

Kinetics and Overvoltage of the Electrodeposition of Zinc from Sulfate Solutions in the Presence of Na, Ca, and Mg Ions at a Rotating Disk Electrode

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A study of the effect of temperature on the velocity of electrodeposition and polarization of zinc in the presence of Na, Ca, and Mg ion impurities has been undertaken by the method of polarization curves using a rotating disk electrode.

In the presence of Na, Ca, and Mg ion impurities, crystallization overvoltage occurs; probably caused by difficulties in penetration of metal atoms to the growing crystal faces. The influence of metal ion impurities is probably of adsorptive character.

The results are consistent with the suggestion that metal ion impurities act to eliminate the retarding action of hydrogen. The metal ion impurities do not directly promote discharge of zinc but suppress the inhibiting action of hydrogen.

Commercial electrolytes always contain additives in the form of salts of electronegative metals: sodium, magnesium, calcium, aluminium, and manganese. The latter of these is usually introduced into the electrolyte in dioxide form for the purpose of oxidizing the ions of divalent iron to the trivalent state to effect deposition of iron as hydrate.

Most investigators consider that the ions of alkali and alkali earth metals do not exert any influence on the electrolysis of zinc.^{1,2} Izgaryshev and Maiorova³ found that the cations of the alkali and alkali earth metals serve to reduce polarization of the zinc cathode and explain this phenomenon by formation of complex ions.

Studies of hydrogen overvoltage, by Iofa *et*

*al.*⁴ have shown that addition of neutral salts to acid solutions usually causes a rise in hydrogen overvoltage; however, this effect occurs only in dilute solutions.

Pecherskaya and Stender⁵ noted that the admixtures of alkali and alkali earth metals salts cause a considerable rise in the specific resistance of zinc sulfate and they noted that the ions of electronegative metals are carried to the cathode where they do not discharge. The ions accumulate in the layers of the electrolyte adjacent to the cathode blocking access of zinc to the cathode. This phenomenon is capable of causing reduction in the current efficiency. In further work, Turomshina and Stender⁶ studied the effect of admixtures of the ions of electronegative metals upon the current efficiency and cathode potential. They concluded that the sodium, calcium, magnesium, and manganese ions present in a zinc electrolyte are capable of discharging jointly with the zinc ions forming intermetallic compounds with the zinc which serve as microanodes in short-circuited elements on the cathode surface. However, Kletenik,⁷ in a study on the effect of manganese in the electrodeposition of zinc, reported that attempts to detect manganese in electrodeposited layers of zinc, obtained at very different current densities and concentrations of manganese in the electrolyte, were unsuccessful.

Published data do not permit an unambiguous conclusion to be reached on the influence of ions of electronegative metals on the cathodic deposition of zinc in zinc sulfate solutions or on

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the nature of the polarization accompanying this process. Because of the complexity of these effects, it would be highly desirable to study the electrodeposition process under conditions where the number of uncontrolled variables were minimal.

The present work is concerned with a study of the influence of temperature on the rate of deposition of zinc at a rotating disk electrode in the presence of Na, Ca, and Mg.

To determine the rate-limiting stage in the cathodic processes and to elucidate the type of cathodic polarization in the electrodeposition of zinc in the presence of electronegative metal ion impurities, Gorbachev's temperature-kinetic method⁸ was used.

An important stage in the development of the temperature-kinetic method is its application under conditions of forced convection. The use of forced convection — rotating disk electrode — in the study of electrochemical reactions makes it possible to control the stage involving the transport of the reactants to the electrode surface and to eliminate experimental errors due to natural convection.

EXPERIMENTAL

The experiments involved the measurement of polarization curves using a rotating disk electrode recently described.⁹ The polarization measurements were made by a galvanostatic method. The electrolytic cell consisted of a glass cylinder 340 ml vessel. The large volume of the catholyte combined with a small surface area of the cathode ensured the constancy of

the composition of the solution during the measurements of the polarization curve. The electrolytic cell was fitted in a jacket through which water from a precision thermostat circulated. The auxiliary electrode consisted of a 2.26 cm diam. platinum plate. A saturated calomel half-cell served as the reference electrode.

