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> APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

## Cathodic Deposition of Zinc from Dilute Solutions onto a Rotating Disc Electrode

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**Abstract**—The cathodic deposition of zinc onto a rotating disc electrode was studied. The influence exerted by various parameters on the process was examined. The observed phenomena were explained in terms of corrosion and the positive difference-effect.

Purification of sewage to remove heavy-metal ions is a problem of current importance for many industries. Various methods can be used for sewage purification, but electrochemical methods, such as electrocoagulation, electroflotation, electrodestruction, and electrodeposition of metals, are of particular interest. The electric treatment makes it possible to purify wastewater of varied composition and dispersity without raising the content of salts in a water being purified and, rather frequently, with precipitates not formed at all or formed in a considerably decreased amount [1]. Among the electrochemical methods mentioned above, the electrolysis is of special interest, since it can be performed without use of chemicals in the course of purification and yields a metal in the form of a target product, which simplifies its further processing.

The electrodeposition of metals from dilute solutions has its own specific features, which consist in that the process rate is limited by delivery of a reagent to the electrode surface. This problem can be solved by using a rotating disc electrode instead of an immobile electrode. As shown previously [2], using a rotating disc cathode allows the rate of copper electrodeposition from dilute solutions to be increased by a factor of 5-10, with a high current efficiency (CE) retained.

In this study, we continue to examine the electrodeposition of metals onto a rotating disc electrode and the cathodic deposition of zinc from solutions with concentrations of up to 1 g  $l^{-1}$ .

## **EXPERIMENTAL**

Zinc was electrodeposited in a glass cell with a rotating cathode. The cell volume was 0.5 l. As cathodes were used discs made of stainless steel, sheet copper, and aluminum. The cathode area was 160 cm<sup>2</sup>. Semi-discs made of titanium gauze coated with ruthenium(IV) oxide served as anodes. Prior to the experiments, the cathodes were trimmed with an emery paper and washed in the electrolyte solution.

The electrodes were polarized in the galvanostatic mode with a B5-49 source of stabilized current and voltage. The voltage was monitored with a V7-27 A/1 voltmeter.

The rate of rotation of the disc electrode was determined and controlled using a tachometer.



**Fig. 1.** Effect of the rotation rate  $\omega$  on the current efficiency CE by zinc in cathodic deposition from dilute solutions. Supporting electrolyte 0.5 M Na<sub>2</sub>SO<sub>4</sub>,  $c_{Zn^{2+}} = 100 \text{ mg l}^{-1}$ , pH 6, copper cathode.

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The electrolyte solutions were prepared by the gravimetric method by dissolving the appropriate dry salts in distilled water. The current efficiency was determined from the difference of the zinc concentrations before and after the electrolysis. The content of zinc(II) was determined by direct complexometric titration.

The duration of electrolysis was calculated on the basis of the initial concentration of zinc ions in the solution, so that the amount of electricity passed through the cell corresponded to the complete recovery of metal.

The dependence of CE on the rate of cathode rotation is shown in Fig. 1. It can be seen that CE is 5% for the immobile electrode. As the rotation rate is raised to 52.3 rad  $d^{-1}$ , CE increases to 35–40%. With the rotation rate raised further, CE somewhat decreases.

The pH value of the electrolyte solutions also affects the current efficiency. The dependence of CE on the solution pH passes through a maximum at pH 7 (Fig. 2).

Irrespective of the initial concentration of zinc ions, the dependences of CE on current density also pass through a maximum (Fig. 3), whose position shifts to higher current densities as the concentration of zinc ions in the electrolyte increases.

With a stainless steel electrode, no zinc is deposited onto the cathode, whereas with copper and aluminum electrodes, the cathodic deposition of zinc is rather effective (Fig. 4).

To account for the dependences obtained, it is necessary to note that the electrodeposition of metals, which stand to the left of hydrogen in the electrochemical series, is almost always complicated by a concurrent reaction of hydrogen evolution. In addition, electronegative metals can displace hydrogen from water, i.e., they may be subject to corrosion with a hydrogen and oxygen depolarization. Therefore, the CE by zinc in cathodic deposition will be determined by the relative rates of three processes: zinc recovery, hydrogen evolution, and corrosion of zinc from the electrode surface. It is also necessary to note that amphoteric metals, such as zinc, exhibit a positive difference-effect in cathodic polarization, which originates from destruction of a protective zinc oxide film upon alkalization of the near-cathode layer of the solution through cathodic evolution of hydrogen.

The flux N of a solution across the boundary diffusion layer, which appears on a rotating cathode and



**Fig. 2.** Effect of the pH of the initial solution on the CE by zinc in cathodic deposition. Supporting electrolyte 0.5 M Na<sub>2</sub>SO<sub>4</sub>,  $c_{Zn^{2+}} = 100 \text{ mg l}^{-1}$ ,  $i = 1 \text{ mA cm}^{-2}$ ,  $\omega = 52.3 \text{ rad s}^{-1}$ , copper cathode.



**Fig. 3.** Current efficiency CE by zinc in cathodic deposition from dilute solutions with various concentrations vs. current density *i*. Supporting electrolyte 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 6,  $\omega$  = 52.3 rad s<sup>-1</sup>, copper cathode. Zinc concentration (mg l<sup>-1</sup>): (a) 5, (b) 100, and (c) 1000.

