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Electrodeposition of Zinc on Glassy Carbon from $ZnCl_2$ and $ZnBr_2$ Electrolytes

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ABSTRACT

The initial stages of the electrocrystallization of zinc from 3M $ZnCl_2$ and 3M $ZnBr_2$ on glassy carbon has been investigated using cyclic voltammetry, the potential step method, and scanning electron microscopy. Particular care was taken to ensure electrolyte purity and to eliminate resistance effects in the measurements. The nucleation overvoltage in 3M $ZnCl_2$ was ~ 17 and ~ 12 mV in 3M $ZnBr_2$. In 3M $ZnCl_2$, the current transients from the potential step measurements could be fitted to a simple model that assumes instantaneous nucleation followed by growth of three dimensional centers under kinetic control. A similar mechanism is operative for 3M $ZnBr_2$ at low overvoltages. At higher overvoltages, the current transient is governed by mixed kinetic and diffusion control and cannot be fitted to a simple model. The lower nucleation overvoltage and the faster kinetics in 3M $ZnBr_2$ is correlated with the lower stability constants for the zinc bromide complexes. Erroneous results are obtained when resistance effects are not accounted for.

The zinc electrode is common to both zinc/chlorine and zinc/bromine batteries. Although considerable progress has been made in engineering these batteries, there are still problems with the zinc electrode (1-8). These are related to changes in zinc electrode morphology which result in dendritic growth and nonadherent deposits. These problems are more severe under conditions of random shallow cycling.

There have been several publications on the kinetics of zinc deposition from zinc chloride electrolytes (9-16). There have been reports on the dependence of zinc morphology on additives (17) and a-c modulation of the charging current (18). The kinetics of dendrite growth in zinc chloride electrolytes has been reported recently (19). Except for brief references in a few publications (2, 6), there is no information in the open literature on the electrodeposition of zinc from zinc bromide electrolytes. In the case of zinc chloride, the publications deal mainly with the electrodic reactions (10-16) and the electrode morphology after prolonged deposition (17-19). There are no publications on the processes involved in the initial stages of nucleation and growth of zinc on foreign substrates.

In zinc halogen batteries, zinc is deposited on an inert current collector. Materials that have been used are plastic bonded carbon (5), dense graphite (7), vitreous carbon (6), or silver plated titanium. In the present study, the initial stages of zinc deposition on glassy carbon were investigated using the potential step technique (20). This included studies in both 3M $ZnCl_2$ and 3M $ZnBr_2$ electrolytes.

Experimental

Reproducible results, which fitted reasonable nucleation and growth models, could only be obtained after careful attention was given to current distribution, resistance effects, and electrolyte purity.

Cell design.—The cell used in these studies was a modification of the design of Cahan *et al.* (21). The cell, which was machined from PTFE, is shown in Fig. 1. The three PTFE parts were held together by aluminum flanges and tiebolts. The bottom two parts were sealed with a CTFE O-ring and a 0.25 mm PTFE spacer. The counter and reference electrodes were 1 mm diam zinc wires (99.9999% pure). These were covered with heat shrinkable PTFE tubing to a level below the top of the electrolyte. This cell design ensured uniform current distribution over the electrode surface. The working electrode was a 7.5 mm diam glassy carbon electrode with a PTFE collar (Pine Instrument Company). The collar formed a tight leak free slip fit with the bottom part of the cell.

Electrolyte preparation.—High purity 3M $ZnCl_2$ was prepared by reacting high purity zinc (99.9999%) with the distilled azeotrope of HCl. Concentration adjustments were made by additions of triply distilled water. High purity 3M $ZnBr_2$ was prepared by reacting high purity zinc with high purity bromine under triply distilled water. The reaction was carried out in an Erlenmeyer flask immersed in an ice bath.

Electric circuitry.—Cyclic voltammetry measurements were made using a Stonehart BC-1200 potentiostat in conjunction with a PAR 175 programmer and a Soltec 3316 X-Y recorder. Resistance correction was

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Key words: battery, SEM, nucleation.

