length and 2 cm in width. The thickness of the electrolyte layer was 50 μ m in the present experiment. The cathode was made of a platinum foil, which was polished by diamond paste and rinsed by acetone before use. The anode was lead plate with purity 99.9%. The electrolyte solution was 0.5 M Pb(BF₄)₂ with reagent grade. The electrodeposition was performed at a constant applied voltage -10 V.

The process of electrodeposition growth was viewed by an optical microscope equipped with a charge-coupled device (CCD) video camera, as shown in Fig. 1. The CCD device connected with a personal computer. With this optical system, we can make a real-time observation on the growth of deposit and simultaneously save the video image for analysis later.

2.2. Measurement methods

Kinetic measurements in the present experiment involved three aspects: conductivity of the electrolyte solution, electrode potential and I-V properties for different electrode reactions.

Conductivity of the electrolyte solutions was determined by a conductivity meter (DDSJ-308A, Shanghai, China). The frequency was 1 kHz. Considering that the glass plate might have an impact on the transport of ions in the thin layer electrochemical cell, we designed a setup to measure the conductivity of electrolyte solution confined in a very thin cell. The measurement setup is shown in Fig. 2(a). The length and width of the glass plate were 4 and 2 cm, respectively. Two thin platinum wire electrodes (50 μ m in diameter) were placed at the two ends of the cell.

To investigate the change in the overpotential at the two ends of a disengaged dendrite, the electrode potential was measured. In our experiments, a regular metal band made



Fig. 2. Schematic diagrams of the measurement setup. (a) The setup measuring the conductivity of the thin solution layer. (b) The setup measuring the electrode potential at the two ends of the metal band sandwiched in the thin electrochemical cell.

of lead foil substituted for the irregular disengaged deposits. The thickness of the band was 50 μ m and the width 0.5 mm. The measurement method was illustrated in Fig. 2(b). A copper wire, 30 μ m in diameter, was welded on the band, and it extended from the band to the cell. The surface of the copper wire was coated with a layer of insulating paint to prevent distorting the distribution of electric field in the cell. A platinum microprobe was used to detect the electrode potential around the ends of the metal band. Since the microprobe was very thin (30 μ m in diameter) and soft, it was welded on a steel plate to firm up. In this way, we could operate the microprobe and the steel plate were protected by insulating paint except the tip of the probe. A digital potentiometer was used to measure the electrode potential.

Polarization curves for the different electrode reactions were obtained by linear voltage scanning (LVS) technology. The experiments were conducted on electrochemical analyser (CHI 6200, Shanghai, China). The measurement was performed in a 3D electrochemical bath. The working electrode was lead with the surface area of 1 mm². The auxiliary electrode was platinum plate and the reference electrode was a saturated calomel electrode (SCE). The sweep rate was 10 mV s⁻¹. Our measurement consisted of these electrode reactions: dissolution of Pb, deposition of Pb and electrolysis of water. For the electrode reaction of Pb, the measurement was carried out in Pb(BF₄)₂ solution with the concentration of 0.5, 0.1 and 0.02 M, respectively. For the anodic and cathodic reaction of the electrolysis of water, considering these reactions mainly depend on the pH value of the water, we

first measured the pH values of the $Pb(BF_4)_2$ solution with the concentration of 0.5, 0.1 and 0.02 M by a pH-meter, which are 2.5, 3.8 and 5.5, respectively. Then, $H_2(BF_4)_2$ solutions with the same pH values were used to survey the polarization properties of the electrolysis of water.

3. Results and discussion

When an external voltage is exerted on at the electrodes, Pb began to deposit on the platinum cathode and formed dendrite deposit [18]. Because the cell was thin, the dendrite deposit was thin and brittle. During the course of the growth, one could find small bubble of hydrogen gas generating by the electrolysis of water. Generation of the bubble disturbed the growth of the Pb dendrites and even made the deposit break down. In general, electrodeposits grow out of the electrodes; once a part of the deposit separates from the deposit and becomes an isolated segment, the segment will stop growing. However, in the present experiment we found that the segment moved toward the anode in the thin cell after it broke away from the dendrite deposit linked to the cathode. Fig. 3 illustrates this interesting process with in situ observations. Fig. 3(a) and (b) show the growth of the dendrite deposit without any disturbance from hydrogen gas bubbles. After a few seconds, the deposit began to break, as shown in Fig. 3(c). Then this disengaged dendrite segment began move [see Fig. 3 (d), (e) and (f)]. The movement velocity was about $0.5 \,\mathrm{mm}\,\mathrm{s}^{-1}$ and the direction was toward the anode.

