

KINETICS OF DISSOLUTION OF ZINC IN ZINC CHLORIDE SOLUTION

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ABSTRACT

The kinetics of dissolution of zinc in acidic zinc chloride solution have been investigated in order to understand and optimize its performance in zinc-chlorine hydrate battery. Polarisation experiments were carried out using pure zinc rods and electrodeposited zinc as electrodes. For a concentration change of zinc chloride from 0.5 to 1.5 M, the exchange current densities were found to vary from 1.4 to 2.4 mA/cm² in the case of cast zinc rod electrodes, and from 2.2 to 6.2 mA/cm² in the case of electrodeposited zinc; this increase is attributed to the greater reactivity as well as the increased surface area of the freshly electrodeposited zinc.

Key Words: Kinetics, Zinc-chlorine battery, Dissolution of zinc

INTRODUCTION

The zinc-chlorine battery has been under intensive investigation and development during recent years for vehicular and load levelling applications [1,2]. It is a flowing aqueous zinc-chloride electrolyte battery which utilises porous graphite flow through chlorine electrode and dense graphite zinc electrode substrate. The inter-electrode distance is 2 mm to 4 mm and no separator is employed. Hence the zinc has to be deposited in a non-dendritic form to avoid any shorting. During the charging process, zinc is deposited on the graphite substrate, which, during discharge, dissolves to form the zinc chloride solution. The simple representation of the cell reaction is as follows:



$$x \approx 5.9$$

In an earlier paper [3] it has been shown that the deposition and dissolution of zinc is reversible and proceeds at an efficiency of 98%. It was also observed that the rate of dissolution of deposited zinc was much larger than that of the cast zinc. Hence the kinetics of dissolution of both cast zinc and electrodeposited zinc have been studied here.

EXPERIMENTAL

For polarisation studies a 'H' shaped electrolytic cell was used. Cast zinc electrodes were prepared from super pure (5N) zinc rods by mounting it in araldite. The surface of the electrodes were well polished on a disc polisher and degreased with trichloroethylene. Electrodeposited zinc electrodes were prepared by depositing zinc galvanostatically on stainless steel electrode at a c.d. of 35 mA/cm² for 2 hours duration. Electrolyte solutions were prepared from AR grade zinc oxide and hydrochloric acid. The desired concentrations were achieved by dilution with double distilled water. The potential-current values were determined potentiostatically in various concentrations of zinc-chloride solutions. The potential-current data were recorded. Faradaic efficiency was obtained galvanostatically in different concentrations of zinc-chloride solution and have already been reported [3]. During the study the concentration overpotential was eliminated by agitating the solution. The concentration of zinc chloride was varied from 0.5 M to 1.5 M in three steps (0.5, 1, 1.5 M). The potential was varied from the rest potential of -1.000 to -0.8000 V. The applied potential was varied by 10 mV steps from -1.000 V to -0.950 V and from -0.950 V the potential was varied by 2 mV steps. The electrodes were stabilised in the electrolyte for 5 minutes before each

experiment. At each applied potential the electrode was polarised for 2 minutes in order to ensure constancy of current.

RESULTS AND DISCUSSION

The overpotential vs current plot for the cast zinc rods are presented in fig. 1 for three different concentrations of zinc chloride.

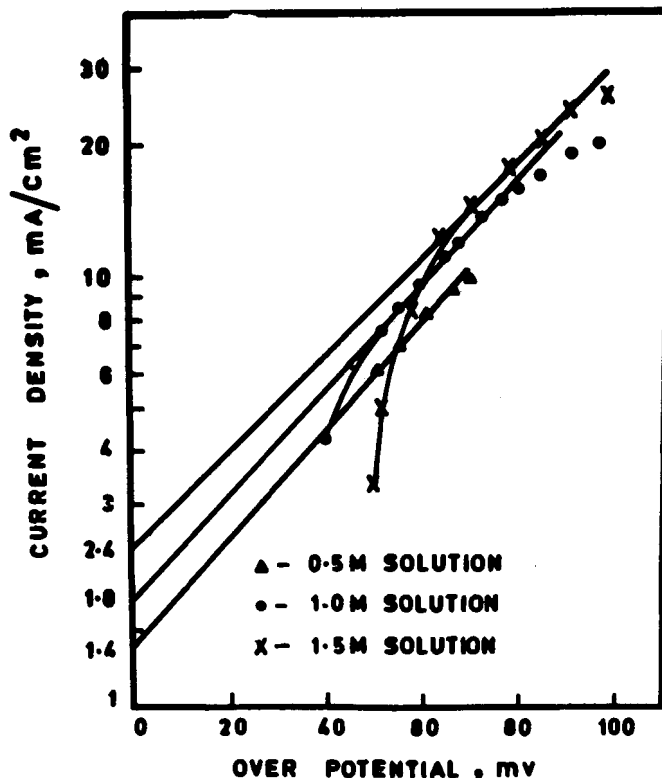


Fig. 1: Anodic Tafel polarisation of cast zinc electrode in zinc chloride solutions

