Magnetic Field Effects on the Current Oscillations in Anodic Zinc Dissolution

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In order to investigate the magnetic field effects on chemical feedback systems, the oscillation behavior of the anodic currents of a zinc electrode was studied in an 8 mol dm^{-3} NaOH aqueous solution under magnetic fields using a liquid-helium-free large-bore superconducting magnet.

The understanding of biological responses to magnetic fields has been of scientific interest for a long time. Recent development of a cryocooler-cooled large-bore superconducting magnet,[1] which is easily handled without liquid helium, is expected to provide a breakthrough in magneto-biological and magneto-biochemical researches.

Periodic oscillations of either current or potential in electrochemical systems serve for years as a model experiment for feedback cycles and information transfer in biological systems.[2-6] It is known that a zinc electrode exhibits spontaneous current oscillations in the vicinity of the Flade potential in concentrated aqueous hydroxide.[7,8] The mechanism of this oscillation is considered to be a feedback reaction cycle of active dissolution, passivation, and reactivation of the electrode.[8] The magnetic field effect on such a system is of great potential interest to not only magneto-electrochemical but also magneto-biochemical studies. Here we report on the experimental studies of the current oscillation behavior of zinc in magnetic fields using a liquid-helium-free large-bore superconducting magnet.

The experimental setup is schemed in Figure 1. The electrode system consists of a zinc disk (ϕ 3 mm) as a working electrode, a platinum wire as a counter electrode, and a Ag/AgCl electrode as a reference one. A H-type electrochemical cell with a G2 glass filter was employed to eliminate the affect of the convection caused by the generation of hydrogen on the counter electrode. A time series of potentiostatic currents was measured using an electrochemical workstation BAS100B/W. Periodic current oscillations were observed at a constant potential of -1.17 V (vs Ag/AgCl) in an 8 mol dm^{-3} NaOH aqueous solution.

The magneto-electrochemical measurements were done with the liquid-helium-free large-bore superconducting magnet in the High Field Laboratory for Superconducting Materials, Tohoku University, which can generate static magnetic fields of up to 5.5 T in a 220 mm room-temperature bore.[1] The working electrode was placed at the center of the magnet, and the magnetic field was applied perpendicularly to the electrode surface. The temperature in the experimental bore was controlled at 20 ± 0.1 °C by a water-circulating thermoregulator.

Figure 2 shows the magnetic field dependence of the time

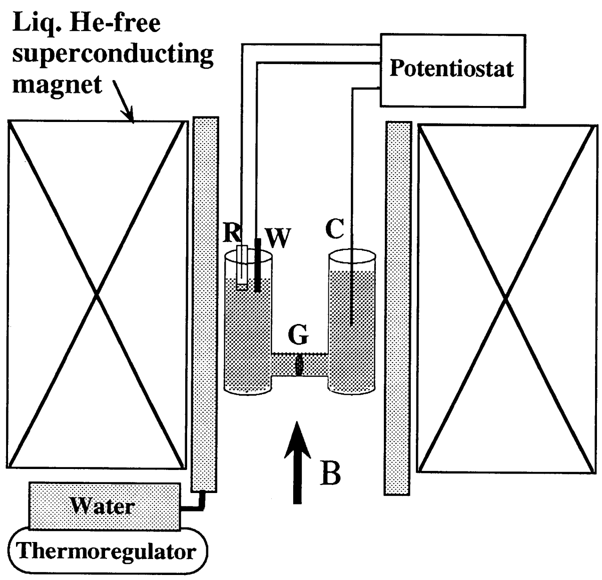

Figure 1. Schematics of the electrochemical measurements in the liquid-helium-free superconducting magnet. W; working electrode, R; reference electrode, C; counter electrode, G; glass filter and B; magnetic field.

