Effect of Chloride Ions in Electrowinning Solutions on Zinc Deposition Behavior and Crystal Texture

Keisuke Kashida¹,*, Satoshi Oue² and Hiroaki Nakano²

¹Department of Materials Science & Engineering, School of Engineering, Kyushu University, Fukuoka 819–0395, Japan
²Department of Materials Science & Engineering, School of Engineering, Kyushu University, Fukuoka 819–0395, Japan

To clarify the effect of chloride ions on Zn electrowinning in terms of deposition behavior and crystal texture, the partial polarization curve, current efficiency, and AC impedance for Zn deposition as well as its morphology and crystal orientation were investigated. In solutions containing chloride ions, the partial polarization curve for Zn deposition was evidently depolarized, and the degree of depolarization increased when increasing the concentration of chloride ions from 300 to 6,000 mg/L. The exchange current density for Zn deposition increased with increasing chloride ion concentration. Conversely, the capacity of the electric double layer increased with increasing chloride ion concentration from 300 to 1,200 mg/L; however, from 3,000 to 6,000 mg/L, the capacity decreased and approached that obtained from a chloride ion-free solution. On the other hand, the partial polarization curve, current efficiency, and AC impedance for Zn deposition as well as its morphology and crystal orientation were investigated. In solutions containing chloride ions, the partial polarization curve for Zn deposition was evidently depolarized, and the degree of depolarization increased when increasing the concentration of chloride ions from 300 to 6,000 mg/L. The exchange current density for Zn deposition increased with increasing chloride ion concentration. Conversely, the capacity of the electric double layer increased with increasing chloride ion concentration from 300 to 1,200 mg/L; however, from 3,000 to 6,000 mg/L, the capacity decreased and approached that obtained from a chloride ion-free solution. On the other hand, the partial polarization curve for hydrogen evolution was almost unchanged by the presence of chloride ions. As a result, the current efficiency of Zn deposition increased by 5–7% and 1.7% in the initial stage of deposition (up until the thickness of Zn reached approximately 2.1 μm) and at 500 A/m² for 6 hours (482 μm), respectively. With the addition of 300 to 1,200 mg/L of chloride ions, the deposited Zn exhibited a preferred orientation of [0001] plane, and it increased with increasing chloride ion concentration, which is attributed to a decrease in the overpotential for Zn deposition; however, no preferred orientation of a specific plane was shown in the deposits when increasing the concentration of chloride ions above 3,000 mg/L. Some spherical concavities resulting from traces of evolved hydrogen gas were observed on the surface of deposited Zn, and the size of the concavities increased with increasing chloride ion concentration. The size of platelet crystals of the deposited Zn decreased with increasing chloride ion concentration, which indicates that the chloride ions possibly promote the nucleation rate of Zn crystals due to specific adsorption onto the cathode.

(Received April 27, 2017; Accepted June 28, 2017; Published August 4, 2017)

Keywords: zinc, electrowinning, chloride ions, current efficiency, polarization, depolarization