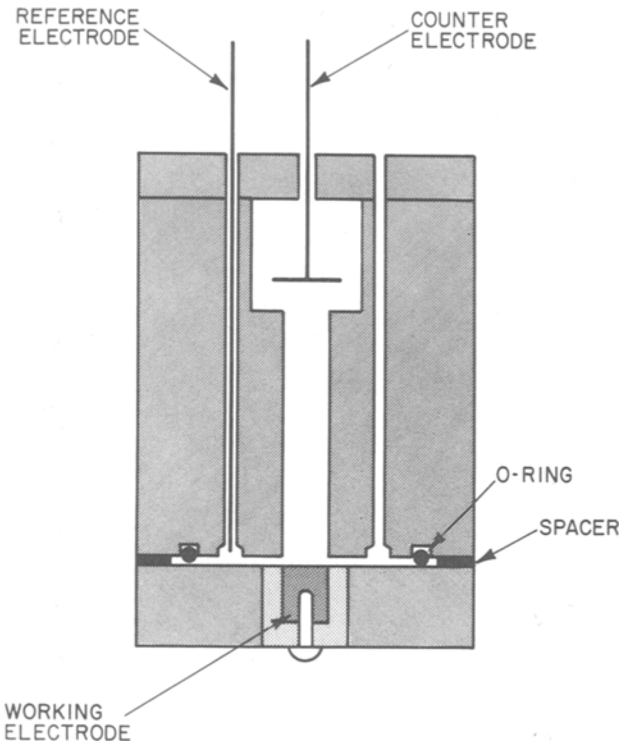

Fig. 1. Schematic of cell for zinc deposition studies

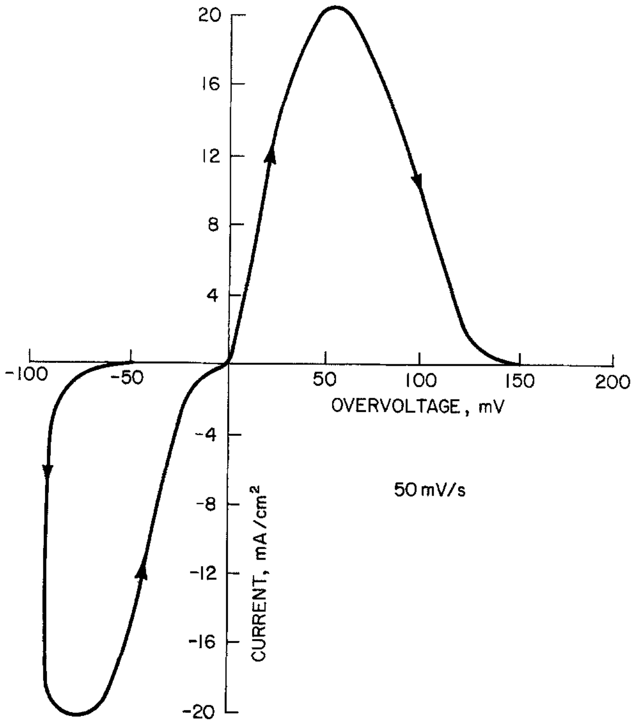

Fig. 2. Cyclic voltammogram for zinc deposition on glassy carbon in 3M $ZnCl_2$, pH = 2.8, sweep rate 50 mV/sec.