The electrode was prepared as described recently.⁹ Its surface area was 0.196 cm². The electrode was rotated by a synchronous motor, the rate of rotation being 771 rev. min⁻¹. In the determination of the polarization curves the potential was measured at 2 min after the attainment of a specific current density. This time was sufficient for a virtually steady value of the potential to be established. To ensure reproducible results, each polarization curve was measured for a fresh deposit. The potential of the zinc electrode in absence of current was determined immediately after completion of the polarization curve. Measurements were made with current densities of 0.5–60 mA cm⁻² at intervals.

The polarization potential of the zinc cathode was measured in solutions of 1 M zinc sulfate, reagent grade, with additions of Na, Ca, and Mg, introduced into the zinc electrolyte as sulfate. Sodium and magnesium effects were studied at three different concentrations: 0.1, 0.5, and 1.0 g/l. Because calcium sulfate is relatively insoluble in solutions of zinc sulfate only one concentration, 0.1 g/l, was studied; all concentrations were studied at four different temperatures: 20, 30, 40, and 50°C. The solutions were treated with activated carbon to remove all surface-active material from the electrolyte.

RESULTS

Sodium. The effect of the concentration of the sodium ion on the polarization potential of the zinc cathode at 20°C is shown in Fig. 1. The

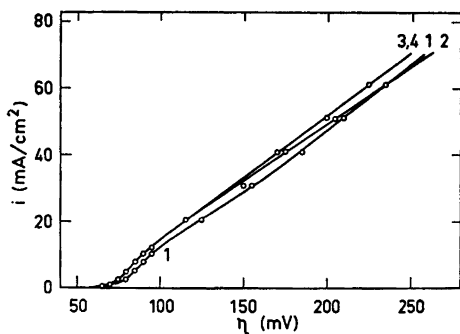


Fig. 1. Effect of sodium ion concentration on the cathode potential-current density relation in 1 M ZnSO₄ solution at 20°C; concentration of sodium (g/l): 1, 0; 2, 0.1; 3, 0.5; 4, 1.0.

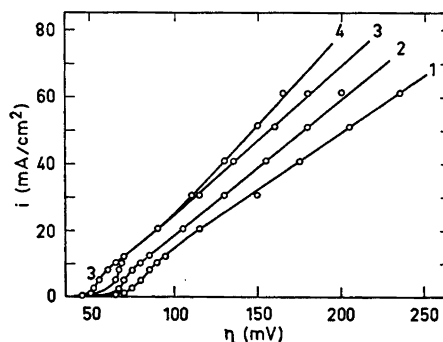


Fig. 2. Effect of the temperature on the cathode potential-current density curve in 1 M ZnSO₄ containing 0.1 g/l Na; temperature (°C): 1, 20; 2, 30; 3, 40; 4, 50.

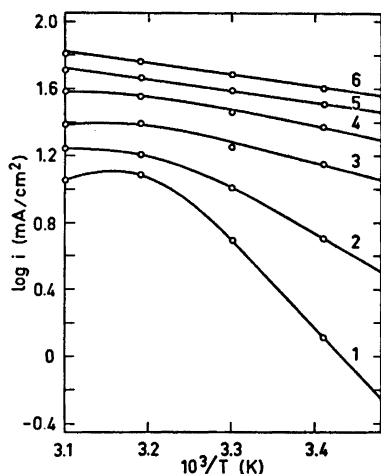


Fig. 3. Dependence of $\log i$ on $1/T$ in 1 M ZnSO_4 containing 0.1 g/l Na at constant polarization potential (mV): 1, 70; 2, 80; 3, 100; 4, 125; 5, 150; 6, 175.

addition of sodium ions to 1 M zinc sulfate shifts the electrode potential in the positive direction. This depolarizing effect is less noticeable at increasing temperatures.

Fig. 2 shows that the polarization potential of the zinc cathode in 1 M zinc sulfate solution containing 0.1 g/l Na decreases with increasing temperature. However, at 50°C an increase is observed, relative to 40°C, at low cathode potential. Similar effects were observed at other concentrations of sodium.

To ascertain the nature of the cathodic polarization accompanying the deposition of zinc in the above solutions, plots for the different concentrations of sodium were made of the logarithm of current density against the reciprocal of the absolute temperature at a constant polarization potential (Fig. 3).

The characteristic of the curves representing $\log i$ as a function of $1/T$ is that it passes through a maximum at high temperatures in the region of low cathode potentials. With increase in the polarization potential the first non-linear portion of the curve becomes linear and the shape of the equipotential curves is characterised by a linear section of definite slope.

