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DECAY OF THE ZINCATE CONCENTRATION
GRADIENT AT AN ALKALINE ZINC CATHODE
AFTER CHARGING

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SUMMARY

This is a study of the transport of the zincate ion to the alkaline zinc cathode. The study was carried out by observing the decay of the zincate concentration gradient at a horizontal zinc cathode after charging. This decay was found to approximate first order kinetics as expected from a proposed boundary layer model. The concentrations were calculated from polarization voltages. The decay half life was shown to be a linear function of the thickness of porous zinc deposit on the cathode indicating a very rapid transport of zincate through porous zinc metal. The rapid transport is attributed to an electrochemical mechanism. From the linear dependence of the half life on thickness the boundary layer thickness was found to be about 0.010 cm when the cathode was at the bottom of the cell. No significant dependence of the boundary layer thickness on the viscosity of electrolyte was observed. The data also indicated a relatively sharp transition between the diffusion and convection transport regions. When the cathode was at the top of the cell, the boundary layer thickness was found to be roughly 0.080 cm. The diffusion of zincate ion through asbestos submerged in alkaline electrolyte was shown to be comparable with that predicted from the bulk diffusion coefficient of the zincate ion in alkali.

INTRODUCTION

Because of recent interest in rechargeable batteries, we began a study of the alkaline zinc electrode (Ref. 1). The knowledge resulting from such a study can be a guide in the design of future batteries so that they can exhibit longer cycle life. The cycle life of a zinc electrode is highly dependent on its morphology. In turn, the morphology is dependent on the zincate concentration (Ref. 1) present at the cathode-electrolyte interface and the transport of the zincate ion to the cathode. The concentration at the interface is not the bulk concentration because of a concentration gradient in the region of the cathode (Refs. 1 and 2) which corresponds to the concentration polarization of the electrode.

This present report concerns the transport of zincate ion to the alkaline zinc cathode. The study involved the measurement of the decay of the zincate concentration gradient at the cathode after shutting off the current. From these data, the gradient's half life was determined and used to understand better the operation of the alkaline zinc electrode. The

zincate concentrations at the electrode were computed from potential measurements. The measurements were made for various plating currents, bulk ion concentrations, thicknesses of deposit, and modifications of the cell. The measurements were made for various thicknesses of asbestos on the cathode as well as for various amounts of electrodeposited porous zinc. The results are compared with those predicted from a proposed model. The dependence of decay half life on the thickness of deposit and viscosity of the electrolyte are discussed. The boundary layer thickness was calculated from an equation relating it to the half life and compared with a value obtained from the literature. An explanation is offered as to why the transport of zincate in porous zinc is much greater than predicted from the bulk diffusion coefficient.

EXPERIMENTAL DETAILS

A schematic of the disassembled cell is shown in Fig. 1(a); the assembled cell is shown in Fig. 1(b). It consists of a polymethylmethacrylate chamber containing three zinc-zincate electrodes. The bottom one is the cathode; the top, the anode; and the middle, the reference. The electrolyte was aqueous potassium hydroxide KOH containing potassium zincate $K_2Zn(OH)_4$. From experience we have found that the zincate concentration at the reference electrode C_R remains constant during an experiment, that is during the time when current is flowing through the cell. This is due to the fact that the amount of zincate removed from the electrolyte solution at the cathode is equal to the amount of zincate added to the anode.

For each new experiment, new 0.005 cm thick zinc sheets were used for the electrode collectors; new electrolyte was also used. With the cell in the position shown in Fig. 1(b) (cathode at the bottom), a constant current (4 to 50 mA) was controlled by a signal generator-potentiostat combination. Via this current, porous zinc deposited on the zinc cathode. In general, mossy zinc deposits at low current densities and large crystalline zinc deposits at high current densities (Ref. 3). The thickness of the deposit could be approximated from the total time at the plating current. When the zinc deposit was near the desired thickness (zero to 0.15 cm), E_i, the potential between the reference electrode and cathode was read off an oscilloscope during a 1 millisecond zero current pulse. The current was then shut off and E_t, the potential between the reference electrode and cathode, was recorded as a function of time after shut off. A long time value of E_t was recorded, corresponding to E_∞. The method of converting values of E_t to concentration values is given in a subsequent section.

Finally, the electrolyte was washed out of the cell, the cell was disassembled, and the cathode was air dried. The value of g, the thickness of the zinc deposit, was measured via a ×10 magnification of a cross section of a slice of the cathode. Attempts to measure the thickness in situ via change in the focal plane of the top surface of deposit proved to be unsatisfactory. Likewise, use of the product of current and on-time as a measure of thickness was not accurate enough; a plot of g versus time for a particular current apparently does not go through the origin.

The experiments were run at a series of current densities and for a series of electrolyte concentrations. The coefficient of viscosity was measured for each electrolyte solution so that viscosity could be taken into account when comparing results between different electrolytes.

When concentration decay occurs with the cell in the position shown in Fig. 1(a), the more dense bulk solution is above the less dense zincate depleted region. In an attempt to eliminate the convection which such a situation would induce, a set of concentration decay experiments were run with the cell in the inverted position. The plating was still done with the cell in the normal position (Fig. 1(a)) but after the current was shut off, the cell was inverted and values of E_t were recorded.

Still another set of concentration gradient decay experiments were performed using known thicknesses of asbestos on the top of the cathode in the normal position. These were intended to simulate the battery type environment of the zinc electrode. The current density used for all of these experiment was 0.4 mA/cm^2. Measurement of the effective thickness of asbestos was very difficult, we finally took the thickness to be the product of the number of layers of asbestos times the average measured thickness of one. The thickness measurements were performed while the asbestos was wet with electrolyte.