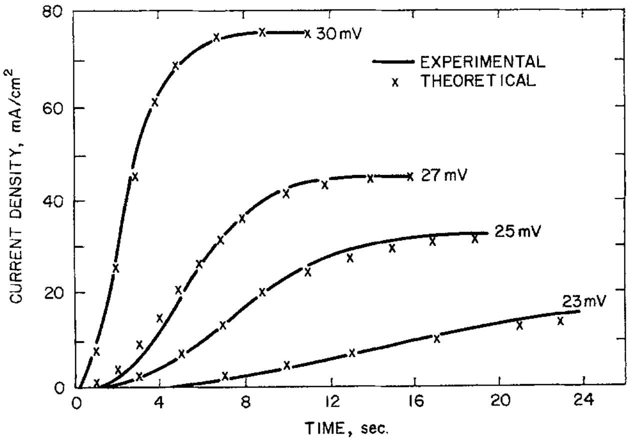

Fig. 3. Current transients (solid lines) for zinc deposition on glassy carbon in 3M $ZnCl_2$, pH = 2.8. Overvoltages are indicated on the figure. Calculated values for the current based on Eq. [2] in the discussion and the constants in Table I are also shown (X).

made using the potentiostat in conjunction with a Hewlett-Packard 3325A function generator and a Tektronix 7634 oscilloscope. Potential step measurements were made using the potentiostat in conjunction with the X-Y recorder.

Experimental procedure.—The electrodes were successively polished with 320 and 600 grit sandpaper, 3 and 1μ diamond polish. The electrodes were then rinsed with triply distilled water and assembled in the cell. Particular care was taken to ensure that the electrode surface was flush with the top surface of the bottom part of the cell. The cell was filled with 20 ml of deaerated electrolyte, and the electrochemical measurements were immediately carried out. When samples were prepared for scanning electron microscopy, the cell was quickly disassembled and the electrode was rinsed with water and methanol. Samples were stored under deaerated methanol prior to carrying out the electron microscopy. In some cases, the electrodes were weighed so as to determine the current efficiency for zinc deposition.

Results

Figure 2 is a cyclic voltammogram for zinc deposition from 3M $ZnCl_2$ on glassy carbon. The cyclic voltammogram exhibits a nucleation loop in that cathodic current on reversal of the sweep is higher than that found on going in the cathodic direction. Qualitatively, the results, in zinc bromide, were similar. There was no evidence of underpotential deposition of zinc.

Figures 3 and 4 show the results of the potential step measurements in 3M $ZnCl_2$ and 3M $ZnBr_2$, respectively. The current transients show a small induction time followed by a smooth rise to a current plateau. The potential step measurements indicate that the critical overvoltage for zinc deposition is ~17 mV in 3M $ZnCl_2$ and ~12 mV in 3M $ZnBr_2$. For the same overvoltage, the current is much higher in 3M $ZnBr_2$. At the higher overvoltages in 3M $ZnBr_2$, the shape of the current transients change. When the resistance correction is not made the currents are much lower. As the current increases, the iR component increases and the real applied potential decreases with time. This tends to level off the current transient.

Figure 5 shows scanning electron micrographs (SEM) of the deposit in 3M $ZnBr_2$ and 3M $ZnCl_2$. The SEM data indicate that the growth pattern may be described by the growth of equally sized zinc particles dispersed at random over the zinc surface. The number of particles per cm² increases with the applied overvoltage. When deposition was carried out for a long time the deposit morphology was essentially identical to that found by Oren and Landau (19). Weight measurements indicated that the current efficiency for zinc deposition was ~100%.

Discussion

Models for electrocrystallization.—Several models have been developed for describing the nucleation and growth of metals during electrodeposition at constant potential (20, 22-25). These models include various assumptions regarding nucleation and growth of three dimensional centers. Nucleation can be instantaneous or can occur over a period of time, governed by a first order kinetic law. Growth can occur under

