The Effect of Manganese Ion Impurity on the Kinetics and Overvoltage of Zinc Electrodeposition from a Sulfate Solution

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The kinetics of the electrochemical deposition of zinc from pure sulfate solutions and in the presence of manganese ion impurity have been investigated by the method of polarization curves using a rotating disk electrode. Analysis of the data by Gorbachev's temperature-kinetic method demonstrated that deposition of zinc from pure sulfate solution is accompanied by charge-transfer overvoltage; in the presence of manganese ion impurity crystallization overvoltage occurs. The influence of manganese ion impurity is probably of adsorptive character.

The nature of the influence of manganese on the electrodeposition of zinc from sulfate electrolytes, occupies an intermediate position between metal cations more active and less active than zinc. The influence of manganese has been considered by several investigators:

Fedotieff and Stender [1] showed that current efficiency for zinc depends on the manganese concentration in the electrolyte. Marshall [2] found that the current efficiency for zinc was lower in presence of manganese. Weimer et al. [3] consider that manganese is a harmless impurity in the electrodeposition of zinc. Stender et al. [4] showed that permanganate ions formed at the anode migrate to the cathode and depolarize it. According to the data of a number of investigators, [5-7] manganese is harmless up to a definite concentration in solution $(2-3 \text{ g/l})$; on further increase of the manganese content the current efficiency drops appreciably.

Most research has been aimed at the effect of manganese on current efficiency and on the effects of manganese with other impurities but

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the mechanistic details are still obscure.

A study of deposition of zinc in the presence of manganese ion impurity under conditions of known rate of transport of this impurity to the cathode is valuable in furthering the understanding of the mechanism of impurity action. A rotating disk electrode is particularly suitable for such study. Levich [8] has shown that the rate of a transport-controlled reaction is uniform over such a disk and has derived an expression for the limiting rate of reaction. His theoretical results have been verified experimentally by Gregory and Riddiford [9] and by Newson and Riddiford. [10]

In the present study the effect of temperature on the rate of deposition of zinc at a rotating disk electrode in the presence of manganese was investigated. The results were treated in accordance with Gorbachev's temperature-kinetic method. [11]

In the temperature-kinetic method the nature of polarization is assessed by studying the temperature variation of current density under conditions of constant polarization potential. The determination of the effective activation energy makes it possible to distinguish between concentration and charge transfer overvoltage. This allows the individual stages of electrochemical reactions, including those involving a combination of charge transfer and concentration overvoltage, to be studied.

In order to understand how impurities work, it is desirable first to have some concept of how metal ions are discharged and built into a crystal lattice in the absence of impurities. Thus, the determination of polarization curves of zinc

deposition were made at four different concentrations: 0.05 M, 0.1 M, 0.5 M, and 1 M $ZnSO_4$, and the concentrations studied at four different temperatures: 20, 30, 40, and 50°C.

The effect of admixtures of manganese at four different concentrations and at 20, 30, 40, and 50°C was studied with 1 M $ZnSO_4$ as standard.

EXPERIMENTAL

The rotating disk electrode (RDE) used in this work was a modification of that described by Khomutov and Skornyakova [12]. The 0.5 cm diam. aluminium disk (99.998 % Vigeland Metal Refinery A/S) was attached to a 1.6 cm diam. brass extension shaft, precision ground (Fig. 1). The disk and extension shaft pressure fitted into a polyvinyl chloride (PVC) insulating sleeve. The aluminium disk and subsequently the PVC sleeve were accurately machined by using the ground extension shaft to fix the axis of rotation. The electrode face was polished, before each experiment, to a mirror finish on a metallurgical polisher by using AB Microcloth and AB Polishing alumina No. 1 (Buehler Ltd. Evanston Ill., levigated alumina 5.0 μ). The electrode was driven by a 885 r.p.m. synchronous motor, obtaining other rotation speeds with a belt and pulleys of different diameters. The speeds were measured with a stroboscope. The current was fed to the RDE through graphite contacts sliding on a carefully centered
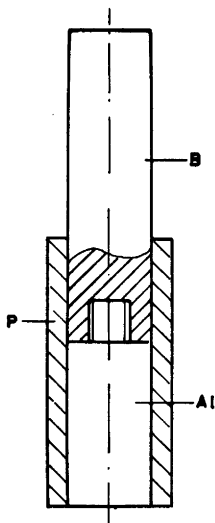