Chemicals

The zinc sheet was 99.999 percent pure. The electrolytes were prepared by dissolving weighed amounts of reagent grade zinc oxide in measured amounts of reagent grade nominally 45 percent KOH (carbonate free) and then diluting with distilled water to the desired concentrations. The final solutions were chemically analyzed for zincate and hydroxide. The asbestos used was the type used in the Astropower battery separator, that is coated with polyphenylene oxide (ppo).

Calculations of Zincate Concentration

The measured voltage is relatable to the effective zincate concentration C_t at the cathode by the following form of the Nernst equation.

$$C_t = MC_R e^{-(\mathscr{F}E_t/nRT)} = MC_R e^{-78.1\ E_t} \tag{1}$$

where M is the relative activity of the cathode zinc metal (activity of reference zinc metal taken as unity) and C_R is the zincate concentration at the reference electrode. The undecayed fraction of the concentration difference $\Delta C_t/\Delta C_i$ is thus given by Eq. (2).

$$\frac{\Delta C_t}{\Delta C_i} = \frac{C_\infty - C_t}{C_\infty - C_i} = \frac{e^{-78.1\,E_\infty} - e^{-78.1\,E_t}}{e^{-78.1\,E_\infty} - e^{-78.1\,E_i}} \tag{2}$$

where C_∞ is the zincate concentration at the cathode at infinite time and C_i is the zincate concentration at the cathode right before the current is shut off.

MODEL

The model for concentration gradient (polarization) decay presented here is intended to apply only to our type of experimental setup, that is to a system having a definable boundary layer at the cathode. In contrast, the principles discovered through the use of our model should be applicable to all electrochemical system including batteries.

Our model for concentration gradient decay is based on Refs. 1 and 2. In Fig. 2(a) the solid line represents the profile expected during steady state electrodeposition of the zinc metal. The dashed line shows how our model differs from what we think is the actual profile. The symbol y is used as the boundary layer thickness dictated by our model. In order to characterize the degree to which the real situation deviates from our model, we have invented a thickness y^* so that the area P in Fig. 2(a) equals area Q. The difference between y^* and y is a measure of the breadth of the interface between the diffusion and convection regions. A more mathematical definition of y^* would be $2\int_g^\infty \Delta C_x \, dx/\Delta C_i$ where ΔC_x is the zincate concentration difference between the bulk value and that at position x in the boundary layer.

Induced convection during current flows keeps the bulk of the electrolyte mixed and at a uniform constant composition as indicated in Fig. 2(a). The conversion of zincate to zinc at the cathode during current flow causes the zincate concentration gradient across the boundary layer. In previous work (Ref. 1), the zinc metal appeared to plate out essentially only at the boundary layer-porous zinc metal interface and not within the porous zinc. If this is true, steady state current conditions would require the zincate concentration within the porous zinc deposit to be essentially constant as depicted in Fig. 2(a).

When the current is shut off, the zincate tends to be transported from the bulk into the porous zinc metal until at infinite time, the concentration difference ΔC_t between the bulk and electrode becomes zero; ΔC_t is a function of distance from collector and time. Figure 2(b) illustrates a possible zincate concentration profile at some time after the current is shut off. The boundary layer is now represented by y_0 in case it is different from the thickness during passage of current.

The transport of zincate within the porous zinc can be quite complicated. Tortuosity exists which can slow down transport. In contrast,

multiplicity of transport modes can lead to unexpectedly rapid transport. Modes of transport include bulk diffusion, surface diffusion, convection and electrochemical transport. In our model we make the simplifying assumption that regardless of the transport mechanism, an equation similar to Fick's second law applies.

$$\frac{dC}{dt} = D_g \frac{d^2C}{dx^2} \tag{3}$$

D_g is the net transport coefficient. To integrate Eq. (3) over both region g and y, the transport coefficient in both regions must be equal; however if they are approximately equal as was first supposed Eq. (4) becomes an approximate solution (Ref. 4)

$$C_t = a_o + \sum a_n \cos(\lambda_n x) \, e^{-\lambda_n^2 D_g/t} \tag{4}$$

There are no sine terms because of symmetry with respect to $x = 0$. The constants $a_n's$ and $\lambda_n's$ can be evaluated from the model profile at zero time in Fig. 2(a) using Fourier series methods (Ref. 5). Thus, Eq. (4) becomes

$$\frac{\Delta C_t}{\Delta C_i} = \frac{C_\infty - C_t}{C_\infty - C_i} = \sum_{\substack{odd \\ n}} \frac{16(g + y_o)}{y(n\pi)^2} \sin \frac{n\pi \left(g + \frac{y}{2}\right)}{2(g + y_o)} \sin \left(\frac{n\pi y}{4(g + y_o)}\right)$$

$$\times \cos \frac{n\pi x}{2(g + y_o)} \, e^{-[n\pi/2(g+y_o)]^2 D_g t} \tag{5}$$

At long times only the first term of Eq. (5) is important so that the equation simplifies to first order kinetics. From the definition of half life,

$$t_{1/2} = \ln 2 \left/ \frac{d \ln(\Delta C_t/\Delta C_i)}{dt} \right. \tag{6}$$

Combining Eq. (6) with the derivation of the first term of Eq. (5) yields

$$\sqrt{t_{1/2}} = \frac{2}{\pi} (g + y_o) \sqrt{\frac{\ln 2}{D_g}} \tag{7}$$

Thus the half life appears not to be dependent on the original concentration profile but only on the transport coefficient and thicknesses of the layers. Equation (7) also states that the half life is the same regardless of where the decay rate is measured; therefore for our experiment, knowledge as to where the concentration is being measured is not necessary. According to Eq. (7) a plot of $\sqrt{t_{1/2}}$ versus porous zinc thickness g should result in a straight line allowing the calculation of D_g and y_o.