1. Introduction

During electrodeposition of Zn from an electrowinning solution containing a large amount of sulfuric acid, hydrogen evolution occurs on the cathode only at low current densities. With an increase in the current density, Zn deposition commences when the cathode is polarized to reach the equilibrium potential of Zn. The minimum current density required for initiating Zn deposition has been named the critical current density. For Zn electrowinning from highly concentrated sulfuric acid solution, the critical current density for Zn deposition increases due to impurities contaminating the solution, resulting in a significant decrease in current efficiency of the deposition. Therefore, there are many studies concerning the effect of impurities on the critical current density and current efficiency of Zn deposition.¹–⁹) Fukushima et al. previously classified the impurities into four groups by comparing the critical current density reported by Ohyama¹⁰ with that by Tainton,¹¹ and reported the effects of the impurities of each group on the critical current density for Zn deposition.¹⁰,¹¹) The critical current density reported by Tainton is the current density at which Zn begins to deposit onto an impurity metal cathode from an impurity-free electrowinning solution,¹¹ and the critical current density by Ohyama is the minimum current density needed to initiate Zn deposition on a pure Zn cathode from an impurity-containing solution.²) These impurities are metal ions such as Co, Ni, Fe, Cu, Cd, Al, Pb and Ag, and semimetal ions such as Sb, As and Ge, which derive from the ore; however, there have been few reports on the effect of nonmetallic ions. Therefore, Nakano et al. selected chloride ions as nonmetallic ions and investigated the effect of chloride ions on the deposition behavior and surface morphology of Zn.¹²) As a result, it was reported that the partial polarization curve for Zn deposition shifted to noble potential direction upon the addition of small amounts of chloride ions, and the current efficiency of Zn deposition in the initial stage of deposition increased with increasing chloride ions.¹²) The shift of cathode potential for reduction reaction to noble potential direction is referred to as depolarization. However, only two concentrations of chloride ions, 600 and 6,000 mg/L, were investigated, and the effect of chloride ions on the Zn deposition behavior was examined only in the initial stage of deposition (up until the thickness of Zn reached approximately 10 μm). There are many ambiguities regarding the effect of chloride ions on the current efficiency and crystal texture of Zn deposited by long-term electrolysis. Therefore, in this study, to elucidate this effect, the partial polarization curve, current efficiency, and AC impedance for Zn deposition were investigated in the solutions containing five different concentrations of chloride ions from 300 to 6,000 mg/L, and the morphology and crystal orientation of Zn deposited with thicknesses of approximately 2.1 and 482 μm were analyzed.

2. Experimental

Table 1 shows the electrolyte compositions and electrolysis conditions for the short-time electrolysis used to investi-
gate the deposition behavior and crystal morphology of Zn in the initial stages of deposition. An electrolytic solution was prepared by dissolving ZnO with purity of 99.999% (0.765 mol/L) in distilled and ion-exchanged water containing sulfuric acid. The concentration of free sulfuric acid was 1.53 mol/L. Chloride ions were added in the form of HCl, at concentrations of 300, 600, 1,200, 3,000, and 6,000 mg/L (0.00846, 0.0169, 0.0338, 0.0846, and 0.169 mol/L). Although the chloride ions were reported to be present in an amount of 41 to 350 mg/L into the practical electrolyte,\textsuperscript{(13)} in this study, a larger amount of chloride ions were added to make their effect on the deposition behavior and crystal texture of Zn clear. An Al sheet and a Pt sheet with the same area of 1 cm × 2 cm were used as the cathode and anode, respectively. Prior to electrodeposition, the working electrode was carefully polished and buffed with Nos. 600, 1,500, and 2,000 emery paper before acid pickling and electrolytic degreasing were performed. The electrodeposition was performed in 0.5 L of a non-agitated solution at 40 °C. The total polarization curve was obtained by measuring the corresponding cathode potential while changing the current density every 3 min in a range from 0.01 to 2,000 A/m². The partial polarization curves were obtained via electrodeposition under coulostatic (50 kC/m²) and galvanostatic conditions for a current density range from 50 to 2,000 A/m². The deposits were dissolved from the cathode using nitric acid, and Zn was quantitatively analyzed using inductively coupled plasma spectroscopy to calculate the current efficiency of Zn deposition. The partial current densities for Zn and H₂ evolutions were calculated in each case by multiplying the half-width of the X-ray diffraction peak corresponding to the 0002 reflection. The cross-sectional morphologies of the deposited Zn was calculated using the Scherrer equation\textsuperscript{(15)} from the half-width of the X-ray diffraction peak corresponding to the 0002 reflection. The AC impedance was measured at 200 A/m² during Zn deposition. To obtain Nyquist plots, the frequency dependence of the AC impedance and the phase difference were measured for 1,600 s using a frequency-response analyzer at 50 A/m² (±10 mA sine wave, 10 × 10⁻³ to 10⁵ Hz, 10 points/decade).