Fig. 1. Interchangeable rotating disk electrode: B, brass extension; P, PVC shield; Al, Aluminium disk electrode, pressure fitted in PVC shield.

shaft mounted in a pair of bearings fitted in a heavy brass cylinder.

The electrolysis cell was a glass cylinder, 7.8 cm diam. by 9.4 cm deep, and was filled with *ca.* 340 ml solution. The dimensions of the cell and cathode were chosen to meet the hydrodynamics requirements of the Levich theory.[9,13,14] The temperature was maintained constant by circulating water from a thermostat set through a water jacket around the cell.

The three-electrode cell consisted of the RDE as the working electrode, a large platinum disk as auxillary electrode and a saturated calomel electrode (SCE) as reference. The platinum auxiliary electrode had a diameter of 2.26 cm and was positioned about 6.5 cm below and parallel to the face of the RDE. The capillary connection to the test solution (Luggin capillary) was made at a point in the solution slightly to the rear and to one side of the disk where the ohmic drop is negligible.[10] The capillary was filled with the electrolyte by drawing solution into the capillary until it made contact with the porous plug of the salt bridge of the SCE.

The electrolyte used in this study consisted of zinc sulfate reagent grade. The cathode potential-current density curves obtained in highly purified solution, zinc sulfate recrystallized 3 times, were not significantly different from the results obtained without improving reagent purity. However, it was important to remove all surface-active material from the electrolyte. This was done by treatment with activated carbon.

The polarization measurements were made by a galvanostatic method. Measurements were made of steady values of the potential attained 1 – 2 min after passage of a given current. Direct measurements gave the cathode potential with respect to the saturated calomel electrode. The overvoltage was calculated by substracting the potential value of the zinc electrode in absence of current from the determined potential values at constant current. The potential of the zinc electrode in absence of current was determined immediately after completion of the polarization curve.

It was shown by Frumkin [15] that when metals dissolve (with evolution of hydrogen) in acidic electrolytes the potential obtained can be either practically equilibrium values or differ substantially from the equilibrium values, depending on the relative rates of the electrode processes occurring on the surface of the metal while dissolving. Kravtsov and Ermolova,[16] in a study of the steady-state potentials of zinc and zinc amalgam in sulfate solutions, have shown that the reduction in the acid concentration and increase in the zinc ion concentration make it possible to bring a shift from nonequilibrium to practically equilibrium values of the zinc potential.

The polarization potential of the zinc cathode was measured in solutions containing 0.05 M,

0.1 M, 0.5 M, and 1 M zinc sulfate; and 1 M zinc sulfate with additions of manganese, introduced into the zinc electrolyte as sulfate. Manganese effects were studied at four concentrations: 0.1, 0.5, 1.0, and 3.0 g/l. Measurements were made with current densities of $0.5-60$ mA cm^{-2} at intervals in the range $20-50°C$. The electrode was rotated at 771 r.p.m.

RESULTS AND DISCUSSION

Electrodeposition of zinc from pure sulfate solutions. Fig. 2 presents the data for the electrolyte solutions containing 1 M zinc sulfate. The polarization curves show that the cathodic polarization varies with temperature and current density. With increase of temperature, the polarization potential of the cathode falls. Similar behavior was observed with various concentrations of zinc sulfate. The cathodic polarization increases with increasing current density.

Fig. 3 demonstrates the effect of the concentration of zinc sulfate on the polarization potential at 20°C. With increasing zinc sulfate concentration, the zinc polarization potential decreases. Similar relations were observed at other temperatures.