D_g is much smaller than the zincate bulk diffusion coefficient D (transport coefficient operating in region y), one can solve Eq. (3) with the assumption that no gradient exists within region y_0. In other words, y_0 can be taken to be zero and thus

$$\sqrt{t_{1/2}} = \frac{2g}{\pi} \sqrt{\frac{\ln 2}{D_g}} \tag{8}$$

If D_g is much larger than D; there will be essentially no gradient in region g during decay. And the rate of the entire process would be governed solely by flow through a uniform but time dependent concentration gradient in the boundary layer. Because of these factors, Fick's first law may be written

$$F = -D \frac{\Delta C_t}{y_0} \tag{9}$$

where F is the flow per unit area at any time through the boundary layer. This value of F is also equal to minus the rate of increase per unit area of the amount of zincate within the porous zinc region. This amount of zincate per unit area is equal to the product of its concentration C_t and its length g plus a small contribution from the boundary layer $y^*/3$. Thus

$$F = -\frac{d}{dt}\left[C_t\left(g + \frac{y^*}{3}\right)\right] = \frac{d}{dt}\left[\Delta C_t\left(g + \frac{y^*}{3}\right)\right] \tag{10}$$

Remember $\Delta C_t = C_\infty - C_t$. The term $y^*/3$ arises from the following: If all the zincate change in the boundary layer involved diffusion through the entire boundary layer, one would use $y^*/2$ $\left(\text{that is } y^*\int_0^1 x' \, dx'\right)$ because the average value of ΔC_x in the y region is $\Delta C_t/2$. To correct for the fact that some changes in concentration involve diffusion through only a portion of the boundary layer, one should use $y^* \int_0^1 (x')^2 \, dx'$ or $y^*/3$.

Then, combining Eqs. (9) and (10) followed by integration yields:

$$\frac{d \ln}{dt}\left(\frac{\Delta C_t}{\Delta C_i}\right) = \frac{D}{\left(g + \frac{y^*}{3}\right)y_0} \tag{11}$$

Combining Eqs. (6) and (11) yields

$$t_{1/2} = \frac{\ln 2 \left(g + \frac{y^*}{3}\right)y_0}{D} \tag{12}$$

Thus if D_g is much greater than D, a plot of $t_{1/2}$ versus g should give a straight line and permit calculation of y^0/D and y^*.

Special mathematical attention should be given to the case where $g = 0$; that is the case where there is no zinc deposit. Under this condition solution of Eq. (3) requires no approximation. Thus, the half life can be found to be

$$t_{1/2} = \left(\frac{2y_o}{\pi}\right)^2 \frac{\ln 2}{D} \tag{13}$$

Actually, no concentration decay experiment can be performed with absolutely no deposit. However, Eq. (13) illustrates that plots of $t_{1/2}$ or $\sqrt{t_{1/2}}$ versus g may have deviations from straightness near $g = 0$; see Eqs. (7), (8), and (12).

In our experiments with layers of asbestos on the cathode and essentially no zinc deposit, one can let D_g be the zincate transport coefficient within the asbestos and g, the thickness of the asbestos. For this situation, solution of Fick's law for the three cases ($D_g \cdot D$; $D_g < D$; and $D_g > D$) yield the same equation for $t_{1/2}$ as were found for the case of g equalling the thickness of the porous zinc and D_g equalling its zincate transport coefficient. Refer to Eqs. (7), (8), and (12). Note that the original zincate profile in the asbestos will differ from that in the porous zinc; but the final equations are independent of the original zincate profiles.

RESULTS AND DISCUSSION

Concentration Gradient Decay as Function of

Zinc Deposit Thickness

Normal position. - Figure 3 shows a typical concentration gradient decay curve for the horizontal cathode at the bottom of the cell. It approximates first order decay after a short period of time in accord with our model. From such plots, values of $t_{1/2}$ were calculated via Eq. (6). In Figs. 4 and 5, respectively, we have plotted $\sqrt{t_{1/2}}$ and $t_{1/2}$ as a function of g as suggested by Eqs. (7) and (12). The purpose was to determine which is the more appropriate equation. The results from four different electrolytes are plotted in both figures. Consider first Fig. 4; near $g = 0$, the curves deviate considerable from linear dependence. Values of the zincate transport coefficients D_g were calculated from the slopes in Fig. 4 via Eq. (7) and tabulated in Row 4 of Table I together with the compositions (Rows 1 and 2) and viscosities (Row 3) of the electrolytes. The value of the zincate diffusion coefficient for each electrolyte (Row 5) was calculated from its respective viscosity via the Stokes-Einstein equation using 1.9 Å as the radius of the moiety (which is based on experimental diffusion and viscosity data; Refs. 5 to 9). Row 6 of Table I lists the D_g to D ratio which is about 7 for all the electrolytes. Thus Eq. (7) which is based on a D_g to D ratio of about one should not be applied. However, we can conclude that D_g is much greater than D although an accurate value of D_g cannot be ascertained.

Comparing Fig. 5 with Fig. 4, one can see that the plots in Fig. 5 appear to be more nearly linear than those in Fig. 4. This is expected because values of D_g are much larger than those for D. The slopes and $t = 0$ intercepts of the data in Fig. 5 are tabulated respectively in Rows 7 and 8 of Table I. The value of y_0 for each electrolyte (Row 9) was calculated via Eq. (12) and the respective slope. The average value is 0.013 cm. The values of y^* were obtained from the $t = 0$ intercepts by multiplying by a minus 3; see Eq. (12). The values of y^* appear to be about 50 percent greater than the values of y_0. This indicates that the actual concentration profile (solid line Fig. 2(a)) does not deviate radically from our model (dashed line Fig. 2(a)) and means that the interface between diffusion and convection transport is moderately sharp. One should point out that the calculated values for y_0 are dependent on the value of D while those for y^* are not. Thus, the results also give credence that the proper values of D have been used. In Table I, a slight increase of both y_0 and y^* with decreasing viscosity can be noted; however, these variations may well be within our experimental error.. A value of y during current flow was calculated from data in Ref. 4; see Row 11, footnote b in Table I. This value for y is about half the corresponding value of y_0. Whether the difference between y and y_0 is real or not, we cannot say at present; however, the data in Ref. 1 indicate y is essentially independent of current density.

