

(*Electrochemical System*, 1973) and have been derived for $\text{ZnCl}_2\text{-H}_2\text{O}$ from the transport data of Agnew and Paterson (*J. Chem. Soc. Far. Trans. 1*, 74 (1978) 7986). The results appear to reflect increasing complexation. To estimate these binary diffusion coefficients from $\text{ZnCl}_2\text{-KCl-H}_2\text{O}$, effective diffusion coefficients reacting at $E = 1.35$ V are used. Consequently, only four species, K^+ , Cl^- , Zn^{2+} , and ZnCl_3^- , will be assumed present in the $\text{ZnCl}_2\text{-}^3$ M KCl solution as a first approach to the concentrated-solution transport formalism in this electrolyte.

For the experimental investigation of growth of dendritic zinc in these electrolytes, a cell with a concentric inner rotating cylinder electrode is being used. Alternatively, a rectangular cell with a free-convection flow pattern has been designed.

In 1983 the multicomponent diffusion equation in solution-side transport processes will be used to formulate the migration effect making use of known or estimated diffusion coefficients. Experiments will be conducted under two different conditions, *i.e.*, galvanostatic and potentiostatic deposition at initially smooth and initially profiled electrodes. Rotating speed, coulombs passed, concentration of zinc halide, and applied potential will be the main parameters to be investigated.

The microscopically nonuniform current distribution at a dendrite-like protrusion will be analyzed as part of the effort to understand better the interaction of dendrites with mass transfer in solution. A model for predicting the growth rate of dendrite will be developed. The theory will be compared with the results from the cell with inner rotating concentric cylinder electrode and the free convection cell.

Recent publications

- 1 M. L. Gopikanth, W. C. Hsie and J. R. Selman, Effective diffusivities of zinc in concentrated zinc halide solutions, to be submitted to *J. Electrochem. Soc.*, 1982.

ZINC ELECTRODE MORPHOLOGY IN ACID ELECTROLYTES

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The purpose of this research is to elucidate the factors affecting zinc electrode morphology in acidic zinc chloride and zinc bromide electrolytes. The results will provide fundamental information needed to improve the design and performance of zinc/halogen batteries.

Significant advances have been made in elucidation of the mechanisms of the nucleation and growth of zinc in high purity zinc chloride and zinc

bromide electrolytes. This has included an investigation of zinc-on-zinc deposition and zinc on foreign substrates, such as glassy carbon, graphite, silver, and copper. In addition, some preliminary exploratory work has been done on the effect of superimposed a.c. square waves, fluorinated surfactants, and inorganic cation (Pb^{++} , Bi^{+++}) additions on zinc electrode morphology.

The experimental approach taken was to use the potential step technique with careful attention to eliminate extraneous resistance effects. Baseline data were obtained in high purity electrolytes. High purity 3 M ZnBr_2 was prepared by the direct reaction of high purity (99.9999 percent) zinc and bromine and high purity 3 M ZnCl_2 was prepared by the reaction of high purity zinc with the distilled azeotrope of HCl.

The results for zinc deposition from 3 M ZnBr_2 and 3 M ZnCl_2 on glassy carbon may be summarized as follows. The nucleation overvoltage is approximately 12 mV in 3 M ZnBr_2 and is approximately 17 mV in 3 M ZnCl_2 . In 3 M ZnBr_2 , the critical overvoltage for dendrite initiation coincides with the nucleation overvoltage. In 3 M ZnCl_2 , the exchange current is lower than in 3 M ZnBr_2 , and growth in the overvoltage region of 20 mV to 35 mV can be described by a mechanism involving instantaneous nucleation and growth of three-dimensional centers under kinetic control.

Zinc-on-zinc deposition is quite different. When zinc is deposited on a smooth annealed zinc surface, growth occurs through simultaneous layer growth along with instantaneous nucleation and growth of three-dimensional centers. The density of the latter increases with the overvoltage. When zinc is deposited on silver or copper, the growth pattern is very similar to that found in the zinc-on-zinc case. Apparently the occurrence of underpotential deposition of zinc on these metals and alloy formation yields a zinc-like surface that promotes layer growth. On zinc, silver, and copper, there is no detectable nucleation overvoltage for zinc deposition.

Plans for the next period involve the following efforts:

- The work on collection and analysis of baseline data in high purity electrolytes will be completed shortly.
- The effects of superimposed a.c., surfactants and inorganic additives on the various nucleation and growth processes will be investigated.
- Promising approaches to control zinc morphology will be evaluated in small flow-by cells.

Recent publications

- 1 J. McBreen, E. Gannon, D. T. Chin and R. Sethi, Effect of AC charging methods on zinc electrode morphology, *American Chemical Society Meeting, Las Vegas, March 28 - April 2, 1982*.
- 2 J. McBreen, E. Gannon, D. T. Chin and R. Sethi, Zinc deposition in acid electrolytes, *Extended Abstracts, 82-2, The Electrochemical Society, Inc., Pennington, NJ, 1982*.