To investigate the effect of chloride ions on the current efficiency and crystal texture of Zn deposited by long-term electrolysis, Zn electrodeposition was performed by circulating 3.0 L of solution under galvanostatic conditions of 500 A/m² at 40 °C for 6 h. An Al sheet and a Zn sheet with the same area of 6 cm × 8 cm were used as the cathode and anode, respectively. Zn sheet was used to prevent chloride ions from oxidizing at anode. The size of the electrolytic cell was 8.5 cm (length) × 13 cm (width) × 9.5 cm (depth), and the capacity of the electrolyte and the anode–cathode distance were 1.05 L and 3 cm, respectively. Table 2 lists the conditions used for long-term electrolysis. 2.52 mol/L of Zn²⁺ ions were continuously supplied into the circulation tank at a rate of 0.26 mL/min, and the inflow from the circulation tank to the electrolysis tank was 150 mL/min. The current efficiency of Zn deposition was calculated from the mass difference of the cathode before and after electrolysis. The surface and cross-sectional morphologies of the deposited Zn were observed using a scanning electron microscope (SEM). The crystal orientation of the deposited Zn was determined using the method introduced by Wilson and Rogers\textsuperscript{(4)} with an X-ray diffraction intensity of 0002 to 1122 reflection. The crystallite size of the deposited Zn was calculated using the Scherrer equation\textsuperscript{(15)} from the half-width of the X-ray diffraction peak corresponding to the 0002 reflection. The cross-sectional texture of the deposited Zn was investigated by electron backscatter diffraction (EBSD). Prior to obtaining EBSD, the sample was embedded in a conductive resin, and the cross section was polished to a mirror finish using aluminum powders with grain sizes of 1, 0.3, and 0.1 µm, after which etching was performed by Ar ion milling. Using EBSD, the crystallographic orientations of the reference direction (RD, i.e., the direction normal to the surface of the deposited Zn) were examined.

### 3. Results and Discussion

#### 3.1 Effect of chloride ions on Zn deposition behavior during the initial stage of deposition

Figure 1 shows the effect of chloride ions on the total polarization curve for Zn deposition. In total polarization, the current for hydrogen evolution was detected at the potential region more noble than the equilibrium potential of Zn, \( E_{Zn}^{0} \approx \) (−0.766 V), regardless of whether chloride ions were present or not, whereas Zn deposition began near the equi-
librium potential of Zn. Although the effect of chloride ions on the polarization curve in the region of hydrogen evolution was not observed, the polarization curve in the region of Zn deposition evidently shifted to noble potential direction with the coexistence of chloride ions. Therefore, the effect of chloride ions on the partial polarization curves for Zn deposition and hydrogen evolution in the potential region less noble than the equilibrium potential of Zn was also investigated.

Figure 2 shows the partial polarization curves for Zn deposition in solutions containing various amounts of chloride ions. The partial polarization curves significantly shifted to noble potential direction with 300 mg/L of chloride ions compared with chloride ion-free solution. When increasing the chloride ions to more than 300 mg/L, the degree of depolarization increased with increasing chloride ion concentration. The partial polarization curve curved greatly at Zn partial current densities of 500 to 700 A/m² regardless of whether chloride ions were present or not. The depolarization effect increased with increasing chloride ion concentration in both regions where the charge-transfer overpotential occurred at current densities less than 500 A/m² and the diffusion overpotential increased at current densities more than 700 A/m². The exchange current density \( i_0 \) for Zn deposition was measured at the equilibrium potential of Zn (−0.766 V) by extrapolation of the Tafel plot of the Zn partial polarization curve at current densities less than 200 A/m².

Figure 3 shows the relationship between the exchange current density for Zn deposition and the concentration of chloride ions in solution. The exchange current density with 300 mg/L of chloride ions was two times larger than that without chloride ions, and increased significantly with the concentration of chloride ions above 300 mg/L. This indicates that chloride ions promote the charge-transfer process for Zn deposition.

