Electrodeposition Behavior of Zn–Ni Alloys from an Alkaline Zincate Solution Containing Ethylenediamine

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Electrodeposition behavior of Zn–Ni alloys was investigated at current densities of 5–500 A·m−2 and a charge of 5 × 10^4 C·m−2 at 308 K in an unagitated zincate solution containing ethylenediamine (EDA), which forms a stable complex with Ni^{2+} ions. In the case of the TEA solution, the Zn–Ni alloy exhibited normal codeposition at low current densities, wherein electrochemically more noble Ni deposited preferentially, while it exhibited anomalous codeposition at high current densities, wherein less noble Zn deposited preferentially. In the EDA solution, the alloy exhibited anomalous codeposition at high current densities; on the other hand, even at low current densities, the Ni content in the deposit was almost identical with the composition reference line, showing a behavior similar to anomalous codeposition. In the EDA solution, Ni deposition and H₂ evolution were significantly suppressed over a larger region of current densities, showing the formation of an inhibitor for deposition, which results from Zn^{2+} ions in the cathode layer. The dependence of the current efficiency for alloy deposition on the current density was smaller in the EDA solution than in that containing TEA. In the TEA solution, the underpotential deposition of Zn apparently occurred with Ni, while in the EDA solution, the underpotential deposition of Zn never occurred, because Ni deposition was suppressed by the coexistence of Zn^{2+} ions even at low current densities. The throwing power of Zn–Ni alloys in the EDA solution was better than that in the TEA solution.

KEY WORDS: zincate; zinc-nickel alloys; electrodeposition; underpotential deposition; anomalous codeposition; normal codeposition; ethylenediamine; triethanolamine.

1. Introduction

Zn–Ni alloy coatings are applied on automobiles, household electric products, and building materials owing to its superior corrosion resistance in comparison with Zn coatings.1–3) These alloy coatings are particularly useful for automobile engine parts, which require high corrosion resistance at elevated temperatures. Although the electrodeposition of Zn–Ni alloys is usually performed from sulfate and chloride solutions, cyanide and zincate solutions are better from the perspective of throwing power.4,5) However, since hydrogen cyanide is toxic, this study focuses on the electrodeposition of Zn–Ni alloys in a zincate solution containing ethylenediamine (EDA), which forms a stable complex with Ni^{2+} ions. In the case of the TEA solution, the Zn–Ni alloy exhibited normal codeposition at low current densities, wherein electrochemically more noble Ni deposited preferentially, while it exhibited anomalous codeposition at high current densities, wherein less noble Zn deposited preferentially. In the EDA solution, the alloy exhibited anomalous codeposition at high current densities; on the other hand, even at low current densities, the Ni content in the deposit was almost identical with the composition reference line, showing a behavior similar to anomalous codeposition. In the EDA solution, Ni deposition and H₂ evolution were significantly suppressed over a larger region of current densities, showing the formation of an inhibitor for deposition, which results from Zn^{2+} ions in the cathode layer. The dependence of the current efficiency for alloy deposition on the current density was smaller in the EDA solution than in that containing TEA. In the TEA solution, the underpotential deposition of Zn apparently occurred with Ni, while in the EDA solution, the underpotential deposition of Zn never occurred, because Ni deposition was suppressed by the coexistence of Zn^{2+} ions even at low current densities. The throwing power of Zn–Ni alloys in the EDA solution was better than that in the TEA solution.

In addition, the effect of additives on the throwing power of a Zn–Ni alloy deposited from the zincate solution was investigated by the authors; the throwing power of a deposited Zn–Ni alloy was improved by the addition of ethylenediamine (EDA) as a complexing agent for Ni^{2+}. The deposition of Zn–Ni alloys from a zincate solution containing tartaric acid,6) TEA,9) and N-[1-(2-pyrrolidonyl) ethyl] methacrylamide10) as a complexing agent for Ni^{2+} has been reported. However, there is an ambiguity in the deposition behavior of Zn–Ni alloys from a zincate solution containing EDA. In this study, the deposition of a Zn–Ni alloy was performed in a zincate solution containing EDA as a complexing agent for Ni^{2+}, and the deposition behavior was compared with that reported6,7) from a zincate solution containing TEA.

