Mechanism of Oscillatory Electrodeposition of Zinc, Revealed by Microscopic Inspection of Dendritic Deposits during the Oscillation

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(Received March 7, 2003; CL-030195)

Electrodeposition of Zn shows a potential oscillation in a diffusion-limited current region, accompanied by dendritic deposits. Detailed microscopic investigations of the deposits during one cycle of the oscillation have revealed a new mechanism including autocatalytic Zn growth, which is closely related to Mullins-Sekerka instability.

Electrodeposition reactions sometimes show current or potential oscillations.[1–5] They also give deposits with peculiar shapes such as dendrites[1–4] and layers.[5] The results suggest that the coupling of electrodeposition and oscillation is an interesting way to produce micro- or nano-sized crystallites with regulated morphological structures. However, knowledge on the mechanism of oscillatory metal deposition is too limited to control the size and shape of deposits. This is most probably because a general mathematical model for electrochemical oscillations was established very recently (around 1995).[6]

We reported previously[5] that oscillations for Cu and Sn–Cu deposition, leading to layered deposits, arose from a negative differential resistance (NDR) caused by adsorption of a protonated organic amine. These may be regarded as the first example of oscillatory metal deposition with clarified mechanisms on the recent theoretical level. There is another type of oscillatory metal deposition that leads to dendritic deposits such as deposition of zinc. A number of studies were made on the oscillations of this type,[1–3] but reported mechanisms have not necessarily been verified by experiments. In a previous paper,[4] we reported a new mechanism for oscillatory Zn deposition, including autocatalytic Zn growth which is closely related to Mullins-Sekerka instability.[7] In the present paper, we will report confirmative evidence for the mechanism obtained by detailed microscopic investigations of deposits.

A polycrystalline zinc disc (6 mm ϕ) was used as the working electrode, together with a Pt plate as the counter electrode and an Ag/AgCl/saturated-KCl electrode as the reference electrode. The Zn disc was polished with alumina powder and etched with 0.01 M H_2SO_4 before use. An electrolyte solution was prepared by dissolving ZnO powder into 4.0 M NaOH. Current density (j) vs potential (U), and U vs time (t) were measured with a potentiostat and a potential programmer, and recorded digitally at 100 Hz with a storing system (instruNET, GW Instruments). The electrode surface was inspected with a Hitachi S-5000 scanning electron microscope (SEM).

Figure 1a shows j vs U for a Zn-disc electrode in 0.2 M Zn(II) + 4.0 M NaOH under a current-controlled condition. A cathodic current due to Zn deposition starts to flow at about −1.46 V. When the j reaches the diffusion-limited current density, the U shifts suddenly to the negative until hydrogen evolution occurs, and a potential oscillation follows in a higher-j region. Figure 1b shows U vs t at a constant j of $-21\,\mathrm{mA\,cm^{-2}}$, as measured for the apparent electrode surface area. The potential oscillation is sustained for more than 10 min.

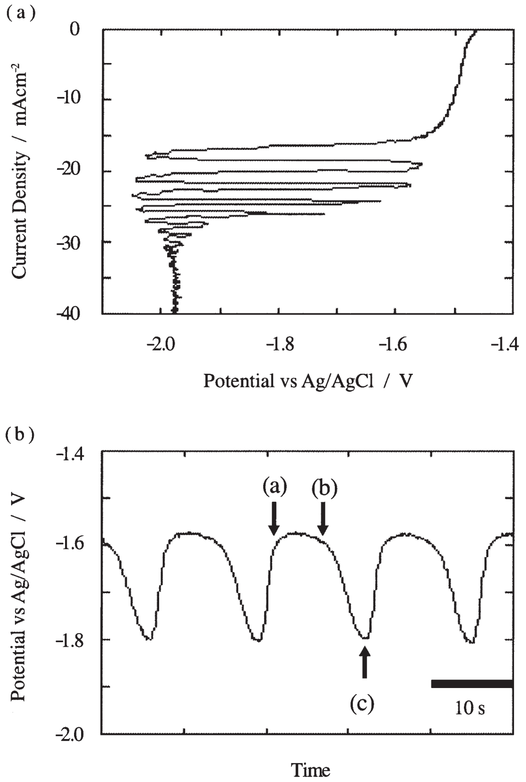

Figure 1. (a) j-U curve for a Zn-disc electrode (6 mm ϕ) in 0.2 M Zn(II) + 4.0 M NaOH under a current-controlled condition, and (b) a potential oscillation at $j = -21\,\mathrm{mA\,cm^2}$.

Figure 2 shows how Zn deposits change their shape during one cycle of the potential oscillation. Figures 2a, 2b, and 2c were obtained by pulling out a Zn-disc electrode from the electrolyte at the oscillation stages (a), (b), and (c) of Figure 1b, respectively. Upon pulling out the electrode,together with successive water rinsing, the electrode potential was kept negative with a potentiostat in order to prevent chemical dissolution of Zn deposits during these procedures. Note that the Zn deposit in Figure 2a consists of dendritic aggregates of very thin leaflets with ample openings. The leaflets become thicker and the openings become narrower in Figure 2b, and the thickened leaflets are finally in contact with each other in Figure 2c. Similar results were reproducibly obtained by repeated experiments.