It is observed that there is no variation in the slopes (≈ 120 mV for all concentrations), but there is a shift in the curves, showing a higher current value with increase in concentration. The exchange current density is found to increase with concentration. Fig. 2 represents the Tafel plots of the electrodeposited zinc under identical conditions. The behaviour is found to be similar.

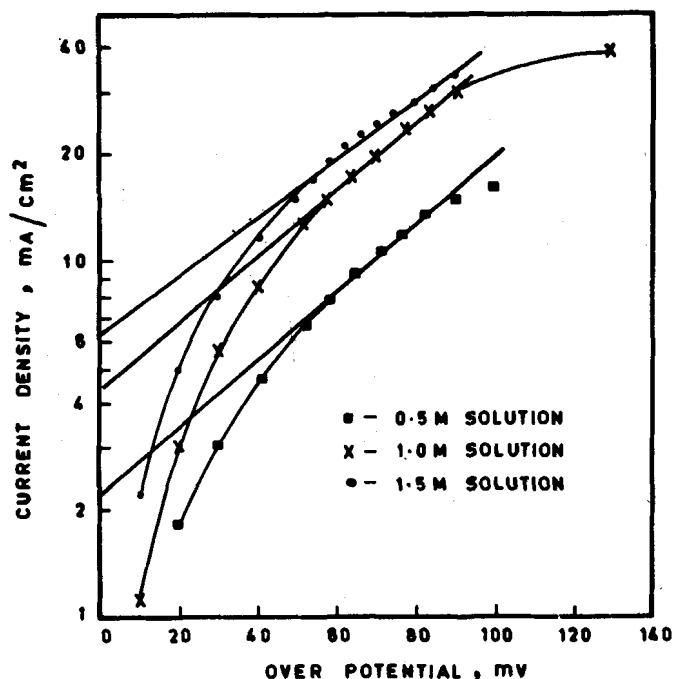


Fig. 2: Anodic Tafel polarisation of electrodeposited zinc electrode in zinc chloride solutions

The values of the Tafel slopes and exchange current densities are given in Table I.

Table I: The kinetic Tafel parameters of cast and electrodeposited zinc in zinc chloride solutions

ZnCl ₂ conc. Molar	Cast Zinc		Electrodeposited zinc	
	<i>i</i> ₀ , mA/cm ²	<i>b</i> _a , mV	<i>i</i> ₀ , mA/cm ²	<i>b</i> _a , mV
0.5	1.4	107.5	2.2	111.4
1.0	1.8	107.5	4.4	103.2
1.5	2.4	103	6.2	104

The exchange current density for the freshly deposited zinc electrodes under all the three concentrations was found to be higher than that for cast zinc rods as can be seen from Table I.

For anodic dissolution, the Tafel slope (Table I) is in good agreement with theoretical values. This is also in agreement with the values reported earlier [4]. In fig. 3 the exchange current density is plotted against concentrations of zinc chloride. It is very well known that the exchange current density (*i*₀) depends on concentrations of the reactants as well as the products:

$$i_0 = nF k_a^a k_c^{(1-a)} C_1^a C_2^{(1-a)} \quad \dots (1)$$

where *a* is symmetric transfer coefficient, *k*_a, *k*_c represent the anodic and cathodic rate constants and *C*₁, *C*₂ represent the concentrations of the reactants and products. In the present case, the exchange current density increases with zinc chloride concentration, as seen from fig. 3.