This novel observation aroused our interest to investigate the mechanism inducing the movement of the isolated deposit segment in the two-dimensional (2D) electrochemical cell. Did the deposit move by the driving force of the electric field? Or was this movement caused by the flow of the local electrolyte solution? Both appear incorrect. Further investigations revealed that the 'movement' of the segment was caused by concurrent dissolution and deposition reactions occurring at the two ends of the dendrite segment. At the end toward to the anode, electrodeposition took place, which allowed the deposit to grow forward. At the end toward to the cathode, the electrodissolution took place, which consumed the deposit continuously. These concurrent dissolution and deposition reactions caused the dendrite segment to move in the cell. In addition, we also found that under different experimental condition, the behavior of the disengaged dendrite segment in the cell was varied. When the concentration of the solution was low (e.g. 0.02 M), the dendrite segment shortened gradually rather than moved. When the length of the disengaged segment along the line of the field was very short, the disengaged dendrite segment neither moved nor shortened, did not change. In these experiments, we never observed the disengaged segment to grow up. In the view of the competition between the dissolution and deposition reactions taking place at two ends of the deposit segment, we can expect that if the amount of dissolving lead was larger than the deposited lead, the segment appeared to shorten gradually; if the dissolution and deposition reactions did not occur, the disengaged deposit remained stationary.

In electrochemistry, the conjugate dissolution–deposition reactions have been reported [19–23]. When a metal rod is placed in an electric field, the field will induce polarization. Anodic and cathodic polarization at the two sides of the metal rod will give rise to appropriate anodic and cathodic overpotentials. Once the overpotential is beyond a critical value, electrochemical reaction will take place at the two ends of the metal rod. The amount of dissolution and that of deposition should meet the charge conservation principle. Because the two ends of the metal rod serve as the anode and cathode, the



Fig. 3. The movement of the disengaged segment of the dendrite deposit in the 2D electrochemical cell. The photographs were obtained with an in situ observation setup (t = 0, 2, 4, 6, 8, 10 s from (a) to (f)).

process is referred as bipolar electrochemistry. This kind of phenomenon has been investigated using fluidized or packed bed electrode for industrial applications in metal recovery [20,21] and electrosynthesis [22-23]. However, in published studies the phenomenon shown in Fig. 3 has not been observed. The reason, we suppose, is that the rates of the electrode reactions are very slow, and the species dissolving and those deposition are generally not the same in those investigations. In the present experimental system, the rate of electrode reaction is large enough and the dissolving mater and deposited product are the same metal lead. In addition, 2D thin layer systems have the advantage that the change of the dendrite segments resulting from a small amount of dissolving mater or deposited product can be observed clearly. Therefore, the movement of the dendrite segment can be viewed in the present electrochemical deposition experiment. In order to verify this conclusion, an experiment was performed in a 3D bath under the same experimental conditions. It was found that in the 3D bath the dissolution-deposition behavior still occurred, but the rates of electrode reactions were very low and the movement of the disengaged deposit was not observed.

According to electrochemical principles [24], the rate of an electrode reaction depends on the overpotential on the reaction interface for a charge transfer controlled process. If the overpotential η is low, the rate of reaction is small. Contrarily, if η is high, the rate of reaction is large. Why are there large overpotentials at the two ends of the isolated metal band in the 2D electrochemical cell? To answer this question the equivalent resistance model was used [25,26]. Fig. 4 shows the equivalent resistance model describing the 2D electrochemical cell with an isolated metal band sandwiched in the cell. As shown in Fig. 4, the total current I_t flowing through the cell can be written as

$$I_{\rm t} = I_{\rm p} + I_{\rm b},\tag{1}$$

where I_p is the current flowing through the metal band and I_b the bypass current flowing through the solution. When the current I_p comes through the metal band placed in the electrolyte solution, polarization overpotential will be induced at the two ends of the band. The relation between overpotential



Fig. 4. Equivalent resistance model for current pathways in bipolar electrochemical system. I_t : total current; I_b : current flowing through the metal band; I_p : current flowing through the solution; R_b : equivalent resistance of the metal band; R_p : equivalent resistance of the solution.