Figure 4 shows the partial polarization curves for hydrogen evolution in solutions containing various amounts of chloride ions. The partial polarization curve for hydrogen evolution was almost linear at potentials from −0.8 to −0.88 V, and rarely changed despite the coexistence of 300 to 6,000 mg/L of chloride ions.

Figure 5 shows the current efficiency of Zn deposition at each current density in solutions containing various amounts of chloride ions. Whether chloride ions were present or not, the current efficiency increased with increasing current density in a range less than 1000 A/m², reached maximum at 1,000 A/m², and then decreased somewhat at 2,000 A/m². The current efficiencies at all measured current densities were higher with chloride ions than without. The current efficiency increased with increasing chloride ion concentration. When increasing the concentration of chloride ions to 6,000 mg/L, the current efficiency was 5–7% higher than that without chloride ions at all measured current densities. The current efficiency of Zn deposition increased with the coexistence of chloride ions, which is expected from the polarization curves for Zn deposition and hydrogen evolution shown in Figs. 2 and 4. That is, with the coexistence of chlo-
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The presence of chloride ions in electrowinning solutions affects the deposition of zinc. This study explores the impact of varying chloride ion concentrations on the efficiency and morphology of zinc deposition.

### Current Efficiency of Zinc Deposition

Current efficiency is a measure of the effectiveness of the electrode process. Figure 5 illustrates the current efficiency of zinc deposition at various chloride ion concentrations. The efficiency decreases as the chloride ion concentration increases, indicating a decrease in the reaction rate. This is due to the electron transfer process being rate-determining and the Tafel equation being completed, as can be seen from Figure 2.

### Nyquist Plots

Figure 6 displays Nyquist plots obtained at 200 A/m² in solutions containing various amounts of chloride ions. The plots show a decrease in the capacitive double layer resistance with increasing chloride ion concentration, which is indicative of the formation of weak complexes or reaction intermediates involving chloride ions.

The Nyquist plots are significant as they provide insight into the electron transfer process. By observing the diameter of the semicircle, the capacity of the electric double layer in solutions containing various amounts of chloride ions can be calculated. The semicircle diameter increases with increasing chloride ion concentration due to decreasing the capacity of the electric double layer with chloride ion concentration.

### Polarization Resistance

Figure 7 illustrates the polarization resistance for zinc deposition and the capacity of the electric double layer under different chloride ion concentrations. The polarization resistance significantly decreases upon the addition of 300 mg/L of chloride ions and further decreases with increasing chloride ion concentration. Conversely, the capacity of the electric double layer increases with increasing chloride ion concentration from 300 to 1,200 mg/L; however, it decreases from 3,000 to 6,000 mg/L, the capacity decreases and approaches that obtained from a chloride ion-free solution. It has been reported that the specific adsorption of chloride ions increases the capacity of the electric double layer. The increase in the capacity of the electric double layer with chloride ion concentration from 300 to 1,200 mg/L demonstrated by this study can be attributed to the specific adsorption of the chloride ions.

The reason for the decrease in the capacity of the electric double layer with chloride ion concentration from 3,000 to 6,000 mg/L is unknown and should be investigated further in future.

It has been reported that the exchange current density of a reaction at a metal electrode is affected by the anion in the solution. The electron shell of ions becomes a dipole due to polarization which shows the forming regions of positive and negative charge. It is known that there is a correlation between the polarization and the exchange current density of the metal electrode in the reaction, and the exchange current density of the reaction increases with increasing polarization of the anion in solution. The polarizability of chloride ions is larger than that of other anions; as a result, the chloride ions promote the deposition of most metal. For example, it was reported that the polarizability of chloride ions (8.9 cm³/mol) is larger than that of sulfate ions (3.9 cm³/mol); the exchange current density for zinc deposition in a sulfate solution is 3 × 10⁻⁴ A/cm², and it is 3 × 10⁻² A/cm² in chloride solutions.