The deviation of the equipotential curves from linearity which passes through a maximum is characteristic of crystallization overvoltage.⁸

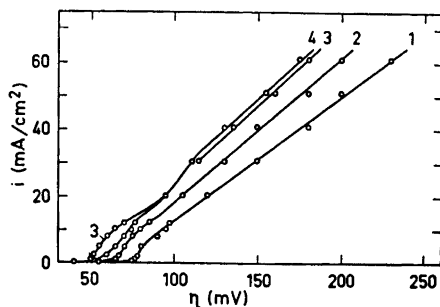


Fig. 4. Effect of the temperature on the cathode potential-current density curve in 1 M ZnSO_4 containing 0.1 g/l Ca; temperature (°C): 1, 20; 2, 30; 3, 40; 4, 50.

More generally, divergence from linearity is due to the cumulative effect of some additional, secondary factor, which distorts the normal temperature variation of the electrode process.¹⁰

The deposits of zinc on the cathode were more porous and darker with increasing concentrations of sodium in the electrolyte.

Calcium. Calcium showed a depolarizing effect at all temperatures except at 50°C in which an opposite effect is observed.

Fig. 4 exhibits the degree to which the presence of 0.1 g/l Ca affects the cathode potential-current density curve with temperature. The polarization potential of the zinc cathode decreases with increase in temperature up to 40°C.

The equipotential plots based on the polarization measurements show deviation from linearity in the variation of the logarithm of the current density with reciprocal of the absolute temperature (Fig. 5). The equipotential plots show a maximum in the region of high temperatures, characteristic of crystallization overpotential; at higher potentials the curve approaches linearity.

The deposit of zinc in the presence of 0.1 g/l Ca in the electrolyte did not differ from that obtained with pure solutions.

Magnesium. The presence of magnesium in the electrolyte caused a depolarization in the cathode potential at all temperatures studied except at 50°C where a polarization was obtained in the low cathode potential region. This was observed at all concentrations investigated. The effect of the concentration of magnesium

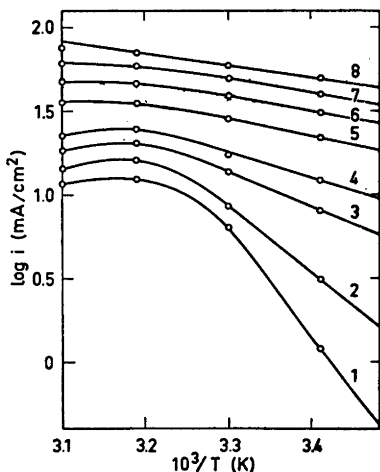


Fig. 5. Dependence of $\log i$ on $1/T$ in 1 M ZnSO_4 containing 0.1 g/l Ca at constant polarization potential (mV): 1, 75; 2, 80; 3, 90; 4, 100; 5, 125; 6, 150; 7, 175; 8, 200.

on the polarization potential of the zinc cathode at 20°C is shown in Fig. 6.

Fig. 7 depicts the effect of the temperature on the cathode potential-current density curve in the zinc sulfate solution containing 0.5 g/l of magnesium. The polarization potential of the cathode decreases with rise in temperature except at 50°C. This was observed at all the concentrations investigated.

The characteristic of the equipotential plots (Fig. 8) in the variation of the logarithm of the current with the reciprocal of the absolute temperature, at the different concentrations, is the

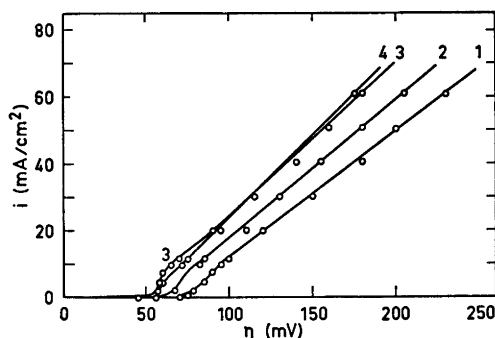


Fig. 7. Effect of the temperature on the cathode potential-current density curve in 1 M ZnSO_4 containing 0.5 g/l magnesium; temperature (°C): 1, 20; 2, 30; 3, 40; 4, 50.