2. Experimental

Table 1 shows the composition of the zincate solution and

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the electrolysis conditions for Zn–Ni alloy deposition. The electrolytic solutions were prepared by dissolving reagent-grade ZnO (0.15 mol·dm⁻³), NiSO₄·6H₂O (0.016 mol·dm⁻³), NH₄CH₂CH₂NH₂ (0.36 mol·dm⁻³), and NaOH (2.5 mol·dm⁻³) in distilled and deionized water. In some experiments, deposition was conducted from pure Zn or Ni solutions to avoid the presence of ZnO or NiSO₄·6H₂O, respectively, from the standard solution described above. Electrodeposition was performed in unagitated solutions under coulostatic (5<5 C·m⁻²) and galvanostatic (5–500 A·m⁻²) conditions at 308 K. Copper sheets measuring 1×2 cm² and platinum sheets measuring 1×2 cm² were used as the cathode and anode, respectively. Cathode deposits were dissolved using nitric acid. The Zn and Ni contents of the deposited Zn–Ni alloys were quantitatively analyzed by inductively coupled plasma spectroscopy. As a result, the Ni content of the deposit and the cathode current efficiency for Zn and Ni deposition were calculated. The partial current densities for Zn and Ni deposition and H₂ evolution were calculated, in each case, by multiplying the total current density by the current efficiency. The current efficiency for H₂ evolution was calculated by subtracting the current efficiency for Zn and Ni deposition from 100%. Cathode potentials were measured using a saturated KCl, Ag/AgCl reference electrode (0.199 V vs. NHE, 298 K). Potentials were plotted with reference to the saturated KCl, Ag/AgCl reference electrode.

Table 1. Solution compositions and electrolysis conditions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mol·dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.15</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.016</td>
</tr>
<tr>
<td>NH₄CH₂CH₂NH₂</td>
<td>0.36</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.5</td>
</tr>
</tbody>
</table>

NHE. The throwing power of deposited Zn–Ni alloys was evaluated by the Hull cell test, which was performed in unagitated solutions under coulostatic (5×10⁴ C·m⁻²) and galvanostatic (5–500 A·m⁻²) conditions at 308 K. Copper sheets measuring 1×2 cm² and platinum sheets measuring 1×2 cm² were used as the cathode and anode, respectively. Cathode deposits were dissolved using nitric acid. The Zn and Ni contents of the deposited Zn–Ni alloys were quantitatively analyzed by inductively coupled plasma spectroscopy. As a result, the Ni content of the deposit and the cathode current efficiency for Zn and Ni deposition were calculated. The partial current densities for Zn and Ni deposition and H₂ evolution were calculated, in each case, by multiplying the total current density by the current efficiency. The current efficiency for H₂ evolution was calculated by subtracting the current efficiency for Zn and Ni deposition from 100%. Cathode potentials were measured using a saturated KCl, Ag/AgCl reference electrode (0.199 V vs. NHE, 298 K). Potentials were plotted with reference to the NHE. The throwing power of deposited Zn–Ni alloys was evaluated by the Hull cell test, which was performed in unagitated solutions, Table 1, at an average current density of 200 A·m⁻² at 308 K using copper sheets measuring 1×2 cm² and platinum sheets measuring 1×2 cm² as the cathode and anode, respectively. The morphology of the 5-μm-thick deposits obtained at 50 and 100 A·m⁻² was observed by scanning electron microscopy (SEM). The atomic structure of the alloys was examined by X-ray diffraction (XRD).

3. Results and Discussion

3.1. Deposition Behavior of the Zn–Ni Alloy

Figure 1(a) shows the total polarization curve and the partial polarization curves of Zn and Ni for Zn–Ni alloy deposition conducted from the solution containing EDA. Results reported previously from the solution containing TEA are also shown in Fig. 1(b) for comparison. As shown in Fig. 1(a), in the total polarization curve obtained from the EDA solution, the cathode potential shifted rapidly in the less noble direction at a current density above 5 A·m⁻², and the current density rapidly increased at approximately –1.27 V. In the partial polarization curves for Zn and Ni deposition, both current densities began to increase at approximately –1.27 V and gradually increased with polarization.