Although the current density does affect the concentration gradient, no effect of current density on $t_{1/2}$ is predicted by our model and none was found experimentally. Moreover, when the values of $t_{1/2}$ are compared on the basis of thickness, as is done in Figs. 4 and 5, the data seem to be independent of the type of zinc deposit, mossy or large crystalline.

Cell in inverted position. - Figure 6 shows a typical concentration gradient decay curve for the horizontal cathode at the top of the cell. One can notice that the extrapolated intercept of the straight line position to zero time deviates drastically from unity compared with the data in Fig. 3. This may be attributable to premature mixing caused during the inversion of the cell. Via Eq. (6), the values of $t_{1/2}$ were obtained from the straight portions of such graphs. The $\sqrt{t_{1/2}}$ values for Electrolyte I (9.46 M KOH; 1.15 M potassium zincate) were plotted as a function of g; the resultant D_g via Eq. (8) was again found to be about seven times the respective D. Thus we plotted $t_{1/2}$ values against g as shown in Fig. 7. Via Eq. (12) values of y_0 and y^* were calculated from the slope and the $t = 0$ intercept of this curve in the same manner as they were for the curves in Fig. 5: $y_0 = 0.081$ cm and $y^* = 0.125$ cm. Again y^* is about 50 percent greater than y_0. But these values are an order of magnitude larger than those for the same electrolyte with the cell in the normal position; see Table I, Electrolyte I: $y_0 = 0.010$ cm; $y^* = 0.016$ cm. This difference in boundary layer thickness indicates that gravimetric induced convection has a great bearing on the thickness of the boundary layer.

Concentration Gradient Decay as a Function

of Asbestos Thickness

A concentration gradient decay curve for a cell with asbestos on the cathode is shown in Fig. 8. The intercept of the straight line portion is close to unity indicating very little deviation from first-order kinetics. In Fig. 9 we have plotted values of $\sqrt{t_{1/2}}$ for Electrolyte I against the thickness of asbestos. The most reliable point in Fig. 9 is at zero thickness which corresponds to the zero thickness point for Electrolyte I given in Figs. 4 and 5. The slope via Eq. (7) yields a D_g in asbestos of 0.98×10^{-6} cm^2/sec a value about 30 percent lower than the bulk diffusion coefficient. The closeness of D_g to D validates the use of Eq. (7). One can expect D_g in asbestos to be smaller than D because of tortuosity; however, our low experimental value may well be accountable to uncertainty in the slope of Fig. 9.

A plot of $t_{1/2}$ versus g (not shown) yielded via Eq. (12) a y_0 value of 0.13 cm which is not a reasonable value, being an order of magnitude greater than the y_0 values listed in Row 9 of Table I. This unreasonableness in the value of y_0 adds credence for the application of Eq. (7) rather than Eq. (12) to our asbestos data.

FURTHER DISCUSSION

The rapid transport of zincate through porous zinc deserves further consideration. First, our data do not allow us to calculate with any degree of certainty the magnitude of the transport coefficient involved; but an educated guess would be that D_g is at least about an order of magnitude greater than D. Second, the rapid transport appears to be operative even when the cell is in the inverted position: thus, the cause of the rapid transport of zincate is probably not due to gravitationally induced convection.

We believe the apparent rapid transport of zincate through porous zinc to be due to an electrochemical mechanism. Our belief arises from the following observation. In several of our normal position gradient decay experiments where the zinc deposit had the large crystalline morphology, we observed mossy zinc growing at the zinc-boundary layer interface during the decay period when no current was passing through the cell. We believe this mossy zinc deposit is caused by local electrochemical reaction with the driving force arising from the small local concentration gradients present within the porous zinc. The zinc metal would deposit at high zincate concentration regions and dissolve in low zincate concentration regions. The phenomenon would decrease the zincate concentration near the place where the zinc metal is deposited and increase the zincate concentration where the zinc dissolves. The net effect as far as the zincate is concerned is rapid transport from regions of higher concentration to regions of lower concentration.

Another topic that warrants further attention is the observation that the concentration gradient half life is dependent on the thickness of zinc plate. This suggests the possible use of the half life as a measure of the thickness of deposit. In the present state of the method, it is not precise but it might be helpful when deposits cannot readily be observed. The general method is neither limited to battery applications nor to the zinc electrode. Of course feasibility experiments and calibration would be required for a specific application. One must emphasize that the method is a measure of thickness and not of moles of deposit. One application might be the detection of morphology of deposit by plotting $t_{1/2}$ against the number of coulombs. A change in slope particularly an abrupt one should indicate a change in effective density of deposit and thus a change in morphology.

SUMMARY OF RESULTS

The results from our study of the decay of the zincate concentration gradient at an alkaline zinc horizontal cathode collector after charging can be summarized as follows:

1. Zincate concentration gradient decay curves approximate first order kinetics.

2. The zincate concentration gradient half life increases with increasing thickness of zinc deposit on the cathode; there is no effect of current density.

3. The transport of zincate through porous zinc is much faster than predicted from the bulk diffusion coefficient; it is attributed to a localized electrochemical mechanism.

4. The boundary layer thickness for a cathode at the bottom of the cell is about 0.01 cm with very little if any dependence on the viscosity of the electrolyte.

5. The boundary layer thickness for a cathode at the top of the cell is about 0.0f cm; this is attributed to less gravitationally induced convection when the cathode is on top.