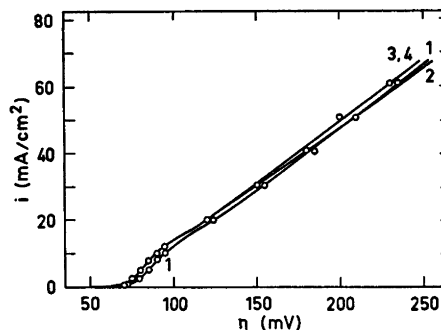


Fig. 6. Effect of magnesium ion concentration on the cathode potential-current density relation in 1 M ZnSO_4 solution at 20°C; concentration of magnesium (g/l): 1, 0; 2, 0.1; 3, 0.5; 4, 1.0.

deviation from linearity with passage through a maximum at high temperatures in the region of low cathode potentials. This is depicted in Fig. 8 for a solution containing 0.5 g/l of magnesium.

The deposition of zinc in the presence of small quantities of magnesium, 0.1 g/l, did not differ in appearance or color from that obtained with pure solutions. As the concentration of magnesium increased the cathode deposits of zinc became somewhat darker and more porous.

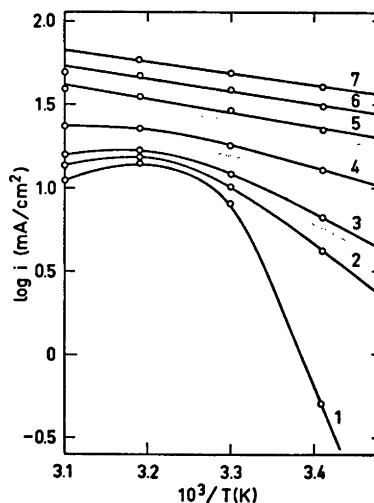


Fig. 8. Dependence of $\log i$ on $1/T$ in 1 M ZnSO_4 containing 0.5 g/l magnesium at constant polarization potential (mV): 1, 75; 2, 80; 3, 85; 4, 100; 5, 125; 6, 150; 7, 175.

DISCUSSION

The results obtained from the treatment of experimental data applying the temperature-kinetic method showed that admixtures of ions of electronegative metals affect the deposition of zinc, hindering the process by which atoms are incorporated into crystal lattice, namely the appearance of crystallization overpotential as a rate controlling step.

The impurities of electronegative metals appear to affect the crystal growth of zinc electro-deposits by a mechanism involving the adsorption of impurities at growth sites. This supposition is confirmed by the following experimental facts:

(i) The zinc deposits in presence of admixtures of ions of electronegative metals are irregular and loose. At a low adsorption rate the electro-deposition is less uniform, because the electrode surface is unequally covered by the species of the added impurities.¹¹

(ii) A general feature of the cathodic deposition of zinc in presence of admixtures of ions of electronegative metals is that zinc deposition is strongly affected in the region of low cathode potential – kinetically-controlled range – and slightly affected at higher potentials – diffusion-controlled range. The action of impurities, which act as surface-active agents, would be expected to be more pronounced as the current density is lowered. At high current densities on fast growing crystallite facets, the surface-active agents do not accumulate sufficiently to stop growth.¹¹

(iii) Zinc is deposited at potentials on the negative side of the zero-charge potential of zinc [$\phi_N = -0.63$ V (NHE)].¹² Therefore surface-active cations can be adsorbed on the cathode.

(iv) There is a very slight deviation between the stationary potential with and without impurities.

In the absence of effective surface inhibitors and at low overvoltage, metal crystals will grow without the formation of nuclei.

In this case, the ad-atoms will preferentially enter existing dislocations. But with increasing coverage of the electrode surface by adsorbed species, the mean free path for lateral diffusion of the ad-ions will be shortened. This is equivalent to a decrease in the diffusion coefficient of ad-ions which can result in an increase in surface diffusion control or an increase in ad-ion concentration at steady state to a point such that the rate of two-dimensional nucleation becomes appreciable. Hence, a decrease in surface diffusion control due to the reduction in the distance between growth steps. Therefore, with high inhibition the diminished surface diffusion may be the rate-controlling step or with very high inhibition, nucleus formation or diminished surface diffusion both may become the rate-controlling steps. If two-dimensional nucleation is rate-determining, the logarithm of the current density should be a linear function of the reciprocal overvoltage.¹³ Figs. 9 – 11 show that linear relationships are obtained in $1/\eta$ vs. $\log i$ coordinates for the different solutions con-

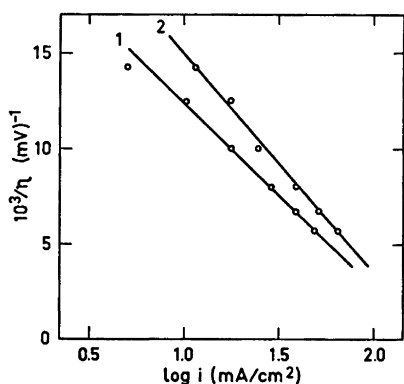


Fig. 9. Variation of $\log i$ on $1/\eta$ in 1 M ZnSO_4 containing 0.1 g/l sodium; temperature ($^\circ\text{C}$): 1, 30; 2, 50.