At potentials more noble than –1.27 V, the partial current densities for Zn and Ni deposition were not detected. On the other hand, as shown in Fig. 1(b), in the TEA solution, the total current density and partial current densities for Zn and Ni deposition began to increase at approximately –0.9 V, and all cathode potentials for the total polarization curve and the partial polarization curves of Zn and Ni rapidly shifted in the less noble direction at a total current density above 50 A·m⁻². Then, the total current density and partial current densities for Ni and Zn deposition increased for a second time at approximately –1.3 V. In the EDA solution, no partial current densities for Zn and Ni deposition were detected at potentials more noble than –1.27 V, but the current densities began to increase at approximately –1.27 V in a manner similar to that for the TEA solution. The equilibrium potential for Zn deposition is calculated to be –1.27 V, assuming that the deposit is pure Zn. On the other hand, the equilibrium potential for Ni deposition is calculated to be –0.78 V based on the complex stability constant $K = 10^{17.53}$, which is formed by the coordination of three EDA molecules with each Ni²⁺ ion, assuming that the deposit is pure Ni.

Figure 2 shows the effect of current density on the Ni content in deposits and the current efficiency for Zn–Ni alloy deposition. The broken line in the figure shows the composition reference line (CRL) of Ni, which means that the Ni content in the solution is identical to that in the deposits. When the Ni content in the deposits is greater than CRL, normal codeposition occurs, in which electrochemically more noble Ni is deposited in preference to Zn. In contrast, when the Ni content in the deposits is less than CRL, anomalous codeposition occurs, in which less noble Zn is deposited in preference to Ni. As can be seen from Fig. 2(a), in the EDA solution, the Ni content in the deposits was near CRL and scarcely changed regardless of current density. At current densities above 100 A·m⁻², the Ni content in the deposits was below CRL, exhibiting anomalous codeposition; however, even at low current densities below 100 A·m⁻², the Ni content in the deposits was near CRL, showing a behavior similar to anomalous codeposition. The current efficiency for Zn–Ni alloy deposition was 50–60% at low current densities of 10–20 A·m⁻², but it increased to approximately
80% with increasing current density. On the other hand, as shown in Fig. 2(b), in the TEA solution, the Ni content in the deposits significantly changed at current densities of 50 to 100 A·m\(^{-2}\). At current densities below 50 A·m\(^{-2}\), the Ni content in the deposits was approximately 85 mass% above CRL, exhibiting normal codeposition, while the Ni content was less than CRL at current densities above 100 A·m\(^{-2}\), exhibiting anomalous codeposition. The current efficiency for Zn–Ni alloy deposition was low at 20–40% in the region of normal codeposition. However, the maximum value of current efficiency was higher in the TEA solution than in that containing EDA. As mentioned above, the current density dependence of the Ni content in deposits and the current efficiency for Zn–Ni alloy deposition were smaller in the EDA solution than in that containing TEA. In the TEA solution, the deposition behavior significantly changed at current densities of 50 to 100 A·m\(^{-2}\), while in the EDA solution, the behavior similar to the anomalous codeposition was evident at all current densities. In the TEA solution, the current efficiency for Zn–Ni alloy deposition significantly decreased at 500 A·m\(^{-2}\), while in the EDA solution, the degree of decrease at 500 A·m\(^{-2}\) was small. The decrease observed at 500 A·m\(^{-2}\) is attributed to the approach of the diffusion limit of Ni\(^{2+}\) and Zn\(^{2+}\) ions, as can be determined from the polarization curves shown in Fig. 1, suggesting a delay in the approach of the diffusion limit of Ni\(^{2+}\) and Zn\(^{2+}\) ions in the EDA solution.

Figure 3 shows the partial polarization curves for Zn deposition from pure Zn and Zn–Ni alloy solutions. Focusing on the initiation of Zn deposition, Zn began to deposit at approximately –1.27 V (i.e., the equilibrium potential for pure Zn deposition) from pure Zn and Zn–Ni alloy solutions containing EDA, but Zn deposits had already begun to form at potentials about 0.4 V more noble than the equilibrium potential when it was deposited from the Zn–Ni alloy solution containing TEA. This result suggests that the underpotential deposition of Zn may occur in the Zn–Ni alloy solution containing TEA, but this peculiar phenomenon does not occur in the EDA solution.