On the other hand, it has been reported that the overpotential for a cathode reaction decreases due to a decrease in the potential at the inner Helmholtz plane by the specific adsorption of anions on the cathode, according to the model of electrode potential distribution in Helmholtz double layers. By increasing the polarizability of the anions, both the adsorption ability of the anions onto the cathode and complexation ability with the metal ions increase. In this study, the depolarization of the zinc deposition potential observed in the presence of chloride ions is possibly caused by a decrease in the potential at the inner Helmholtz plane due to the specific adsorption of chloride ions or by a promoting effect on deposition due to the formation of weak complexes or reaction intermediates involving chloride and Zn²⁺ ions.

Figure 8 shows the surface morphology of zinc deposited at different current densities in solutions containing various amounts of chloride ions. The size of blocks comprising crystal grains became larger with the coexistence of chloride ions. This tendency is more evident upon increasing the concentration of chloride ions to 6,000 mg/L. The surface of...
blocks comprising crystal grains became smoother with the coexistence of chloride ions. On the other hand, the block size of crystals decreased with increasing current density.

3.2 Effect of chloride ions on the crystal texture of Zn obtained by long-term electrolysis

Figure 9 shows the current efficiency of Zn deposition at 500 A/m² for 6 hours in solutions containing various amounts of chloride ions. The current efficiency increased by 1.1% upon the addition of 300 mg/L of chloride ions and further increased with increasing chloride ion concentration above 300 mg/L. The current efficiency with 6,000 mg/L of chloride ions was 1.7% higher than that without chloride ions.

Figure 10 shows the surface morphology of Zn deposited at 500 A/m² for 6 hours in solutions containing various amounts of chloride ions. Some spherical concavities were observed on the surface of deposited Zn regardless of whether chloride ions were present or not. This concavity may result from traces of evolved hydrogen gas. The size of spherical concavities increased with increasing chloride ion concentration. In particular, when increasing the concentration of chloride ions to 6,000 mg/L, numerous layered spherical concavities were observed all over the surface of deposited Zn. The amount of hydrogen evolution seems to decrease with increasing chloride ion concentration because the current efficiency of Zn deposition increased with increasing chloride ion concentration. The decrease in the number of spherical concavities suggests a decrease in the desorption capability of hydrogen gas from the deposited Zn or an increase in the nonuniformity of Zn crystal growth, with increasing chloride ion concentration.

Figure 11 shows the surface morphology of areas without the concavities of deposited Zn, which was observed at a higher magnification. Zn deposited from the chloride ion-free solution comprised platelet crystals which significantly inclined to the substrate. On the contrary, with 300 to 1,200 mg/L of chloride ions, Zn platelet crystals became parallel to the substrate, and the [0001] Zn basal plane of the hcp structure was observed on the outermost surface. Upon increasing the concentration of chloride ions to 3,000 mg/L, Zn platelet crystals became smaller and layered inclining to the substrate. With further increasing the chloride ions to 6,000 mg/L, the clear Zn platelet crystals disappeared and the grain size became smaller.

Figure 12 shows the crystal orientation of Zn deposited at 500 A/m² for 6 hours in solutions containing various amounts of chloride ions. Zn deposited from the chloride ion-free solution showed somewhat preferred orientation of the {10-13} plane. On the contrary, with 300 to 1,200 mg/L of chloride ions, the preferred orientation of [0001] plane was significantly observed. Upon increasing the concentration of chloride ions to 3,000 mg/L, the preferred orientation of [0001] plane disappeared, and the orientation of {1013} plane increased somewhat, which was almost the same trend.
as that from the chloride ions-free solution. With further increasing the concentration of chloride ions to 6,000 mg/L, the deposited Zn showed a texture close to a non-oriented dispersed type without the preferred orientation of a specific plane. Comparing the surface morphology of deposited Zn (Fig. 11) with the crystal orientation (Fig. 12), the angle of inclination of Zn platelet crystals to the substrate decreased upon increasing the orientation index of the {0001} plane, suggesting that the crystal orientation of deposited Zn corresponds to the macro surface morphology.