6. The transport of zincate through asbestos is comparable with that predicted from the bulk diffusion coefficient.

7. The results are consistant with a model in which for a constant current the zincate concentration within a porous zinc cathode is not a function of position and a uniform concentration gradient exists in the boundary layer.
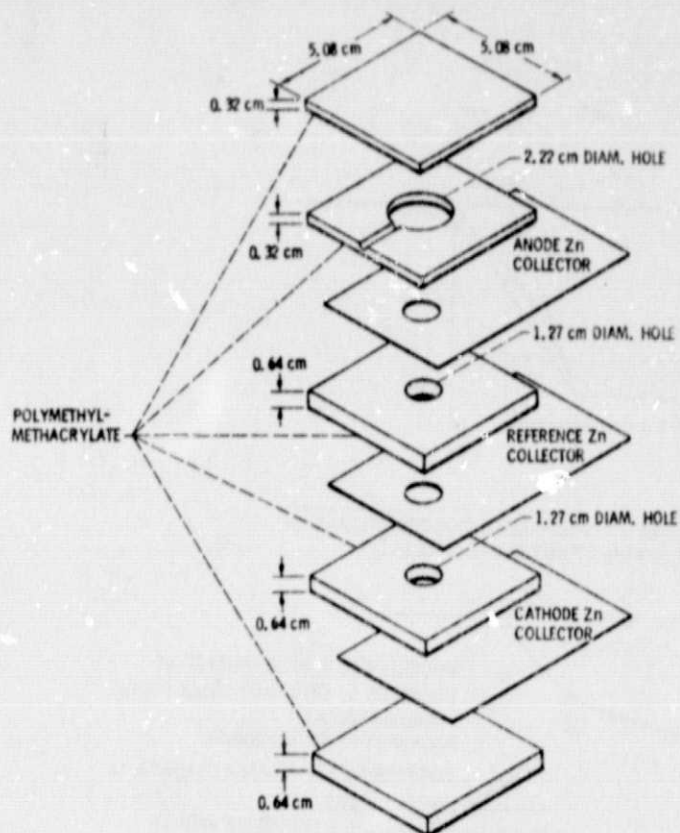
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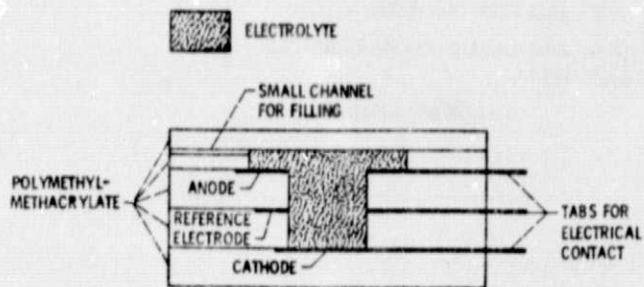
TABLE I. -- CALCULATION OF BOUNDARY LAYER THICKNESS

No.	Electrolyte	I	II	III	IV
1	OH^- conc.; M, l^{-1}	9.46	7.37	4.93	2.30
2	Zincate conc.; M, l^{-1}	1.15	0.91	0.61	0.31
3	Viscosity; cP	7.742	3.990	2.323	1.441
4	D_g, zincate transport coef. through zinc; cm^2, sec^{-1}	1.19×10^{-5}	1.85×10^{-6}	3.60×10^{-5}	5.78×10^{-5}
5	D, zincate diffusion coef.; cm^2, sec^{-1}	1.47×10^{-6}	2.86×10^{-6}	4.93×10^{-6}	7.94×10^{-6}
6	D_g/D	8	6	7	8
7	Slope, Fig. 5; min, cm^{-1}	74	51	31	22
8	t = 0 Intercept, Fig. 5; cm	-0.005	[a]-------	-0.007	-0.007
9	y_o; cm	0.010	0.012	0.013	0.015
10	y^*; cm	0.015		0.021	0.021
[b]11	y; cm	0.005			

[a] Uncertain because of lack of data near g = 0.
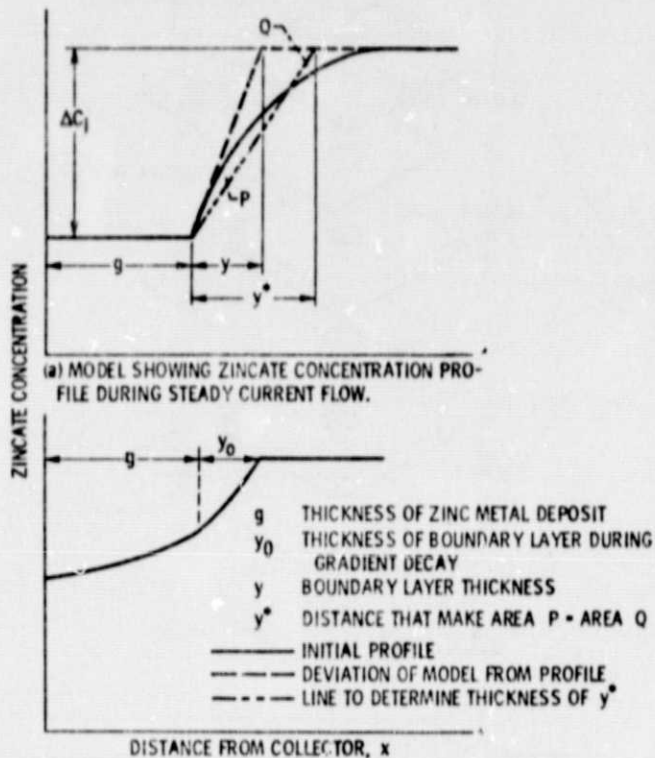[b] $y = 2 \times 96\ 500\ D\gamma_1 a/1000$: $a = 1.26\ cm^2$; $\gamma_1 = 1.35\ M/l \cdot A$ (Ref. 1).