Figure 4 shows the partial polarization curves for Ni deposition from pure Ni and Zn–Ni alloy solutions. In the EDA solution, the cathode potential for Ni deposition from the Zn–Ni alloy solution shifted in the less noble direction in comparison to the equilibrium potential for Zn deposition at all current densities, exhibiting a polarization larger than that from the pure Ni solution. In contrast, in pure Ni and Zn–Ni alloy solutions containing TEA, Ni began to deposit at almost the same potential, exhibiting no effect of Zn\(^{2+}\) ions on Ni deposition at current densities below 7 A·m\(^{-2}\). However, at partial current densities above 8 A·m\(^{-2}\), the cathode potential for Ni deposition from the Zn–Ni alloy solution shifted in the less noble direction in comparison to the equilibrium potential for Zn deposition, exhibiting a polarization larger than that from the pure Ni solution.

Figure 5 shows the partial polarization curves for H\(_2\) evolution from pure Ni and Zn–Ni alloy solutions. In the EDA solution, the cathode potential for H\(_2\) evolution from the Zn–Ni alloy solution shifted in the less noble direction in comparison to the equilibrium potential for Zn deposition at total current densities above 5 A·m\(^{-2}\), exhibiting a polarization larger than that from the pure Ni solution. By contrast, in pure Ni and Zn–Ni alloy solutions containing TEA, H\(_2\) evolution began at almost the same potential, exhibiting no effect of Zn\(^{2+}\) ions on H\(_2\) evolution at cathode potentials.
more noble than −1.0 V. However, when the total current density was increased further, the cathode potential for H₂ evolution shifted in the less noble direction in comparison to the equilibrium potential for Zn deposition because of the coexistence of Zn²⁺ ions, resulting in a polarization larger than that from the pure Ni solution. H₂ evolution behavior from the pure Ni and Zn–Ni alloy solutions containing EDA and TEA showed trends almost similar to that for Ni deposition, as shown in Fig. 4. In other words, H₂ evolution and Ni deposition were significantly suppressed by the coexistence of Zn²⁺ ions. In the TEA solution, H₂ evolution and Ni deposition were suppressed at certain great current densities by the coexistence of Zn²⁺ ions, while in the EDA solution, they were suppressed over a wider current density region.

To clarify the effect of EDA on Zn and Ni deposition and H₂ evolution, the deposition behavior was investigated from the perspectives of pure Zn, Ni and (Zn, Ni)-free solutions containing EDA and TEA. **Figure 6** shows the partial polarization curves for Zn deposition from pure Zn solutions containing EDA and TEA. The partial polarization curve for Zn deposition scarcely changed by the addition of EDA, suggesting that EDA as a ligand appears to marginally affect Zn²⁺ ions. In contrast, the partial polarization curve for Zn deposition was slightly polarized by the addition of TEA, showing the suppression effect of TEA on Zn deposition.

**Figure 7** shows the partial polarization curves for Ni deposition from the pure Ni solutions containing EDA and TEA. The partial polarization curve for Ni deposition was more polarized at all current densities from the EDA solution than from that containing TEA. The complex stability constants K are 10¹⁷.5 and 10⁴.74 which are formed by the coordination of three EDA and two TEA molecules with each Ni²⁺ ion, respectively, showing the formation of a more stable Ni complex in the EDA solution. Therefore, the potential for Ni deposition is thought to be more polarized from the EDA solution than from that containing TEA.

**Figure 8** shows the partial polarization curves for H₂ evolution from (Zn, Ni)-free solutions containing EDA and TEA. At low current densities below 0.5 A·m⁻², H₂ evolution was slightly suppressed by the addition of EDA and TEA, but the effect of EDA on H₂ evolution disappeared at current densities above 0.5 A·m⁻². At current densities above 2 A·m⁻², H₂ evolution was slightly suppressed by the addition of TEA, showing a trend similar to the suppression effect on the Zn deposition shown in **Fig. 6**. The maximum value of the current efficiency for Zn–Ni alloy deposition was higher from the TEA solutions (Fig. 2). This is attributed to a larger suppression effect of TEA on H₂ evolution.