 η and current I_p can be expressed by the Tafel equation [24]

$$\eta = a + b \log\left(\frac{I_{\rm p}}{S}\right),\tag{2}$$

where *a* and *b* are reaction constants and *s* the area of the side surface of the metal band. Eq. (2) indicates that the overpotential at the end of the metal band increases with the current I_p . It can be seen from Eq. (1) and Fig. 4 that for a constant total current I_t the current I_p depends on the proportion of the resistance of metal to that of the electrolyte solution. If the resistance of the solution is very large, nearly all current flows through the metal band and the current I_p becomes large.

Based on above analysis, it can be inferred that the occurrence of the phenomenon shown in Fig. 3 was related to the resistance of the solution in the 2D electrochemical cell. In order to investigate the resistance of the solution in the present system, the setup shown in Fig. 2(a) was used. The experiments showed that the conductivity of the Pb(BF₄)₂ solution $(0.5 \text{ M}, 20 \,^{\circ}\text{C})$ sandwiched in the 50 μ m cell was 0.6 S cm⁻¹. In the present experiment, the conductivity of metal lead was $50,000 \,\mathrm{S \, cm^{-1}}$ [27] and the width of the deposit segment was about 0.5 mm. Thus, in terms of the ohmic model of the resistance of electrolyte solutions, the ratio of the resistance of the deposit segment R_p to that of the solution R_b was calculated to be about 1800:1. In this condition, it can be concluded that nearly all current I_t flowed through the deposit segment and the polarization overpotentials at the two ends of the segment was very large. The large overpotential caused the high rates of the electrode reactions and the movement of the dendrite segment in the 2D cell.

As mentioned above, the phenomenon shown in Fig. 3 was not observed in the 3D system. The reasons, we propose, lie in two aspects: the first is that in 3D electrochemical cell, the distribution of electric field is not limited within the space between the electrodes, but nearly the full electrochemical cell [24]. Thus, the bypass current $I_{\rm b}$ was still large since the area of the current section in solution was very large in comparison with that in the metal band. The second reason was that in the 3D bath the conductivity of the solution was higher than that in the 2D cell. We measured the conductivity of the solution in the 3D bath. Under the same conditions (concentration and temperature), the conductivity of the $Pb(BF_4)_2$ solution was $1.1 \,\mathrm{S}\,\mathrm{cm}^{-1}$. This result indicates that in the thin electrochemical cell, the boundary of the cell indeed made an impact on the transport of ions. The transport process in the 2D electrochemical cell has been investigated in previous studies [18,28]. It has been shown that when the thickness of the cell was very small ($<100 \,\mu$ m), the convection effect is strongly inhibited. Convection is an important mode in transporting ions. Once the convection is eliminated in the transport process, the movement of ions is impeded and the conductivity of the solution would decreases drastically.

In the present thin layer electrochemical experiment, the resistance of the solution was much larger than that of the metal band. So nearly all current I_t flowed through the metal

band, as analysis above. Thus, Eq. (1) becomes

$$I_{\rm t} \approx I_{\rm p}.$$
 (3)