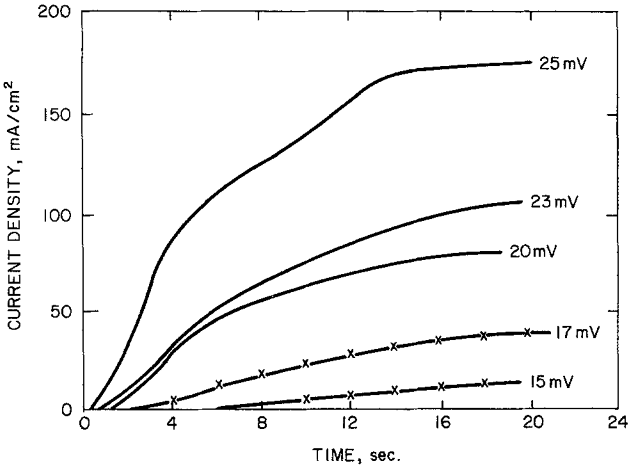

Fig. 4. Current transient (solid lines) for zinc deposition on glassy carbon in 3M $ZnBr_2$, pH = 3.0. Overvoltages are indicated on the figure. Calculated values for the current at 15 and 17 mV (×) are also shown. These are based on Eq. [2] in the discussion. At 15 mV $k^2N_0 = 2.13 \times 10^{-5}$ mol² cm⁻⁶ sec⁻², and at 17 mV, $k^2N_0 = 3.66 \times 10^{-5}$ mol² cm⁻⁶ sec⁻².

either kinetic or diffusion control. In the kinetic control growth models, provisions can be made to account for overlap of growth centers using the Avrami theorem (26). More complicated models have been developed which take into account such things as the death of growth centers (24, 25) and simultaneous layer growth along with the nucleation and growth of three dimensional centers (27-29).

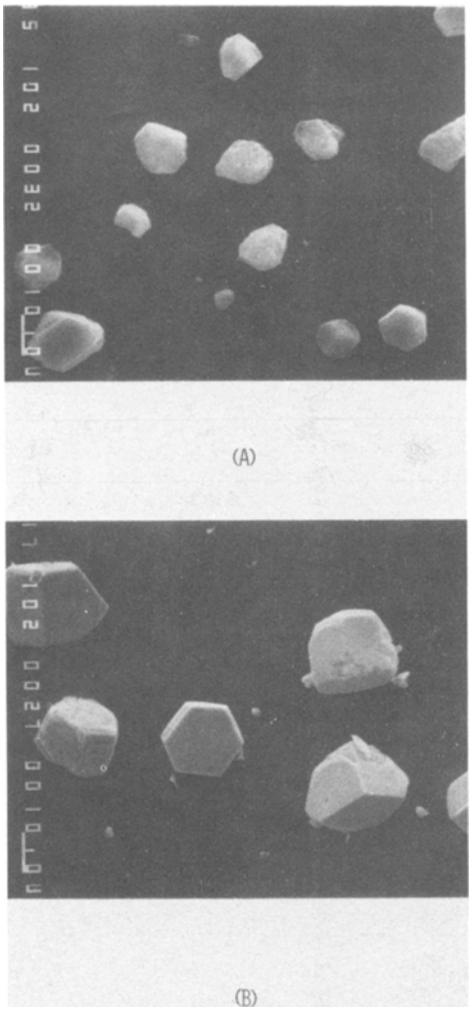

Fig. 5. Scanning electron micrograph of the deposit on glassy carbon after 10 sec of electrodeposition, (A) $ZnCl_2$ at 25 mV, (B) $ZnBr_2$ at 18 mV.

For the simpler models, rising current transients are predicted. For short times the relationship between the current, i, and time, t is

$$i \propto t^n \qquad [1]$$

The exponent n depends on the geometry, the type of nucleation, and the growth conditions. For instantaneous nucleation and growth under diffusion control, $n = 0.5$, and for progressive nucleation and growth under diffusion control, $n = 1.5$. For instantaneous nucleation and growth under kinetic control, $n = 2$, and for progressive nucleation and growth under kinetic control $n = 3$.