To compare the deposition behavior of Zn–Ni alloys from sulfate and zincate solutions, the dependence of the alloy composition in the deposits and the current efficiency for Zn–Ni alloy deposition on the current density in a sulfate solution is shown in **Fig. 9**. For Zn–Ni alloy deposition from the sulfate solution, although normal codeposition, in
which more noble Ni deposited in preference to Zn, was observed at lower current densities, evolution of H₂, which is electrochemically most noble, occurred preferentially, resulting in a current efficiency of approximately zero. \(^{14-18}\) On the other hand, at higher current densities required to obtain practical Zn-Ni alloys with high current efficiency, specific anomalous deposition, in which electrochemically less noble Zn deposited in preference to Ni, was observed.\(^{14-18}\) To explain the anomalous codeposition from a sulfate solution, a hydroxide suppression mechanism is proposed as follows.\(^{14-18}\) (1) Ni deposition from hydrated ions proceeds by a multistep reduction mechanism through the adsorption of intermediate hydroxyl-group-containing NiOH, and the adsorption site for NiOH is limited. (2) Zn(OH)₂, which results from an increase in pH at the cathode layer caused by H₂ evolution during electrolysis, adsorbs on the cathode and obstructs the site for NiOH adsorption, thereby suppressing Ni deposition.

In the case of the zincate solution containing TEA, as shown in Fig. 2(b), normal codeposition occurred at lower current densities, in which more noble Ni deposited preferentially, while anomalous codeposition occurred with increasing current density, exhibiting a behavior similar to that of the sulfate solution. However, in the EDA solution, as shown in Fig. 2(a), a behavior similar to anomalous codeposition was observed even at lower current densities, clearly exhibiting a trend different from that of the sulfate solution. Even in the zincate solution, as shown in Figs. 4 and 5, Ni deposition and H₂ evolution were considerably suppressed by the coexistence of Zn²⁺ ions. Since it has been reported that Zn(OH)₂ formed at the cathode layer suppresses Ni deposition and H₂ evolution in a sulfate solution,\(^{15-18}\) some inhibitor for Ni deposition and H₂ evolution resulting from Zn²⁺ ions also appears to be formed in the zincate solution. Focusing on the difference between EDA and TEA addition, in the TEA solution, Ni deposition was not affected by the coexistence of Zn²⁺ ions at low current densities, while in the EDA solution, Ni deposition was suppressed by the coexistence of Zn²⁺ ions at all current densities (Fig. 4).

Since the Ni complex is more stable in EDA solution than in that containing TEA, Ni deposition was inherently more suppressed in the EDA solution (Fig. 7). As a result, Ni deposition is thought to be more affected by some inhibitor resulting from Zn²⁺ ions in the EDA solution than in that containing TEA. Therefore, in the EDA solution, Ni deposition was suppressed by the coexistence of Zn²⁺ ions even at low current densities, showing a behavior similar to anomalous codeposition. Moreover, in the total polarization curve from the Zn-Ni alloy solution shown in Fig. 1, the cathode potential rapidly shifted in the less noble direction at current densities above a certain value and reached the equilibrium potential for Zn deposition. These current density regions, which rapidly shifted the cathode potential, were 5 to 10 A·m⁻² and 50 to 100 A·m⁻² in the EDA and TEA solutions, respectively, showing that the cathode potential rapidly shifted in the less noble direction at lower current densities in the EDA solution than in that containing TEA. This result is attributed to a greater suppression effect on Ni deposition in the EDA solution than in that containing TEA.

In the TEA solution, since Ni deposition was not suppressed by the coexistence of Zn²⁺ ions at low current densities, Zn is reported to deposit at potentials about 0.4 V more noble than –1.27 V \(\approx \) the equilibrium potential for pure Zn deposition) when it was deposited from the Zn-Ni alloy solution in the form of the intermetallic compound Ni₅Zn₂¹ (Figs. 1 and 3).\(^{6,7}\) In other words, in the TEA solution, the underpotential deposition of Zn apparently occurred with Ni. However, in the EDA solution, since Ni deposition is suppressed by the coexistence of Zn²⁺ ions even at low current densities, the intermetallic compound Ni₅Zn₂¹ cannot be formed, resulting in no underpotential deposition of Zn, as shown in Figs. 1 and 3. Therefore, Zn begins to deposit from the equilibrium potential for pure Zn deposition.

3.2. Structure of the Deposited Zn–Ni Alloys

Figure 10 shows XRD patterns of the deposits obtained at 100 A·m⁻². The Ni content in the deposits obtained from the EDA and TEA solutions were 9.8 and 8.4 mass%, respectively. The deposit obtained from the TEA solution, shown in Fig. 10(b), exhibited single-phase Zn peaks and
peaks from the intermetallic compound Ni$_3$Zn$_{21}$, while that obtained from the TEA solution, shown in Fig. 10(a), exhibited only peaks resulting from the intermetallic compound Ni$_3$Zn$_{21}$. The XRD peaks of the deposits obtained from both solutions were slightly shifted in the higher angle direction. Since the peaks of the Cu substrate were also slightly shifted in the same manner, this shift may be attributed to an incomplete zero-degree adjustment of 2θ.