Figure 13 shows the cross-sectional SEM images of Zn deposited at 500 A/m² for 6 hours in solutions containing various amounts of chloride ions.
from the chloride ion-free solution was slightly rough, but it became smoother with 300 to 1,200 mg/L of chloride ions, probably because the Zn platelet crystals became parallel to the substrate due to the preferred orientation of \{0001\} plane at these chloride ion concentrations. When increasing the concentration of chloride ions to 6,000 mg/L, voids were observed at the surface and inside the deposited Zn, as shown in Fig. 10. These voids probably result from traces of evolved hydrogen gas.

Figures 14 and 15 shows the crystal orientation mapping images by EBSD of Zn deposited at 500 A/m² for 6 hours in solutions containing various amounts of chloride ions. For the EBSD, the crystallographic orientations of the RD, i.e., the direction normal to the surface of the deposited Zn, are shown. In the solution without chloride ions, as shown in Fig. 14 (a), the deposited Zn exhibited a non-oriented dispersed type of fine crystals in the initial stage of deposition, and at a thickness above 10 μm, the deposited Zn shifted to epitaxial growth that the deposits succeed the crystallographic orientation of substrate, resulting in large grains. At a thickness over 50 μm, the deposited Zn comprised both inclined fibrous type crystals with the \langle1013\rangle, \langle1012\rangle and \langle1011\rangle orientations and crystals reflecting the epitaxial growth. On the contrary, with 300 to 1,200 mg/L of chloride ions, as shown in Figs. 14 (b), (c), Fig. 15(d), the deposits exhibited fibrous type crystals with the \langle0001\rangle orientation from the initial stage of deposition. With 1200 mg/L of chloride ions, as shown in Fig. 15(d), although the deposits showed epitaxial growth with orientations besides \langle0001\rangle from the middle of the deposition onward, the deposits mostly comprised crystals with the \langle0001\rangle orientation. Upon increasing the concentration of chloride ions to 3,000 mg/L, as shown in Fig. 15(e), the fibrous type crystals with the \langle0001\rangle orientation disappeared, and the deposits exhibited a non-oriented dispersed type of fine crystals from the initial stage to the outermost surface. Upon further increasing the concentration of chloride ions to 6,000 mg/L,
as shown in Fig. 15(f), although the deposits had voids resulting from traces of evolved hydrogen at the surface and inside the deposited Zn, the deposits exhibited a non-oriented dispersed type of fine crystals from the initial stage to the outermost surface. The crystal orientation of deposited Zn examined by mapping images of EBSD is almost consistent with the surface orientation of Zn shown in Fig. 12.

Pangarov calculated the relative values of two-dimensional nucleation work for various crystal planes. By assuming that two-dimensional nuclei with the smallest nucleation work were formed at a given crystallization overpotential, he examined the overpotential dependence of the preferred orientation of the various metals deposited from aqueous solutions.21,22) According to Pangarov, the preferred orientations of hcp Zn shifted from the {0001} plane to the {1011}, {1120}, and {1010} planes (in that order) with increasing Zn deposition overpotential. In this study, the increase in the {0001} plane of the deposits obtained at 500 A/m$^2$ with the coexistence of 300 to 1,200 mg/L of chloride ions is attributed to a decrease in the overpotential for Zn deposition with chloride ions (Fig. 2). However, although the overpotential for Zn deposition at 500 A/m$^2$ decreased with 3,000 and 6,000 mg/L of chloride ions, the preferred orientation of the {0001} plane disappeared, which cannot be explained by the overpotential theory. Pangarov also suggested that the work of two-dimensional nucleation on the various crystal planes could change regardless of the overpotential when certain foreign additives were adsorbed onto the cathode.21,22) When increasing the concentration of chloride ions above 3,000 mg/L/L, the chloride ions in this study possibly affected the nucleation and growth rate of specific crystal planes.