5.08 cm — 5.08 cm

0.32 cm

2.22 cm DIAM. HOLE

0.32 cm

ANODE Zn COLLECTOR

1.27 cm DIAM. HOLE

0.64 cm

POLYMETHYL-METHACRYLATE

REFERENCE Zn COLLECTOR

1.27 cm DIAM. HOLE

0.64 cm

CATHODE Zn COLLECTOR

0.64 cm

(a) SCHEMATIC OF DISASSEMBLED CELL.

ELECTROLYTE

SMALL CHANNEL FOR FILLING

POLYMETHYL-METHACRYLATE

ANODE

REFERENCE ELECTRODE

CATHODE

TABS FOR ELECTRICAL CONTACT

(b) SCHEMATIC OF CELL (ACTUAL SIZE, CELL IS CLAMPED TOGETHER WITH BOLTS THAT ARE NOT SHOWN).

Figure 1. - Cell.

(a) MODEL SHOWING ZINCATE CONCENTRATION PRO-
FILE DURING STEADY CURRENT FLOW.

g	THICKNESS OF ZINC METAL DEPOSIT
y_0	THICKNESS OF BOUNDARY LAYER DURING GRADIENT DECAY
y	BOUNDARY LAYER THICKNESS
y^*	DISTANCE THAT MAKE AREA P = AREA Q

———— INITIAL PROFILE

— — — DEVIATION OF MODEL FROM PROFILE

— · — · LINE TO DETERMINE THICKNESS OF y^*

DISTANCE FROM COLLECTOR, x

(b) MODEL SHOWING ZINCATE CONCENTRATION PRO-
FILE DURING DECAY.

Figure 2. - Model.

THICKNESS OF POROUS ZINC: 0.041 cm; CHARGING
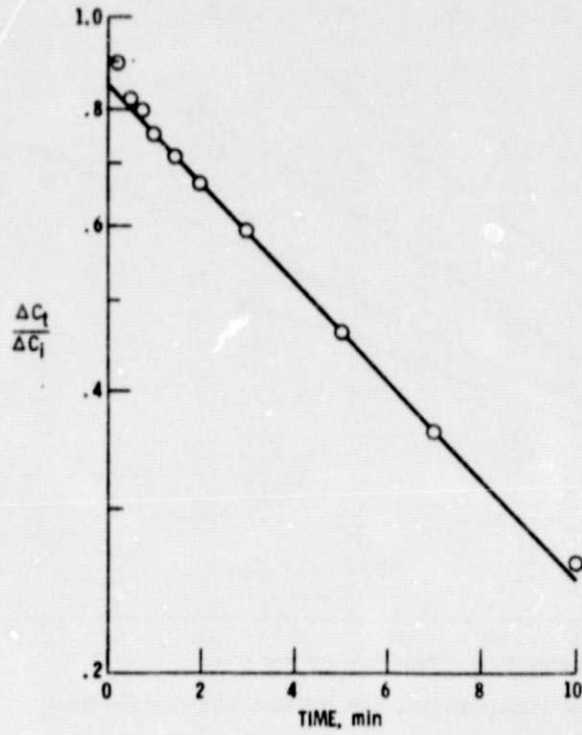CURRENT: 16 mA/cm²; ELECTROLYTE 1; OH⁻ CONC:
9.46 M/ℓ; AND ZINCATE CONC: 1.15 M/ℓ

Figure 3. - Zincate concentration gradient decay with
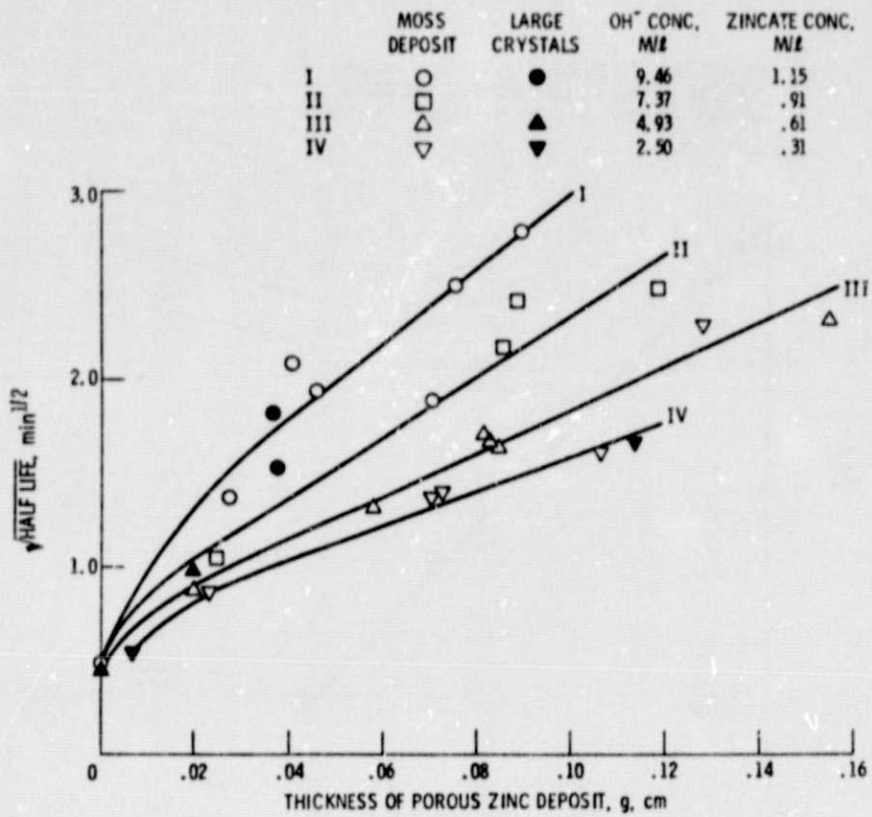layer of porous zinc on cathode; cathode at bottom.

