

formation in alkaline media. In acid media, similar information is required for the Zn/Cl₂ and Zn/Br₂ systems.

(2) Shorting has also been observed at open circuit, and a detailed study is required to outline conditions under which this deleterious phenomenon occurs.

(3) Shape change or slumping at the zinc electrode leads to serious deterioration, and observations of this process during cycling are required in the single-pore microcell.

(4) Nickel oxide exfoliation from the nickel substrate appears to be identified as a cause for nickel electrode performance deterioration. Correlations are needed for various conditions of cycling with the extent of exfoliation.

(5) Continued studies are needed on the effects of cycling zinc electrodes (acidic and basic media) as started in this program in 1979.

Recent publications

- 1 T. Katan, P. T. Bergeron and S. Szpak, Evolution of reaction profiles in porous zinc electrodes, *J. Electrochem. Soc., Ext. Abstr.*, 79-2 (1979) (in press).
- 2 S. Szpak, C. J. Gabriel and T. Katan, Fragmentation of dendritic zinc clusters on electrode cycling, *J. Electrochem. Soc.*, to be submitted.

RESEARCH ON ALKALINE ZINC SECONDARY ELECTRODES WITH EMPHASIS ON LIFE IMPROVEMENT

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The goal of the project is to provide information which will aid in the realization of a reproducibly long-lived zinc secondary battery designed and constructed in such a manner as to retain the high energy density and power density capabilities of the porous zinc electrode. Our approach has been to carry out experiments based on mathematical models of the electrode developed by Professor Douglas Bennion, UCLA, and his colleagues and students. The modelers use their best efforts to construct tractable models which include the essential aspects of physical processes occurring in the electrodes. The results are predictions of observable quantities related to electrode performance; the predictions serve as guidelines for the experimentalist in the laboratory, thus, hopefully, increasing the effectiveness of the laboratory work. Agreement between model prediction and experiment serves to reinforce one's conviction that essential processes are understood and properly incorporated into the model; disagreement defines limits of applicability of

the model and/or calls for changes in the model which might involve fine tuning of an approximation or major changes, such as inclusion of factors previously believed negligible but indicated, by experimental evidence, to be of greater importance.

Early in this report period, emphasis was placed on testing assumptions and predictions based on the Choi model of the zinc-silver oxide cell with normal convection. Cells with convection which incorporated several reference electrodes and electrolyte sampling ports were cycled. Data reported include overpotentials of the zinc electrode as functions of position and time as cycling proceeded, volume average fluid flow rates for selected cycles, and concentrations as functions of position in the zinc electrode compartment during selected cycles. Active material distribution over electrodes subsequent to cycling was also determined. Periodic concentration changes in the zinc compartment within cycles, as postulated in the Choi model, were confirmed; however, drastic cumulative concentration changes predicted at the ends of cycles were not observed, indicating a need for model revision better to reflect actual cell construction and behavior. Analysis of electrodes subsequent to cycling confirmed material redistribution predicted and observed by Choi for cells of similar design, flow rates, and current densities.

Later in the report period emphasis has been placed on evaluation of failure modes of porous zinc electrodes operated under conditions of severely limited convection as predicted by Sunu. The failure mode which has been emphasized is that of short term failure due to OH^- depletion on cell discharge. We have sought, by several means, to measure volume average OH^- concentration decreases in small, 1 cm^2 apparent surface area, 0.1 cm thick porous zinc electrodes, operated under conditions of severely limited convection. The cell being used allows for observation of test electrode overpotentials, and membrane resistance, as well as chemical analysis of the electrolyte in the test electrode. Our results to date fail to support OH^- depletion as a primary failure mode under the given circumstances. The possibility that the disagreement lies in theoretical treatment of membrane behavior is being considered as well as other possibilities.

Further work being done under subject contract involves measurement of hydrostatic pressure changes in the limited convection cell during cycling, and the construction and testing of small, thin, porous zinc electrodes based on a porous nickel conducting matrix. The latter work has been initiated based on our conviction, developed over the past several years, that the kind of porous zinc electrode which will be most effective in a high energy density secondary cell is a very thin electrode of graded pore size which will be operated under severely limited convective flow conditions.

Recent publications

- 1 D. C. Hamby and J. Wirkkala, *J. Electrochem. Soc.*, 125 (1978) 1020.
- 2 D. C. Hamby, N. J. Hoover, J. Wirkkala and D. Zahnle, accepted for publication, *J. Electrochem. Soc.*, June, 1979.