Figure 16 shows the crystallite size of Zn deposited at 500 A/m$^2$ for 6 hours in solutions containing various amounts of chloride ions. The crystallite size of deposited Zn decreased with increasing chloride ion concentration. When the overpotential for metal deposition decreases, the nucleation rate of the deposited metal generally becomes smaller than the growth rate of the metal, thereby resulting in an increase in the crystallite size.23) However, in this study, although the overpotential for Zn deposition decreased with increasing chloride ion concentration, the crystallite size of Zn decreased, which cannot be explained by the overpotential theory. The reason for this is unknown, but the chloride ions possibly promote the nucleation rate of Zn crystals due to the specific adsorption onto the cathode. The measured crystallite size of Zn was approximately 34 to 92 nm, and the size of the platelet crystals was several tens of micrometers, as shown in Fig. 11. It was reported that the hexagonal platelets of deposited Zn comprise many particles that are several tens of nanometers in size.24) In this study, the crystallite size was determined using the half-width of the X-ray diffraction peaks, and it appears to correspond to the size of each particle that formed the platelet crystals of Zn. Upon increasing the concentration of chloride ions, the sizes of both platelet crystals and crystallites of the deposited Zn decreased, which suggests that there is a correlation between the sizes of platelet crystals and crystallites of Zn in this study.

From the above results, the existence of chloride ions in solution is favorable for an increase in current efficiency for Zn deposition from the electrowinning solution. However, the higher concentration of chloride ions cause the voids at the surface and inside of deposited Zn as shown in Figs. 10 and 13, and are known to originate the pitting corrosion of Al cathode and the dissolution of Pb-Ag alloy anode. Therefore, the proper concentration of chloride ions in solution should be hereafter investigated from the perspective of advantages and disadvantages.

4. Conclusion

The partial polarization curve, current efficiency, and AC impedance for Zn deposition and the morphology and crystal orientation of the deposited Zn were investigated to clarify the effect of chloride ions in electrowinning solutions on the deposition behavior and crystal texture of Zn. With the coexistence of chloride ions in solution, the partial polarization curve for Zn deposition was evidently depolarized, and the degree of depolarization increased with increasing chloride ion concentration from 300 to 6,000 mg/L/L. The exchange current density $i_0$ for Zn deposition increased with increasing chloride ion concentration, which indicates that the chloride ions promote the charge-transfer process for Zn deposition. The polarization resistance for Zn deposition measured by AC impedance decreased with increasing chloride ion concentration. Conversely, the capacity of the electric double layer increased with increasing chloride ion concentration from 300 to 1,200 mg/L; however, from 3,000 to 6,000 mg/L, the capacity decreased and approached that obtained from a chloride ion-free solution. On the other hand, the partial polarization curve for hydrogen evolution was almost unchanged with the coexistence of chloride ions. As a result, the current efficiency of Zn deposition increased by 5–7% and 1.7% in the initial stage of deposition (up until the thickness of Zn reached approximately 2.1 $\mu$m) and at 500 A/m$^2$ for 6 hours (482 $\mu$m), respectively.

With the addition of 300 to 1,200 mg/L of chloride ions, the deposited Zn exhibited a preferred orientation of [0001] plane, which is attributed to a decrease in the overpotential for Zn deposition; however, no preferred orientation of a specific plane was shown in the deposits when increasing the concentration of chloride ions above 3,000 mg/L. Some spherical concavities resulting from traces of evolved hydro-
gen gas were observed on the surface of deposited Zn, and the size of the concavities increased with increasing chloride ion concentration. The size of platelet crystals of the deposited Zn decreased with increasing chloride ion concentration, which indicates that the chloride ions possibly promote the nucleation rate of Zn crystals due to specific adsorption onto the cathode.

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