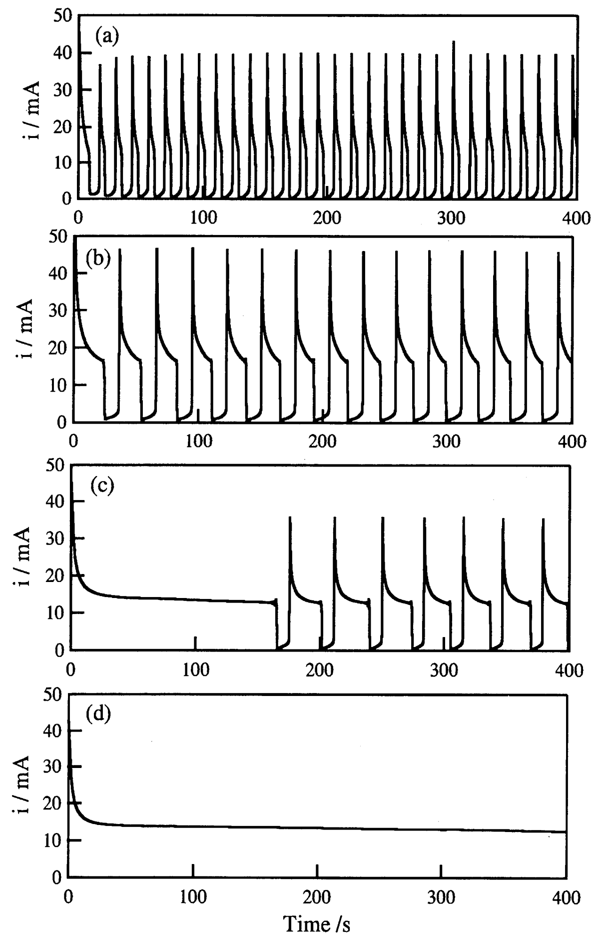

Figure 2. Time series of the anodic currents of zinc in an 8 mol dm^{-3} NaOH solution at a constant potential of -1.17 V under magnetic fields of (a) 0 T, (b) 1.0 T, (c) 1.7 T, and (d) 2.0 T.

series behavior of the anodic current of the zinc electrode. In the absence of a magnetic field periodic oscillations are seen with the period t_0 of 13.5 s (Figure 2(a)) . The oscillation period increases with increasing magnetic field (t_0 = 27.4 s at 1.0 T and 31.5 s at 1.7 T), and a shoulder is clearly seen after each peak (Figure 2(b)). In the field of 1.7 T the oscillation begins after a long current plateau of *ca.* 13 mA, and this current value is nearly equal to that of the shoulders (Figure 2(c)). The oscillation disappears in the higher fields and the dissolution current of *ca.* 13 mA flows continuously in 2.0 T (Figure 2(d)).

The current oscillation of the zinc electrode in concentrated aqueous hydroxide was explained by McKubre and Macdonald[8] in terms of the dissolution-passivation mechanism as following reactions:

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \quad (1)$$
$$Zn(OH)_4^{2-} \rightleftarrows ZnO + H_2O + 2OH^- \quad (2)$$

The oscillations occur in the vicinity of the Flade potential, at which the electrode undergoes the transition from the active to the passive state. In the active state the faradaic current flows by the progress of the reaction (1). The rapid dissolution of zinc reduces a local *p*H around the electrode, and the reaction (2) proceeds forward accompanying the ZnO film formation, resulting in the passivation of the electrode. Once the electrode is passivated, the diffusion of the OH^- ion to the electrode surface increases the local *p*H, and dissolving the ZnO film according to the backward reaction (2). As a result, the electrode is reactivated.

A dominant effect of magnetic fields on electrochemical reactions is the magnetohydrodynamic (MHD) effect, which causes the convection during electrolysis and generally enhances faradaic currents, resulting from the increase in the mass trasnfer.[9,10] In the present case the MHD effect is considered to be effective during the active state of the electrode. Figure 3 shows the oscillation profile of the current in the absence of a magnetic field, where we define three characteristic parameters of the oscillation period t_0, a dissolution period t_d, and a period of the passive state t_p. As seen in Figure 2, t_d increases with increasing magnetic field, while t_p is almost independent of the field. This result indicates that the MHD effect disturbs the passive film formation of ZnO on the electrode and extends the active state. On the other hand, the MHD effect is ineffective on the passive state because of quite small currents. In the fields higher than 1.7 T the MHD effect prevents the electrode from the complete passivation, thus resulting in the disappearance of the oscillations. The nearly same current of the shoulders and the plateaus in the magnetic fields (see Figure 2(c) and 2(d)) suggests the existence of the quasi-stable active state of the electrode, and a more detailed study is in progress.

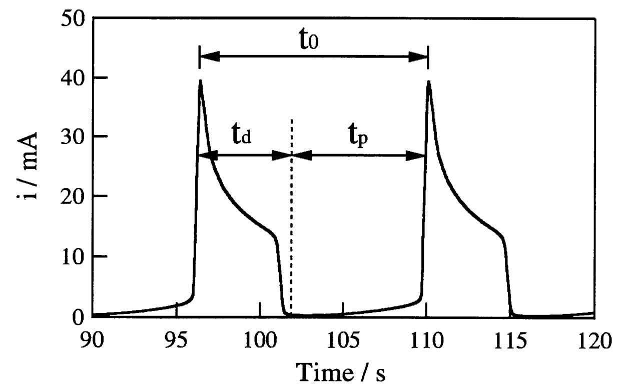

Figure 3. Close-up view of the current oscillation in Figure 2(a) and definition of characteristic parameters in the oscillation.

In conclusion we have examined the magnetic field effect on the feedback reaction system of the anodic current oscillations of zinc and shown that the MHD effect on the passive film formation brings about drastic changes in the oscillation behavior. Our result implies that the influence of the magnetic field is more significant in feedback systems because disturbing only one part of a series of reactions leads to a breakdown of the feedback.

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References and Notes

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