To elucidate the type of polarization in the deposition of zinc in the solutions studied, the logarithm of current density was plotted against the reciprocal of the absolute temperature (log $i-1/T$) at a constant polarization potential ($\eta = $ const.) (Fig. 4). In the range of temperatures and polarization potentials investigated, the log $i-1/T$ plot is linear for all the solutions.
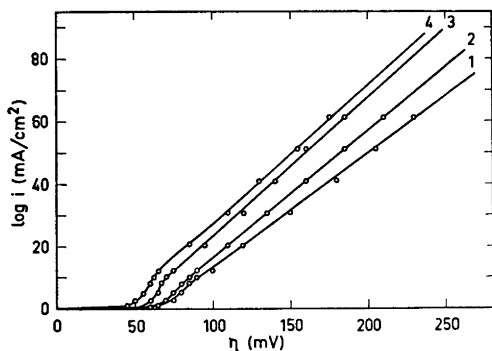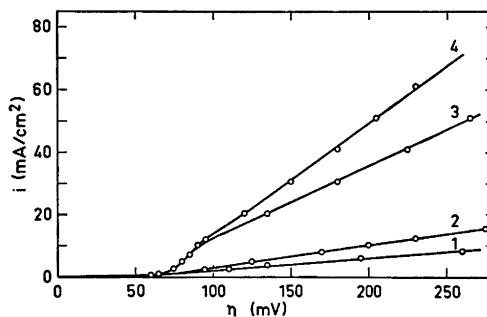

Fig. 3. Effect of zinc sulfate concentration on the cathodic polarization at 20°C: 1, 0.05 M; 2, 0.1 M; 3, 0.5 M; 4, 1.0 M.

The apparent activation energy for the electrode process can be found from the slopes of the log $i-1/T$ plots, with the aid of the relation:

$$2.3 \log i = -\Delta E^{\neq}/RT + \text{constant}$$

It is very interesting to follow the variation of the apparent activation energy with polarization potential. The $\Delta E^{\neq} - \eta$ plot in Fig. 5 shows that the apparent activation energy for solutions containing 1 M and 0.5 M zinc sulfate depends on the polarization potential. With increase in polarization potential from 65 to 150 mV, the apparent activation energy falls from 86.02×10^3 to 13.47×10^3 J/mol and from 44.35×10^3 to 13.39×10^3 J/mol in 1 M and 0.5 M zinc sulfate solutions, respectively.
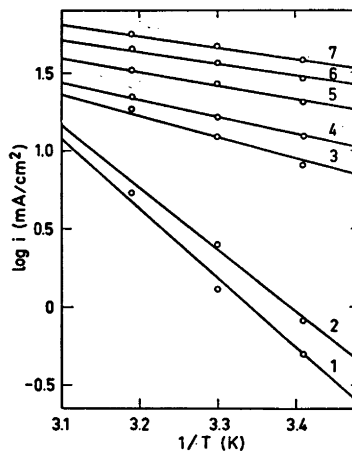

Fig. 2. Effect of temperature on the cathodic polarization curves in solution 1 M ZnSO$_4$; temperature (°C): 1, 20; 2, 30; 3, 40; 4, 50.

Fig. 4. Variation of log i with $1/T$ at constant polarization potential in solution of 1 M ZnSO$_4$; polarization potential η(mV): 1, 65; 2, 70; 3, 90; 4, 100; 5, 125; 6, 150; 7, 175.
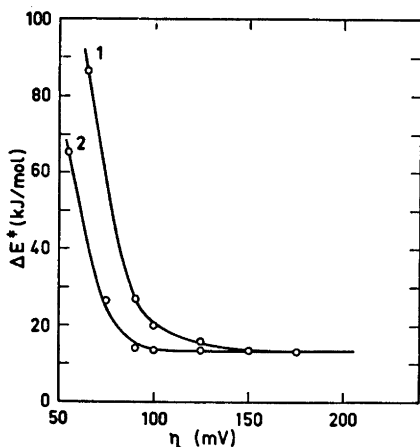
Fig. 5. Variation of the activation energy $\Delta E^{\ddagger}$ with polarization potential η in $ZnSO_4$ solutions: 1, 1 M; 2, 0.5 M.