Eq. (3) offers us the possibility to estimate the overpotential at the two ends of the metal band placed in 2D electrochemical cell. Let *L*, *W* and *d* denote the length, width and the thickness of the cell, and *l*, *w* and *d* denote corresponding parameters of the metal band. When a voltage V_{appl} is applied across the electrodes of the cell, it can be partitioned as follows:

$$V_{\text{appl}} = E^1 + E^1 + E^2 + E^2 + IR_{\text{sol}1} + IR_{\text{sol}2},$$
(4)

where E^{1}_{aed} and E^{1}_{ced} are anodic and cathodic electrode potentials, E^{2}_{aed} and E^{2}_{ced} are electrode potentials at the two ends of the metal band, and $IR_{sol1} + IR_{sol2}$ are the potential drops in the solutions. The calculated model is described in Fig. 5(a). Let\sigma denotes the conductivity of the solution, so the potential drop of the solution can be written as

$$IR_{\rm sol1} + IR_{\rm sol2} = \frac{I_{\rm t}(L-l)}{\sigma dW}.$$
(5)

Under the condition of low current density, the electrode reaction can be considered as a charge transfer controlled process. In this case, the relation between the overpotential η and the current I_p meets Eq. (2). Thus, the overpotentials can be expressed as

$$\eta a^{1} = E^{1} - E_{0} = a_{a} + b_{a} \log\left(\frac{I_{t}}{Wd}\right),\tag{6}$$



Fig. 5. Calculation of the overpotential at the ends of the metal band. (a) A schematic diagram of the calculation model. (b) The overpotential at the ends of the metal band as a function of the length of the metal band.

$$\eta c^{1} = E^{1} - E_{0} = a_{c} + b_{c} \log\left(\frac{I_{t}}{Wd}\right),\tag{7}$$

$$\eta a^2 = E^2 - E_0 = a_a + b_a \log\left(\frac{I_t}{Wd}\right),\tag{8}$$

$$\eta c^2 = E^2 - E_0 = a_{\rm c} + b_{\rm c} log\left(\frac{I_{\rm t}}{Wd}\right),\tag{9}$$

In Eqs. (6)–(9), the equilibrium potential E_0 can be measured by the electrochemical analyser; the reaction constants of lead dissolution a_a , b_a and the reaction constants of lead deposition a_c and b_c can be obtained by fitting of the polarization curves [see Fig. 6(a) and (c)]. For the experiments with the concentration of 0.5 M, we obtained the values of E_0 , a_a , b_a , a_c and b_c were -0.39, 0.18, 0.20, 0.10 and 0.34 V, respectively. Substituting Eqs. (5)–(9) into Eq. (4), we obtain

$$V_{\text{appl}} = 4E_0 + 2(a_{\text{a}} + a_{\text{c}}) + (b_{\text{a}} + b_{\text{c}})\log\left(\frac{I_{\text{t}}^2}{Wwd}\right) + \frac{I_{\text{t}}(L - l)}{sdW}.$$
(10)

For an experimental system, the parameters E_0 , a_a , a_c , b_a , b_c , W, w, d, L, l and σ are fixed, so we can calculate the value of the total current I_t when the applied voltage V_{appl} is given. Then, the overpotential at the ends of the metal band can be determined by using Eqs. (8) and (9). Similarly, fixed the parameters V_{appl} , W, w, d and L, the relation between the overpotential η and the length of the metal band l can be obtained.

Fig. 5(b) is the calculated relationship of the overpotential at the cathodic end of the metal band on the length of the band when the applied voltage $V_{appl} = -10$ V, in company with the experimental value measured by the platinum microprobe. It can be seen from Fig. 5(b) that the experimental value is little less than the calculated value for a certain length of the metal band. The reason is that the microprobe could not be placed close to the end of the band in the experiment, thus causing a small potential different between the microprobe and the end of the band. Fig. 5(b) shows that as the length of the metal band decreased, the overpotential became small. This result presents an interpretation of another phenomenon observed in the present studies that the disengaged deposit segment did not change when the size of the segment was very small. As the length of the segment decreased, the overpotential became small. Once the overpotential was below the critical value, the deposit segment could not grow and kept its stationary status. In the present experiments, we measured the critical length of the metal band $l_c \approx 1$ mm, and the corresponding critical overpotential was about 50 mV. When the length of deposit segment was less than 1 mm, the separate deposit remained stationary, and neither deposition nor dissolution occurred.