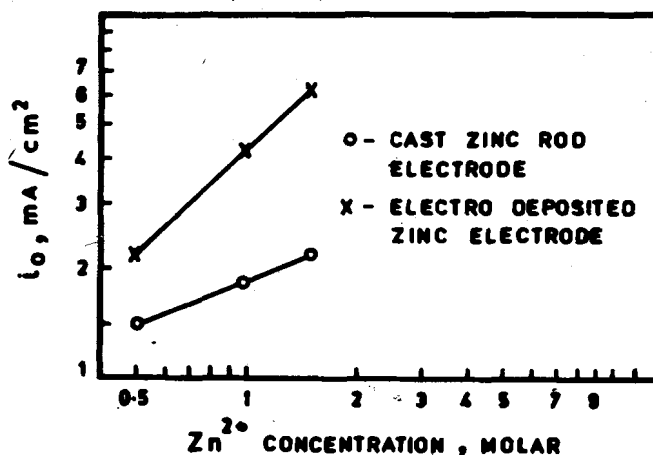
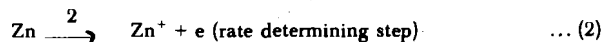


Fig. 3: The exchange current density vs the molar concentration of zinc ions

From the slope of the plot, the concentration index (eqn.1) is obtained as 0.5, which confirms the assumed value of *a* above. From the kinetic parameters, the following mechanism is suggested. The dissolution reaction proceeds in two steps, according to the following equations



If the equation (2) is the rate determining step, the rate expressions are

$$\frac{i_2}{nF} = k_2 \exp \left[\frac{(1-a)FE}{RT} \right] - k_{-2} [\text{Zn}^+] \exp \left(-\frac{aFE}{RT} \right) \quad \dots (4)$$

$$\frac{i_3}{nF} = k_3 [\text{Zn}^+] \exp \left[\frac{(1-a)FE}{RT} \right] - k_{-3} [\text{Zn}^{++}] \exp \left(-\frac{aFE}{RT} \right) = 0 \quad (5)$$

subscripts 2 and 3 have been added corresponding to equation (2) and (3). The reaction (3) is fast and essentially in equilibrium. The equation (5) yields the potential-dependent equilibrium concentration of Zn⁺.

$$[\text{Zn}^+] = \frac{k_{-3}}{k_3} [\text{Zn}^{++}] \exp \left(\frac{-FE}{RT} \right) \quad \dots (6)$$

Substitution into equation (4) gives

$$\frac{i_2}{nF} = k_2 \exp \left[\frac{(1-a)FE}{RT} \right] - \frac{k_{-3}k_{-2}}{k_3} [\text{Zn}^{++}] \exp \left[\frac{-(1+a)FE}{RT} \right] \quad \dots (7)$$

with the overpotential, equation (7) for anodic process can be written as

$$i = nFk [\text{Zn}^{++}] \cdot \frac{1-a}{2} \cdot \exp \left(\frac{(1-a)F\eta}{RT} \right) \quad \dots (8)$$

where $\eta = E - E_{eq}$

$$E_{eq} = \frac{RT}{2F} \ln \left\{ \frac{k_{-3}k_{-2}}{k_3k_2} [\text{Zn}^{++}] \right\}$$

$$k = k_2 \left[\frac{k_{-2}k_{-3}}{k_3k_2} \right]^{(1-a)/2}$$

Alternatively, if equation (3) is the rate-determining step, similarly it can be shown that

$$i = nFk' [Zn^{++}]^{(2-\alpha)/2} \exp \left[\frac{(2-\alpha)F\eta}{RT} \right] \quad \dots (9)$$

$$\text{where } k' = k_3 \left[\frac{k_2 k_3}{k_{-2} k_{-3}} \right]^{(2-\alpha)/2}$$

From the above equations (8) and (9) the following results can be obtained.

1. The Tafel slopes calculated substituting $\alpha = 0.5$ in equation (8) and (9) give a value of 120 mV and 40 mV respectively. From the experimental results given in figs. 1 and 2 the value of Tafel slope obtained is 120 mV. Hence equation (8) corresponding to the reaction (2) gives the actual rate determining step.

2. Similarly from the log-log plot of concentration vs current values within the Tafel region, slopes of 0.259 and 0.224 are obtained. From the rate equation (8) and (9) values of 0.25 and 0.75 are obtained for $\alpha = 0.5$. This also proves that the rate equation (8) which corresponds to reaction (2) gives the actual rate determining step.

REFERENCES

1. PC Symons and P Carr, *Proc 8th Inter-Society Energy Conversion Engineering Conference*, 1973, pp 72-79
2. P Carr, Ch Chi and PC Symons, *28th Power Sources Symposium*, June 1978.
3. Mrs S Nathira Begum, P V Vasudeva Rao and H V K Udupa, *Proc Seminar on Lead, Zinc and Cadmium Retrospect and Prospect*, Organized by ILZIC, November 1981, Delhi.
4. Jung Tack Kim and Jacob Jorne, *J Electrochem Soc.* **127** (1980) 8-15.