Some decrease of the apparent activation energy with polarization potential was observed in solutions containing 0.1 M and 0.05 M zinc sulfate. As polarization is raised from 50 to 150 mV, the apparent activation energy decreases from 55.44×10^3 to 17.32×10^3 J/mol and from 37.53×10^3 to 13.47×10^3 J/mol in 0.1 M and 0.05 M zinc sulfate solutions, respectively.

The absolute values of the apparent activation energy (Fig. 5) and the nature of its variation with polarization potential indicate that the rate of deposition of zinc is limited by the electrode reaction itself, i.e. activation overpotential or charge-transfer overvoltage.

With increase in the zinc sulfate concentration the polarization potential of the zinc cathode decreases, while the rate of cathodic deposition of zinc and the effective activation energy both increase. At the same time the relative proportion of charge-transfer overpotential compared with concentration polarization also increases, i.e. material transport ceases to be the rate-determining stage, the cathodic deposition of zinc being limited by one of the stages in the electrode reaction.

Fig. 6 depicts the polarization curves plotted in terms of Tafel coordinates and shows that these relations are linear. $\eta - \log i$ plots are known to be linear if the charge-transfer at the electrode is rate controlling.[17] Thus the conclusion which follows from the analysis of Fig. 6 is con-
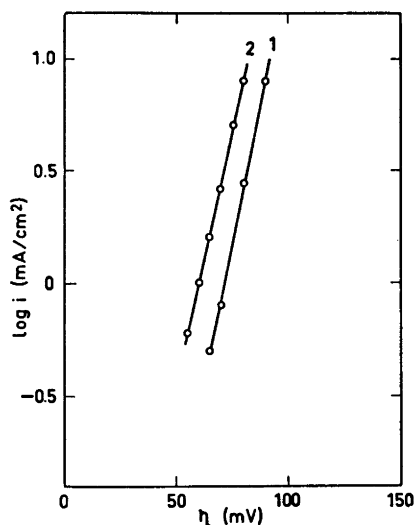

Fig. 6. Dependence of η on $\log i$ at 20°C for $ZnSO_4$ solutions: 1, 0.5 M; 2, 1.0 M.

sistent with the conclusion derived by the temperature-kinetic method.

Effect of manganese. At 0.1 and 0.5 g/l manganese reduced polarization of the zinc cathode at all the temperatures investigated except at 50°C. At a concentration of 1.0 g/l the depolarizing effect ceased at 40°C. At 3.0 g/l a polarization was observed at 20° and 50°C; with small depolarization, in the low cathode potential region, at 30° and 40°C. Fig. 7 shows the effect of manganese ion on the cathode potential-current density relation at 20°C.
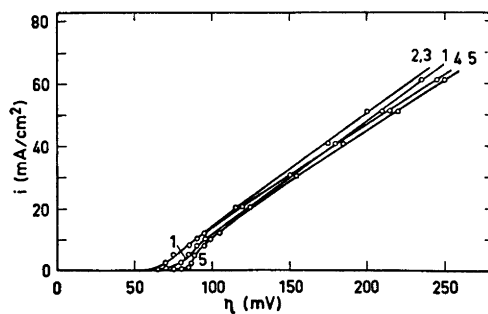

Fig. 7. Effect of manganese ion concentration on the cathode potential-current density relation in 1 M $ZnSO_4$ solution at 20°C; concentration of manganese (g/l): 1, 0; 2, 0.1; 3, 0.5; 4, 1.0; 5, 3.0.