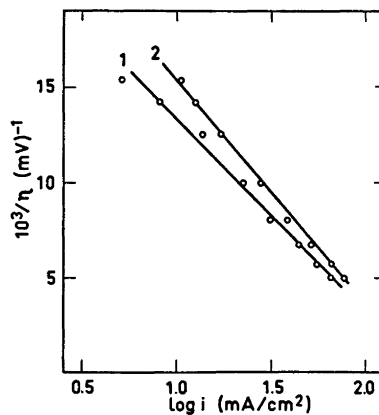


Fig. 10. Variation of $\log i$ on $1/\eta$ in ZnSO_4 containing 0.1 g/l calcium; temperature ($^\circ\text{C}$): 1, 30; 2, 50.

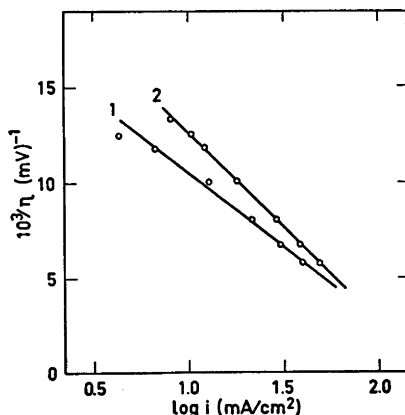


Fig. 11. Relationship between $1/\eta$ and $\log i$ in 1 M ZnSO_4 containing 0.5 g/l magnesium; temperature ($^{\circ}\text{C}$): 1, 20; 2, 30.

taining metal ion impurities. Thus, the conclusion which follows from the analysis of Figs. 9–11 is consistent with the conclusion derived by the temperature-kinetic method.⁸

The depolarizing effect of impurities. As a rule, changes in the structure of the electrolytic deposit are due to adsorption of surface-active substances which block the active sites and cause increased electrode polarization.¹⁴ From the above data it can be seen that in the electrodeposition of zinc electronegative metal ion impurities reduce the electrode polarization. The absence of a direct relation between the polarization and the structure of the electrolytic deposits indicates that surface-active substances added to the electrolyte act on various stages of the electrode process.

Studies of the effect of the concentration of hydrogen ion on the kinetics of the electrolytic deposition of zinc from sulfuric acid solutions,^{15,16} have shown that increase in the pH of the solution causes a reduction in the polarization of the zinc electrode. With increase in temperature, the retarding effect of the hydrogen on the discharge of zinc is removed. Thus, the polarization and structural investigations have shown that the effect of hydrogen on the electrolytic deposition of zinc is associated, not with a change in the condition of the ion undergoing discharge from the solution, but with the adsorption of hydrogen at the electrode surface, which retards the electrode process.

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Therefore, in all probability, the influence of metal ion impurities on the reduction potential of metal ions from electrolyte arises because, in the presence of ions of impurities on the electrode, the metal-hydrogen bond becomes weaker,¹⁷ which promotes adsorption of metal ions, and consequently their reduction. Such a weakening of the bond between hydrogen and the electrode and promotion of discharge is observed in the reduction not only of metal ions, but also hydrogen. Measurements of the overvoltage of hydrogen on zinc in solutions of acids¹⁸ have revealed that hydrogen overvoltage decreases with the nature of the acids in the following sequence: $\text{ClO}_4^- < \text{SO}_4^{2-} < \text{Cl}^-$.

Since the depolarization of the cathode potential is associated with the inhibiting action of surface-active species on the electrode, it might be expected that the depolarization effect would decrease with increasing temperature.¹⁹ In actual fact, experimental results show that depolarization increases until some limit and then falls with rising temperature.

It can be concluded that in the presence of electronegative metal ion impurities the reduction in electrode polarization is associated with elimination of the retarding action of hydrogen. The metal ion impurities do not directly promote the discharge of zinc but suppress the inhibiting action of hydrogen.

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