The results of Figure 2 are quite instructive for the oscillation mechanism. Figure 3 schematically illustrates the change of the Zn deposit during one cycle of the oscillation, after the

SEM images of Figure 2. Let us first consider stage (c) of Figure 3, in which the effective area (S_{eff}) of the electrode surface is not large and thus, in order to maintain the externally applied high current density (j_{ap}), the U is on the negative side of the oscillation where not only the Zn deposition but also hydrogen evolution occur. The important point is that the Zn deposition in Figure 3c is under a diffusion-limited condition, and autocatalytic Zn growth closely related to Mullins-Sekerka instability[7] as reported.[4] Namely, a spherical diffusion layer for Zn(II) ions at a peaked part of the electrode surface leads to a very high rate of Zn deposition at this part, which makes the peaked part more and more peaked (Figures 3c and 3a). This mechanism explains the formation of thin leaflets with ample openings (Figure 2a).

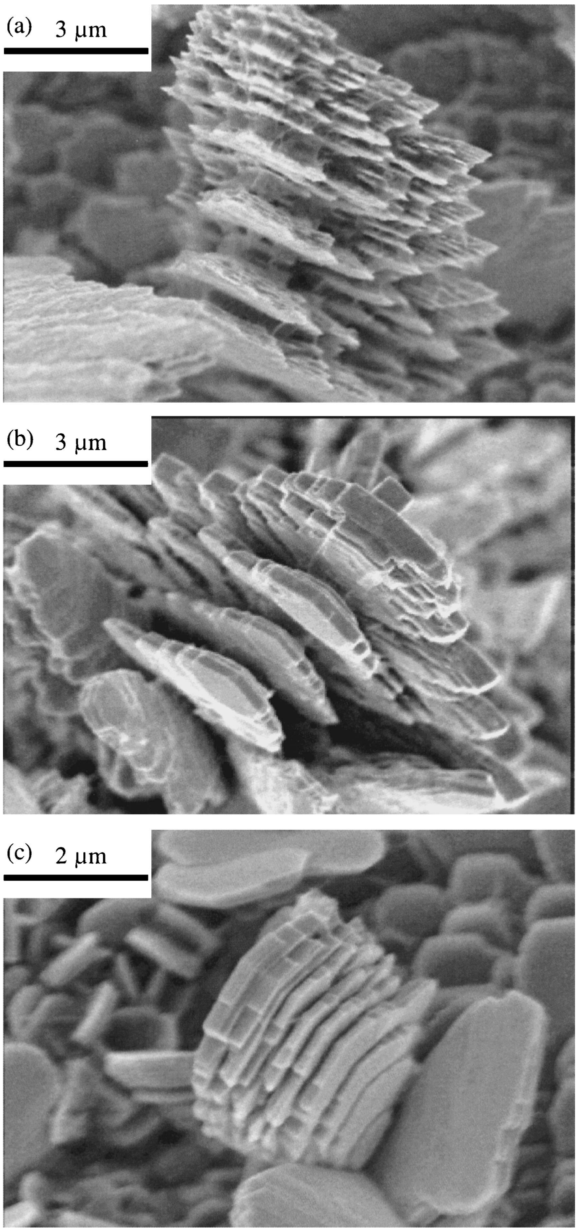

Figure 2. SEM images of Zn deposits, obtained by pulling out the electrode from the electrolyte at the oscillation stages (a),(b), and (c) of Figure 1b.

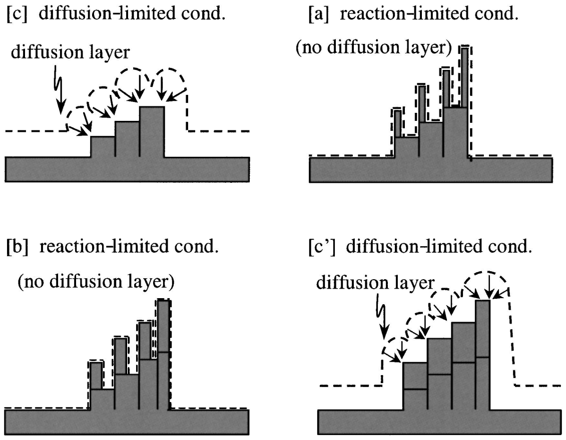

Figure 3. Schematic illustration of formation of dendritic Zn deposits during one cycle of the potential oscillation.

The growth of thin leaflets, on the other hand, causes a large increase in the effective surface area S_{eff} and thus a large decrease in the real current density (j_{r}) under the constant external j_{ap}, which leads to a positive shift in U. The autocatalytic Zn growth and the positive shift in U continue until the diffusion layer (or spherical diffusion) for Zn(II) disappears, i.e., j_{r} reaches the reaction-limited current density. When the reaction-limited current is reached, the Zn deposition occurs all over the electrode surface equally, which leads to thickening of the leaflets[8] (Figure 3b) and finally to their coalescence (Figure 3c′). The coalescence causes a sudden decrease in S_{eff} and a sudden increase in j_{r} to maintain the externally applied constant j_{ap}. Thus, a sudden negative shift in U occurs, and the electrode surface is returned to the initial state (Note that Figure 3c′ is identical to Figure 3c, in that S_{eff} is not large).

It should be emphasized that the mechanism of Figure 3 is given direct experimental support by the SEM images in Figure 2. The sudden shift in U from negative to positive is caused by the autocatalytic Zn growth, whereas the inverse sudden shift in U from positive to negative is caused by the coalescence of thickened Zn leaflets. It is to be noted also that the potential oscillation accompanies the oscillation of the diffusion layer for Zn(II) ions, as is seen in Figure 3. This oscillation of the diffusion layer may play an important role in the synchronization of oscillations on various dendrites at the electrode surface. The present mechanism does not assume any formation of a special layer such as inactive ZnOH reported in the literature,[2] and in this sense, it can be applied generally to various systems.

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Published on the web (Advance View) May 20, 2003; DOI 10.1246/cl.2003.532