New Autocatalytic Mechanism for Metal Electrodeposition Leading to Oscillations and Fern-Leaf-Shaped Deposits

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Zinc electrodeposition on a zinc electrode with a rough surface showed a potential oscillation, accompanied by fern-leaf-shaped deposits, contrary to the case of a zinc electrode with a smooth surface. A new autocatalytic mechanism based on a rough electrode surface is proposed to explain the phenomena systematically.

Electrodeposition of metals such as zinc, tin, and cadmium sometimes shows potential oscillations in a region of high current densities.[1–3] Interestingly, the oscillations are often accompanied by formation of unique fern-leaf shaped deposits.[1,2] Some mechanisms have been reported by assuming either alternate occurrence of hydrogen evolution and metal deposition[1,2] or formation of a zinc-hydroxide surface layer,[3] but the reported mechanisms involve no autocatalytic process[4] and the essence has still not been clarified yet. Fairly long ago, Epelboin et al. reported[5] an S-shaped current vs potential curve for Zn deposition and explained it by assuming that adsorbed Zn^+ as a reaction intermediate acted as an autocatalyst for the Zn deposition, though they gave no experimental evidence. In the present paper, we report a new autocatalytic mechanism for the Zn deposition based on a morphologically rough electrode surface, which can explain both the appearance of potential oscillations and the formation of fern-leaf-shaped deposits.

Polycrystalline zinc (99.99% in purity) discs of 6 mm in diameter were used as the working electrode, together with a $10 \times 10\,mm^2$ Pt plate as the counter electrode and an Ag/AgCl/saturated-KCl electrode as the reference electrode. The Zn electrodes with rough and smooth surfaces were obtained by polishing with alumina powder having the particle size of 3.0 and $0.06\,\mu m$ in diameter, respectively. Scanning electron microscopic (SEM) inspection showed that the unevenness of the rough and smooth surfaces was of the same order in magnitude as the size of the polishing particle. The polished Zn electrodes were etched with 0.01 M HCl for 60 s before use. Aqueous electrolytes containing Zn(II) ions were prepared by dissolution of ZnO powder into 4.0 M NaOH. Current density (j) vs potential (U) curves and oscillations were recorded digitally at 100 Hz with a data-storing system (instruNET, GW Instruments). The inspection of the electrode surface was carried out with a Hitachi S-5000 high-resolution scanning electron microscope.

Figure 1(a) shows a $j - U$ curve for a Zn electrode with the rough surface 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 its current density reaches the diffusion-limited one ($j_{\rm dl} \approx -13\,{\rm mA{\cdot}cm^{-2}}$), the potential ($U$) shifts suddenly to the negative until hydrogen evolution occurs. A potential oscillation appears in a region of j higher than $j_{\rm dl}$. Figure 1(b) shows a time course of the oscillation at $j = -21\,{\rm mA{\cdot}cm^{-2}}$. The oscillation is sustained for more than 10 min. The oscillation in higher j is unstable, decaying soon with time.

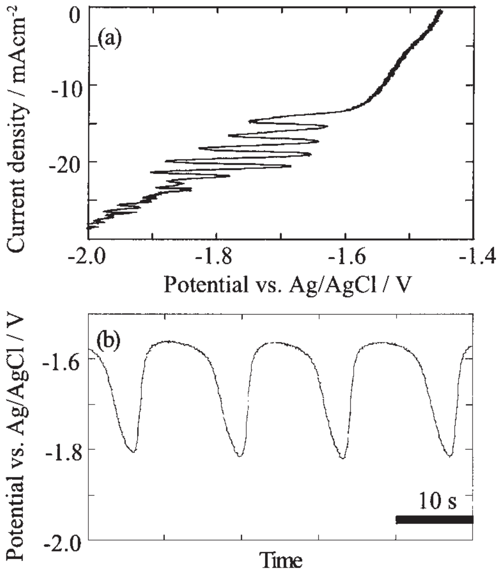

Figure 1. (a) A $j - U$ curve for a rough-surface Zn electrode in 0.2 M Zn(II) + 4.0 M NaOH. The scan rate is 0.1 mA/s. (b) A time course of potential oscillation at $-21\,{\rm mA{\cdot}cm^{-2}}$.

Figure 2 shows SEM images of Zn deposits formed on rough-surface Zn electrodes by the flow of a constant j of (a) $-10\,{\rm mA{\cdot}cm^{-2}}$ (with no potential oscillation) and (b) $-15\,{\rm mA{\cdot}cm^{-2}}$ (with a potential oscillation) for 150 s. The electrodeposition at $j = -55\,{\rm mA{\cdot}cm^{-2}}$ (with a quickly decaying oscillation) gave similar deposits to Figure 2(b). The results show that the electrodeposition with an oscillation at $j > j_{\rm dl}$ gives unique fern-leaf-shaped deposits, quite in contrast to the electrodeposition at $j < j_{\rm dl}$.

The Zn electrodes with the smooth surface, on the other hand, showed neither oscillations nor leaf-shaped deposits even at $j > j_{\rm dl}$, as is shown in Figure 3. The result clearly indicates that an autocatalytic process, responsible for the oscillation and the leaf-shaped deposits, arises from a rough electrode surface. It should be emphasized that any proposed mechanisms[1–3,5] cannot explain this fact.