	MOSS DEPOSIT	LARGE CRYSTALS	OH⁻ CONC, M/l	ZINCATE CONC, M/l
I	○	●	9.46	1.15
II	□	◼	7.37	.91
III	△	▲	4.93	.61
IV	▽	▼	2.50	.31

Figure 4. - Square root of concentration gradient half life as function of zinc deposit thickness.

	MOSS DEPOSIT	LARGE CRYSTALS	OH⁻ CCNC, M/ℓ	ZINCATE CONC. M/ℓ
I	○	●	9.46	1.15
II	□		7.37	.91
III	△	▲	4.93	.61
IV	▽	▼	2.50	.31
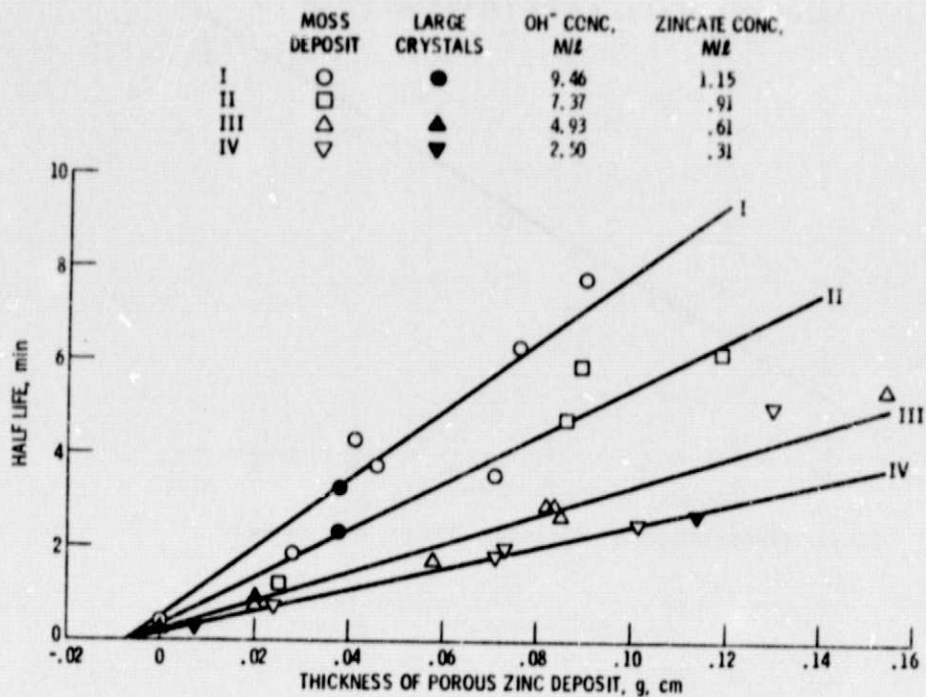
Figure 5. - Dependence of concentration gradient half life in thickness of zinc deposit.

THICKNESS OF POROUS ZINC: 0.05 cm; CHARGING CURRENT: 16 mA/cm²; ELECTROLYTE I; OH⁻ CONC: 9.46 M/ℓ AND ZINCATE CONC: 1.15 M/ℓ
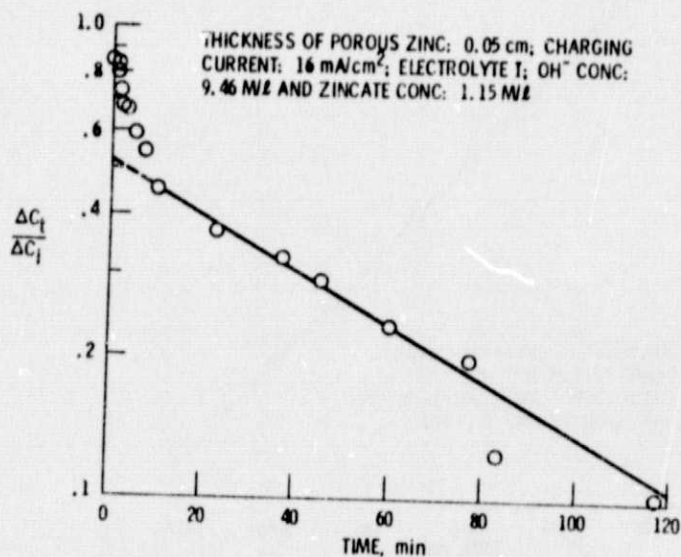
Figure 6. - Zincate concentration gradient decay with layer of porous zinc on cathode; cathode at top of cell.
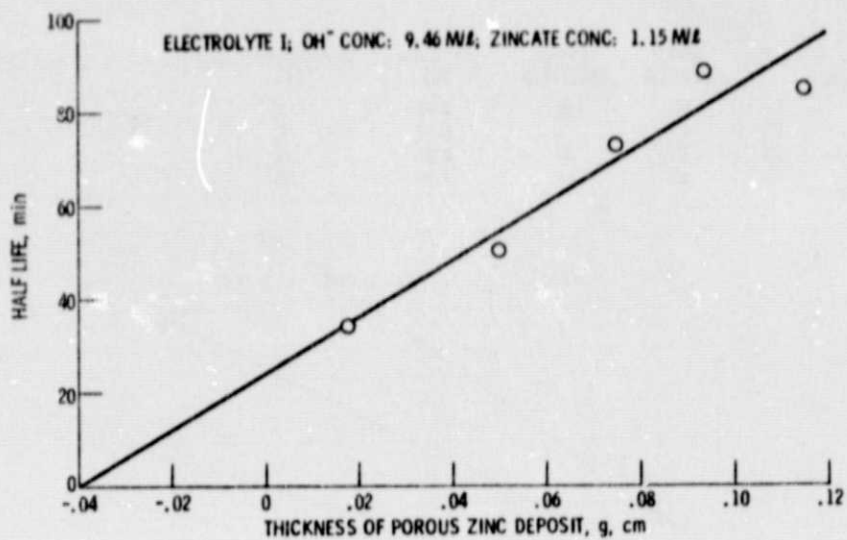
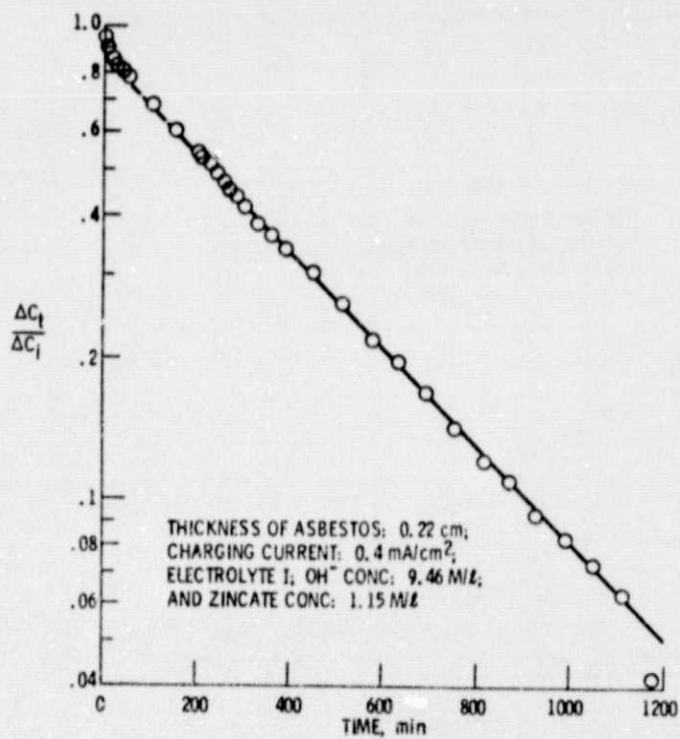Figure 7. - Dependence of concentration gradient half life on g for inverted cell.