Electrodeposition in 3M $ZnCl_2$.—In the case of electrodeposition in 3M $ZnCl_2$, the following conclusions can be drawn from the experimental facts. The results from cyclic voltammetry, potential step measurements, and current efficiency determinations indicate that the contribution of hydrogen evolution to the overall current is negligible. Thus, the data can be treated without considering the contribution from hydrogen evolution. For short times $i \propto t^2$. This would indicate a mechanism involving instantaneous nucleation and growth under kinetic control. The scanning electron microscopy observations indicate that the zinc growths are approximately of equal size. This implies that the nucleation is instantaneous. The current time relationship for the growth of right circular cones under conditions of instantaneous nucleation and growth under kinetic control is

$$i = z\mathbf{F}k^1\left[1 - \exp - \left(\frac{\pi M^2k^2N_0t^2}{\rho^2}\right)\right] \qquad [2]$$

where k^1 and k are the respective rates (mol cm⁻² sec⁻¹) of crystal growth in the direction perpendicular and parallel to the substrate, M is the molecular weight of zinc (65.38 g/mol), ρ is the zinc density (7.14 g cm⁻³), and N_0 the instantaneous nucleation rate; $z = 2$ and $\mathbf{F}$ is the faraday constant.

Theoretical values of i, calculated according to Eq. [2] are shown in Fig. 3. The values of $z\mathbf{F}k^1$ and k^2N_0 for various overvoltages are given in Table I. The agreement between theory and experiment for the current transients is quite good. This, together with the microscopic observations, indicates that a simple mechanism based on instantaneous nucleation followed by growth of three dimensional centers under kinetic control, is operative.

Electrodeposition in 3M $ZnBr_2$.—In the case of zinc deposition from $ZnBr_2$ electrolyte, the contribution of hydrogen evolution can also be neglected. The microscopic observations and the dependence of the current on the square of the time for short times indicates that the mechanism is similar to that found in $ZnCl_2$ electrolyte. However, only the current transients at 15 and 17 mV could be fitted to Eq. [2]. The data at higher overvoltages could not be fitted to any simple theoretical model. Close fits could be obtained for models that assumed the onset of a second set of nuclei after a few seconds. However, the microscopic observations indicated that all the zinc growths were identical in size, and no nuclei beyond those instantaneously formed by the potential step were observed.

Table I. Values of zFk^1 and k^2N_0 for zinc deposition from 3M $ZnCl_2$ electrolyte

Overvoltage (mV)	$z\mathbf{F}k^1$ (mA/cm²)	k^2N_0 (mol² cm⁻⁶ sec⁻²)
23	15.84	1.42×10^{-5}
25	32.59	4.13×10^{-5}
27	45.27	9.75×10^{-5}
30	75.14	4.04×10^{-4}

The divergence from the simple theoretical model is most likely due to the onset of diffusion limitations at high current densities.

Comparison of electrodeposition in 3M $ZnCl_2$ and 3M $ZnBr_2$.—The nucleation overvoltage is lower ($\sim$12 *vs.* $\sim$17 mV) in $ZnBr_2$ than in $ZnCl_2$ electrolytes and the electrode kinetics are faster in $ZnBr_2$. It is known that the complexing halide ions can effect the exchange current density for molybdenum deposition from molten salts (30). A similar effect apparently occurs in the case of zinc in aqueous electrolytes. The stability constants for zinc chloride complexes are much higher than those for zinc bromide complexes (31). This would explain the lower nucleation overvoltage and the faster kinetics in $ZnBr_2$ electrolytes.

Effect of resistance corrections.—When no resistance corrections are made, the potential step measurements yield erroneous results particularly at high current densities. The nucleation rate is not greatly affected since the initial current is very low. However, as the current transient rises the real applied potential at the electrode falls and the current transient rises with a lower time exponent. At high current densities, the current *vs.* the square root of time yields linear plots. Thus, without resistance correction the data could be erroneously interpreted as having growth under diffusion control conditions. These results, and those of Cahan *et al.* in alkaline electrolyte (21), indicate that it is imperative to eliminate resistance effects in zinc electrode kinetic measurements. Otherwise, erroneous conclusions on mechanisms can be easily made.

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