What an autocatalytic process does proceed for the Zn deposition on a rough electrode surface? Let us first consider a smooth surface (Figure 4A), in which the size of the surface unevenness ($\gamma_{\rm SU}$) is about $0.06\,\mu m$, as mentioned earlier, and is much smaller than the thickness of the diffusion layer ($\delta_{\rm DL}$) of about $1\,\mu m$. In such a case, a linear diffusion layer is formed,

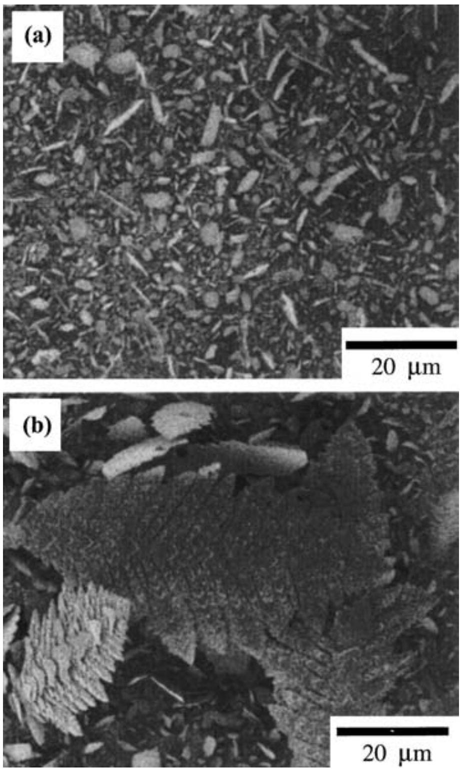

Figure 2. SEM images of Zn deposits on rough-surface Zn electrodes after the deposition (a) at $-10\,\mathrm{mA\cdot cm^{-2}}$ and (b) $-15\,\mathrm{mA\cdot cm^{-2}}$ for 150 s.

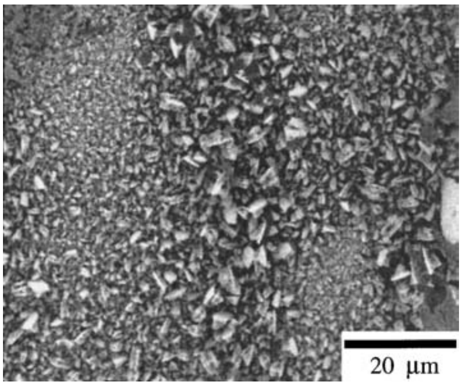

Figure 3. The same as Figure 2(b) except that a smooth-surface Zn electrode was used.

resulting in nearly even deposition of Zn throughout the surface. On the other hand, for a rough surface, in which γ_{SU} is about $3.0\,\mu$m and comparable or larger than δ_{DL}, spherical diffusion layers are formed around tips of peaked parts of the electrode surface (Figure 4B), leading to much higher current densities and thus much higher growth rates at the tips than the other parts. Thus, the peaked parts grow longer and longer autocatalytically. This mechanism works as far as a diffusion layer is formed.

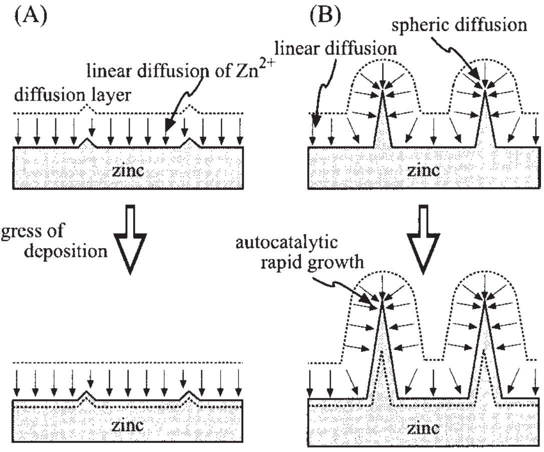

Figure 4. Schematic illustrations of the mode of the Zn electrodeposition on (A) smooth and (B) rough electrode surfaces.

The appearance of the potential oscillation for a rough electrode surface is explained as follows. The rapid growth of peaked parts of the electrode surface leads to a rapid increase in the real electrode area (S_{re}) and thus a rapid decrease in the real current density (j_{re}) under the current-controlled condition, under which j, calculated for the apparent electrode area with neglect of the surface unevenness, is kept constant. The decrease in j_{re} leads to a positive shift in U. This trend continues until j_{re} becomes much smaller than j_{dl} and the diffusion layer for Zn(II) disappears, namely, a state of the reaction-limited current density is realized.

When the diffusion layer disappears, the rate of Zn deposition becomes equal between the peaked and flat parts of the electrode surface. This leads to thickening of peaked parts, and finally to their coalescence, resulting in a large decrease in S_{re}. The large decrease in S_{re} leads to a large increase in j_{re} and a large negative shift in U under the current-controlled condition. Thus, a diffusion layer for Zn(II) is formed again, re-starting the rapid growth of deposits at the tips of peaked parts.

The above mechanism can essentially explain not only the appearance of the potential oscillation but also the formation of fern-leaf-shaped deposits. Also, the mechanism is independent of the kind of deposited metals, in harmony with the reported fact[1–3] that fern-leaf-shaped deposits are commonly formed for Zn, Sn, and Cu deposition. Moreover, the mechanism is in harmony with the inspection by Wang et al.[6] that the curvature of peaked deposits changed periodically during Cu deposition.

In conclusion, the present work has proposed a new autocatalytic mechanism based on a rough electrode surface, which can explain both the potential oscillation and the formation of fern-leaf-shaped deposits. The mechanism can be applied generally to the electrodeposition of various kinds of metals.

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