Figure 8. - Zincate concentration gradient decay with asbestos covering cathode.
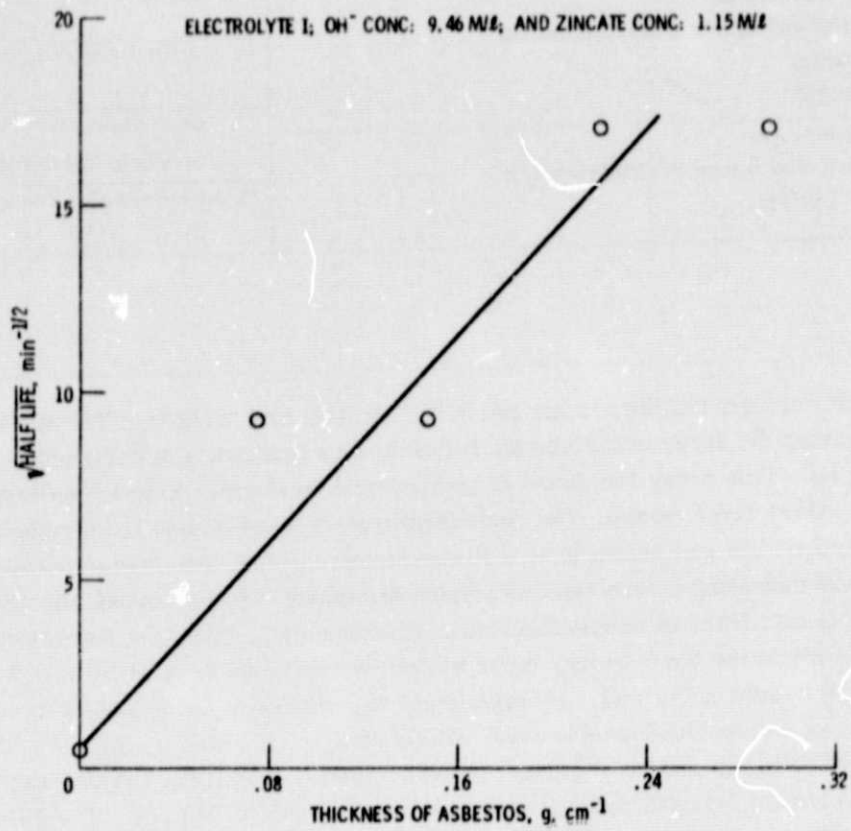
Figure 9. - Dependence of half life on asbestos thickness.

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This is a study of the transport of the zincate ion to the alkaline zinc cathode. The study was carried out by observing the decay of the zincate concentration gradient at a horizontal zinc cathode after charging. This decay was found to approximate first order kinetics as expected from a proposed boundary layer model. The concentrations were calculated from polarization voltages. The decay half life was shown to be a linear function of the thickness of porous zinc deposit on the cathode indicating a very rapid transport of zincate through porous zinc metal. The rapid transport is attributed to an electrochemical mechanism. From the linear dependence of the half life on the thickness the boundary layer thickness was found to be about 0.010 cm when the cathode was at the bottom of the cell. No significant dependence of the boundary layer thickness on the viscosity of electrolyte was observed. The data also indicated a relatively sharp transition between the diffusion and convection transport regions. When the cathode was at the top of the cell, the boundary layer thickness was found to be roughly 0.080 cm. The diffusion of zincate ion through asbestos submerged in alkaline electrolyte was shown to be comparable with that predicted from the bulk diffusion coefficient of the zincate ion in alkali.

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