DENDRITIC ZINC DEPOSITION IN FLOW BATTERIES

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The objectives of this work are to:

- Clarify the solution-side transport processes involved in zinc deposition from acidified halide electrolytes and their effect on the electrode kinetics of zinc deposition and hydrogen evolution;
- Investigate experimentally the growth characteristics, in these electrolytes, of microprofiles of dendritic type in the presence of convection; and
- Relate, insofar as possible, these characteristics to the solution-side transport process and the electrode kinetics of zinc deposition from acidified halide solutions.

Diffusion coefficients for concentrated zinc halide solutions are lacking and can be obtained conveniently by the polarographic method. Extensive data have been obtained for both $ZnCl_2$ and $ZnBr_2$ solutions with 3 M KCl as supporting electrolyte. These data are in fairly good agreement with the few diffusivity data available by other methods; however, they reflect migration and complexation effects of unknown magnitude. A publication reporting these data is being prepared.

To obtain more insight into the significance of these data, the following factors were further explored using solutions very dilute in zinc halide: (1) pH effect on the polarization curve and its plateaus and (2) mercury flow rate and drop time. A simpler system ($CuSO_4$–H_2SO_4; no complexation involved) was also studied by polarographic measurement to verify the technique.

To interpret effective diffusion coefficients, the migration effect was assessed in a preliminary way by assuming a dilute-solution transport formalism including reversible complexation. The program is easily modified for different reacting species and XK values. The variation in XK is due to activity effects that can be related to hydration (see below).

A wide range of stability constants can be found in the literature; there are obvious inconsistencies in the data. The stability constants of Skou *et al.*, (*Electrochemica Acta, 22* (1977) 169 - 174), were chosen; they account for activity effects in terms of hydrated species only. Distribution diagrams for the $ZnCl_2$–H_2O and $ZnCl_2$–KCl–H_2O systems were calculated. In the range of zinc concentration used in zinc/halogen batteries (1 - 3 M $ZnCl_2$), three species are present: in the binary $ZnCl_2$ solutions Zn^{2+}, $ZnCl^+$, and $ZnCl_3^-$; in $ZnCl_2$ solutions with 3 M KCl, $ZnCl_3^-$ is the dominating species.

Binary diffusion coefficients needed in computations that make use of a concentrated-solution transport formalism are those defined by Newman

(*Electrochemical System*, 1973) and have been derived for $ZnCl_2$–H_2O from the transport data of Agnew and Paterson (*J. Chem. Soc. Far. Trans.* I, *74* (1978) 7986). The results appear to reflect increasing complexation. To estimate these binary diffusion coefficients from $ZnCl_2$–KCl–H_2O, 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 $ZnCl_2$–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