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**Fig. 4.** Variation of zinc concentration  $c_{Zn}^{2+}$  in the course of electrolysis with cathodes made of different materials. Supporting electrolyte 0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 6,  $\omega = 52.3$  rad s<sup>-1</sup>. Cathode: (*I*) copper and (*2*) aluminum. ( $\tau$ ) Duration of electrolysis.

is at rest with respect to it, is directly proportional to the diffusion coefficient D of the solution and to the gradient of the solution concentration  $\Delta c$  and inversely proportional to the thickness  $\delta$  of the boundary diffusion layer  $\delta$ : [3]:

$$N = D\Delta c/\delta. \tag{1}$$

In turn,  $\delta$  can be calculated as follows [4]:

$$\delta = 1.61 D^{1/3} v^{1/6} \omega^{-1/2}, \qquad (2)$$

where v is the kinematic viscosity of the electrolyte solution (cm<sup>2</sup> s<sup>-1</sup>), and  $\omega$  is the angular velocity of rotation of the electrode (s<sup>-1</sup>).

The concentration difference is given by

$$\Delta c = c_0 - c_c, \tag{3}$$

where  $c_0$  is the concentration of ions in the solution bulk, and  $c_c$  is the concentration of ions at the electrode surface.

The latter concentration can be calculated as follows:

$$c_{\rm c} = c_0 - i_{\rm c} \delta / (DFz_{\rm i}), \qquad (4)$$

where  $i_c$  is the current flowing to the cathode, and  $z_i$  is the ion charge.

Substituting the expression for the boundary layer thickness into Eq. (4), we obtain

$$c_{\rm c} = c_0 - 1.62 i_{\rm c} v^{1/6} / (D^{1/3} F z_{\rm i} \omega^{1/2}).$$
 (5)

According to (5), the concentration of ions at the cathode surface increases with the rotation rate. This allows electrolysis to be performed at higher current densities.

At the same time, at high flow velocities of the electrolyte, the cathodically formed alkali is removed from, and the oxidant (e.g., oxygen) delivered to the cathode surface. As a result, the surface of freshly deposited zinc has enough time to be covered with a protective oxide film. This explains why CE increases when the rate of cathode rotation is raised to 52.3 rad  $s^{-1}$  (Fig. 1). However, as the rotation rate increases further, CE decreases somewhat, which is probably due to the fact that, at higher flow velocities of the electrolyte, the corrosion becomes the so-called impingement corrosion. In this case, the passivating films, which were formed and existed before the onset of corrosion, are torn off the metal surface by a liquid jet, so that the metal without a protective film undergoes intense corrosion [5].

The shape of the obtained CE-vs.-pH curve (Fig. 2) can be accounted for by the influence of acidity on processes of hydrogen evolution and zinc corrosion, which occur simultaneously at the cathode.

It is known that the dependence of the hydrogen overvoltage on the solution pH passes through a maximum at pH 7 [6]. Because zinc is an amphoteric metal, the rate of its corrosion also depends on the solution pH. The corrosion rate is the lowest in neutral solutions and increases dramatically in acid and alkaline solutions [5, 7].

Thus, the appearance of a peak in the CE-vs.-pH curve (Fig. 2) is due to the fact that, in acid and alkaline solutions, the processes of zinc corrosion and hydrogen evolution prevail over the cathodic deposition of zinc.

The effect of current density on the CE by zinc in cathodic deposition was studied in solutions with initial pH 6. The appearance of extrema in the CE–i dependences is probably due to the fact that, at low rates of the cathodic process, the pH of the nearelectrode layer increases, but does not exceed 7. Under these conditions, the rates of hydrogen evolution and zinc corrosion are the lowest. Therefore, the CE by zinc in its cathodic recovery increases with current density at low polarizing currents. After the current densities at which pH 7 is established in the near-electrode layer are attained, the rates of cathodic hydrogen evolution and zinc corrosion start to increase. Therefore, CE by zinc starts to decrease after a certain polarizing current density is reached.

Presumably, the shift of the peak positions to higher current densities, observed in the CE-i dependences as the concentration of zinc(II) increases, is due to acceleration of the cathodic recovery of zinc

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owing to a decrease in the overvoltage. In this case, the rates of other concurrent processes remain virtually unchanged.

When zinc is deposited onto the surface of metals that have a more positive standard potential than zinc, it forms with them short-circuited galvanic microcells [8], in which the more electropositive metal is a cathode, on which hydrogen evolution occurs, and zinc is a soluble anode. The dissolution of zinc is limited by the cathodic evolution of hydrogen, which, in turn, is dependent on the overvoltage of hydrogen evolution on a given metal.

As is known, the overvoltage of hydrogen evolution on metals that constitute stainless steel (such as iron and nickel) is lower than that on copper and aluminum. Therefore, the rate of electrochemical corrosion of zinc on the surface of a stainless steel electrode is such that we do not observe its deposition. At the same time, the deposition of zinc onto copper and aluminum is rather effective, with the CE by zinc in cathodic deposition being as high as 30-40%.

## CONCLUSION

The study performed demonstrated that the deposition of zinc from dilute aqueous solutions onto a rotating disc electrode is complicated by intense corrosion. On an immobile cathode, the current efficiency does not exceed 5%. On a rotating electrode, the current efficiency by zinc grows with the rotation rate, to reach its maximum value (35-40%) at a rate of 52.3 rad s<sup>-1</sup>. Irrespective of the initial concentration of zinc(II) in a solution, the current efficiency first

increases and then decreases as the current density becomes higher. The pH value of the electrolyte solutions, at which the CE by zinc is at a maximum in electrodeposition from dilute solutions with concentration of up to 1 g  $l^{-1}$ , is 6–7.

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