Besides the movement of the disengaged dendrite segment in the 2D electrochemical cell, another phenomenon observed was the shortening of the segment when the con-



Fig. 6. Polarization curves of four electrode reactions. (a) $Pb^{2+} + 2e \rightarrow Pb$; (b) $H_2O + 2e \rightarrow H_2 + O^{2-}$; (c) $Pb \rightarrow Pb^{2+} + 2e$; (d) $2H_2O \rightarrow O_2 + 4H^+ + 4e$. The concentration of the electrolyte solution is 0.02, 0.1 and 0.5 M, respectively. Corresponding values of pH are 5.5, 3.8 and 2.5. The working electrode was made of lead plate with the area 1 mm². The sweep rate was 10 mV s⁻¹. A saturated calomel electrode (SCE) was used as a reference electrode.

centration of the solution was low. The mechanism inducing this phenomenon can be understood as follows. In the present experiments, there are two kinds of electrode reactions. They are

cathode reaction:

$$Pb^{2+} + 2e \to Pb, \tag{11}$$

 $H_2O + 2e \to H_2 + O^{2-},$ (12)

and anode reaction:

$$Pb \to Pb^{2+} + 2e, \tag{13}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e.$$
 (14)

To find the difference between the reactions in the case of low concentrations and those in the case of high concentrations, we made the measurements on the polarization curves for the four reactions at the concentration 0.02, 0.1 and 0.5 M by using linear voltage scanning (LVS). The results are shown in Fig. 6. The cathodic polarization curves of lead and hydrogen are shown in Fig. 6(a) and (b), respectively. It can be seen from these figures that when the concentration of the solution is 0.5 M, the deposition potential of Pb is about

-0.50 V¹ and the reduction potential of H⁺ is about -1.0 V. Moreover, at the same voltage the current for Pb deposition is much larger than that for H⁺ reduction. This fact indicates that when the concentration of the solution is high, cathodic reaction is dominated by lead deposition, i.e. Eq. (11) is sufficient to describe the cathodic reaction. However, when the concentration of the solution decreases to 0.02 M, the deposition potential of Pb becomes about -1.5 V and the reduction potential of H^+ is about -1.3 V. They are very close. Thus, the cathodic reactions include the deposition of lead and the release of hydrogen gas described by Eqs. (11) and (12), respectively. As for the anodic reaction, Fig. 6(c) and (d) show that the current for the dissolution of Pb is always larger than that for the generation of O₂ over the ranges of concentration and voltage used. Thus, the dissolution of lead (Eq. (13)), no matter whether the concentration of the solution is high or low, is the principle anodic reaction. To sum up, in the case of low concentrations, the anodic reaction is

¹ The polarization curve of Pb electrodeposition [Fig. 6(a)] indicates that when the electrode potential is between -0.50 and -0.39 V (the equilibrium potential), the deposition reaction meets the linear polarization relation, and current is very small (approximately 1 mA). In this case, the deposit cannot grow into a dendrite structure. Thus, in the present experiment we consider the -0.50 V as the deposition potential.

only the dissolution of lead and the cathodic reactions are both the deposition of lead and the generation of hydrogen gas. Conjugate dissolution–deposition reactions require that the charges in the anodic reactions should be equal to those in the cathodic reactions. Thus, the consumption of lead due to the dissolution is more than that for the deposition of lead, and the disengaged deposit segment would shorten gradually.

4. Conclusion

A conjugate electrodissolution-electrodeposition phenomenon was investigated in a 2D electrodeposition cell. Because of the lower conductivity and low thickness of the solution layer, the ohmic resistance of the electrolyte solution became very large, which led to higher polarization overpotentials at the ends of disengaged deposit segments. As a result, the higher overpotential gave rise to the larger rates of the electrode reactions and caused the movement of the disengaged deposit segment. Moreover, we discuss the conditions inducing this novel phenomenon based on a calculation model. It is shown that whether or not the movement of the disengaged deposit segment takes place depends on the polarization overpotential at the ends of the segment. Higher concentrations of the electrolyte and longer length of disengaged segments are necessary for the movement of the segment. When the concentration of the solution is low enough, the disengaged segment will shorten gradually. When the length of the disengaged deposit segment is small, the segment will neither move nor shorten, but keeps a stationary state.

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