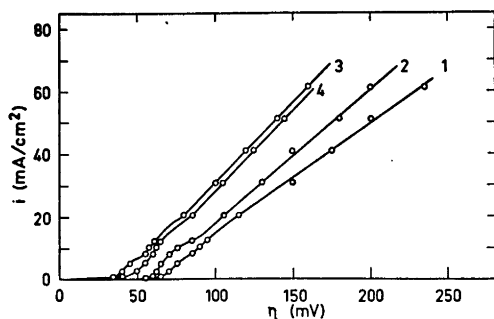*Fig. 8.* Effect of the temperature on the cathode potential-current density curve in 1 M ZnSO$_4$ containing 0.1 g/l manganese; temperature (°C): 1, 20; 2, 30; 3, 40; 4, 50.

A typical behavior of the cathode potential with temperature in solutions containing manganese was a decrease with increase in temperature except at 50°C. Fig. 8 shows the effect of temperature for a solution containing 0.1 g/l manganese.

The deviation of the equipotential curves from linearity with passage through a maximum in the plots of log i against $1/T$ is observed at all concentrations studied. At 0.1 g/l the deviation of the equipotential curves from linearity persist at higher overpotentials (Fig. 9) than in the rest of the concentrations investigated.
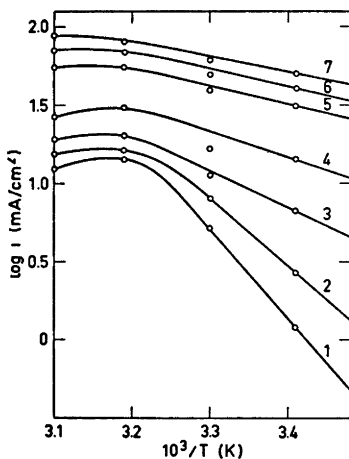

Fig. 9. Dependence of log i on $1/T$ in 1 M ZnSO$_4$ containing 0.1 g/l manganese at constant polarization potential (mV): 1, 65; 2, 70; 3, 80; 4, 100; 5, 150; 6, 175; 7, 200.

The deviation of the equipotential curves from linearity with passage through a maximum is characteristic of crystallization overvoltage.[11]

When the quantity of manganese present in the electrolyte was higher than 0.1 g/l, dark flakes of manganese hydrates were observed to move from the anode into the electrolyte. With increase in manganese content and elevation of temperature, the cathode deposits of zinc become darker.

A characteristic of the cathodic deposition of zinc in presence of admixtures of manganese ion is that zinc is strongly affected in the region of low cathode potential – kinetically-controlled range – and a slight dependence at higher potentials – diffusion-controlled range; this may possibly indicate adsorption of manganese on the electrode. 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.[18] This idea of absorption is also confirmed by the very slight deviation between the stationary potentials in the solution studied with and without manganese.

The absorption of manganese may be supposed to alter either the effective metal charge and, hence, the electrochemical free energy change across the double layer or the number of effective growth sites.[19] If the number of effective growth sites is reduced by adsorbed species, the mean free path for lateral diffusion
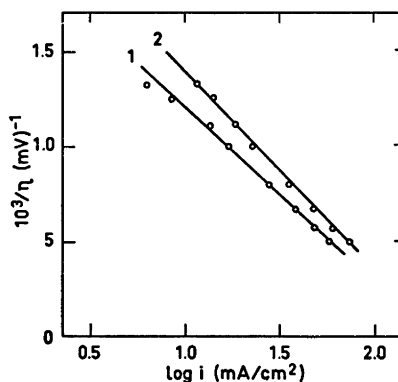

Fig. 10. Relationship between $1/\eta$ and log i in 1 M ZnSO$_4$ containing 0.5 g/l manganese; temperature (°C): 1, 30; 2, 50.

of the adions will be shortened. This is equivalent to a decrease in diffusion coefficient of adions which can result in an increase in surface control or an increase in adion concentration at steady state to a point such that the rate of two-dimensional nucleation becomes appreciable. If two-dimensional nucleation is rate determining, the logarithm of current density should be a linear function of the reciprocal overvoltage.[20] Fig. 10 shows that linear relationships are obtained in $1/\eta$ vs. log i coordinates for the solution containing manganese ion impurity. Thus, the conclusion which follows from the analysis of Fig. 10 is consistent with the conclusion derived by the temperature-kinetic method.

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