Figure 11 shows SEM images of Zn–Ni alloy deposits obtained at 50 and 100 A·m$^{-2}$. The Ni content in the deposits obtained at 50 and 100 A·m$^{-2}$ from the EDA solution were 13.8 and 9.8 mass%, respectively, while those obtained at 50 and 100 A·m$^{-2}$ from the TEA solution were 79.2 and 8.4 mass%, respectively. The deposit obtained at 50 A·m$^{-2}$ from the EDA solution, shown in Fig. 11(a), was composed of a trigonal-pyramid-like smooth surface, while that obtained at 100 A·m$^{-2}$, shown in Fig. 11(b), showed the indistinct edge of a trigonal pyramid. Moreover, on the deposits obtained at 100 A·m$^{-2}$, small granular crystals appearing to be crystalline nuclei were observed over the entire surface. On the other hand, the deposit obtained at 50 A·m$^{-2}$ from the TEA solution, shown in Fig. 11(c), showed a smooth surface composed of small grains, while the deposit at 100 A·m$^{-2}$, shown in Fig. 11(d), was observed to be composed of blocks of platelets. The dependence of surface morphology on the current density in the TEA solution appears to be caused by the alloy composition of the deposits. At 100 A·m$^{-2}$, since the Ni content in the deposits obtained from the EDA solution was almost identical with that from the TEA solution, the surface morphology of both deposits was compared. In the deposits obtained from the EDA solution, the surface of the platelet crystals was smoother, and the gaps between platelet crystals, which were seen in the deposits obtained from the TEA solution, were scarcely observed.

3.3. Throwing Power of the Deposited Zn–Ni Alloys

Figure 12 shows the evaluation of the throwing power determined by the Hull cell test of the Zn–Ni alloy deposits from the EDA and TEA solutions. The throwing power of the deposited Zn–Ni alloys from the EDA solution was better than that of the deposited Zn–Ni alloys from the TEA solution. It is reported that the throwing power of the deposits is improved when the current efficiency for deposition decreases with increasing current density. In both solutions, the current efficiency for Zn–Ni alloy deposition generally increased with current density, as shown in Fig. 2, indicating the disadvantage from the perspective of throwing power. Comparing the dependence of the current efficiency for Zn–Ni alloy deposition on the current density in the EDA solution with that in the TEA solution, the current density dependence was smaller in the EDA solution than in that containing TEA (Fig. 2). As a result, the throwing power of the deposited Zn–Ni alloys from the EDA solution appears to be better than that of the deposited Zn–Ni alloys from the TEA solution.

4. Conclusion

Electrodeposition of Zn–Ni alloys was performed from zincate solutions containing ethylenediamine as a complexing agent for Ni$^{2+}$ and was compared with that from solutions containing triethanolamine. In the solution containing triethanolamine, Zn–Ni alloy deposition exhibited normal codeposition at low current densities, wherein electrochemically more noble Ni deposited preferentially, and the alloy exhibited anomalous codeposition at high current densities, wherein less noble Zn deposited preferentially. In the solution containing ethylenediamine, Zn–Ni alloy deposition exhibited anomalous codeposition at high current densities; on the other hand, even at low current densities, the Ni content in the deposit was almost identical with the composition reference line, showing a behavior similar to anomalous codeposition. In the solution containing ethylenediamine, Ni deposition and H$_2$ evolution were significantly suppressed in a larger region of current densities, showing the formation of an inhibitor for deposition, which results from Zn$^{2+}$ ions in the cathode layer. The dependence of the current efficiency for alloy deposition on the current density was smaller in the solution containing ethylenediamine than in that containing triethanolamine. In the solution containing triethanolamine, the underpotential deposition of Zn apparently occurred with Ni, while in the solution containing ethylenediamine, the underpotential deposition of Zn never occurred, because Ni deposition was suppressed by the coexistence of Zn$^{2+}$ ions even at low current densities. The throwing power of the Zn–Ni alloy was better in the solution containing ethylenediamine than in that containing triethanolamine.
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