

safer, and/or lower-cost batteries. Research on zinc/bromine, calcium/metal sulfide, and iron/chromium (redox) cells will progress toward the technology transfer stage, and exploratory work on such systems as solid electrolyte, organic electrolyte, and molten-salt cells will be pursued.

Engineering Science Research will include morphological studies that address problems hindering the timely development of near-term batteries (lead/lead dioxide, iron/nickel oxide, and/or zinc/nickel oxide); phenomenological studies to provide basic information needed for the rational design, operation and control of electrochemical processes; studies on physiochemical methods for electrochemical research to aid the development of advanced tools for the detailed study of battery materials and processes; and modeling studies aimed at quantitative prediction of the dynamic behavior of cells, cell components and batteries.

Materials Research seeks to identify, characterize, and improve the materials and components to be used in batteries and electrochemical processes. Investigations of solid electrolytes, including those of ceramic (beta-alumina, NASICON), glass, and polymeric compositions, will continue, and advanced liquid electrolytes, such as low-temperature molten-salt mixtures and ionizing organic liquids, will be studied.

BASIC DEVELOPMENT OF NICKEL/ZINC BATTERIES

Lockheed Palo Alto Research Laboratory, Palo Alto, CA 94304 (U.S.A.)

The goal of this program is to gain information on the modes of operation of nickel and zinc electrodes from a study of well-defined, simplified, structural analogs and from the application of semiquantitative, theoretical concepts. The work is designed to yield useful information for hardware development by addressing that domain of dimensions and conditions that exists within the confines of pores in real porous electrodes, approximately 0.1 to 20 μm .

Moving picture photographs have been taken of growing dendrites and of the anodic reaction front as it entered the zinc pore. Coupled with optical microscopic studies, hydrogen bubbles were found to emanate from the base or stems of the dendritic masses. Reaction fronts penetrated at rates of $1 \times 10^{-5} - 1 \times 10^{-3} \text{ cm s}^{-1}$, depending on superficial current densities, corresponding to ca. 50 - 1000 mA cm^{-2} , respectively. In Task II, the maximum accumulated charge of Zn and NiOOH was determined for pores with openings of $1.0 \text{ cm} \times 2 \times 10^{-3} \text{ cm}$. For Zn the accumulated charge depended on current density during charging, being limited by the onset of dendrite

formation when the rate exceeded the $\text{Zn}(\text{OH})_4^{2-}$ diffusive flow, typically being about 600 mC at 50 mA cm^{-2} . For Ni, the charge was *ca.* 15 mC, indicating the need for higher specific surface area than for the Zn.

Aside from the planned tasks, several other advances were made in pursuits prompted by observations during the course of the work.

(1) The movement of isolated Zn particles in a current field was discovered and determined for both the electrokinetic and electrochemical displacement cases, being of the order of $5 \times 10^{-4} \text{ cm s}^{-1}$ and $1 \times 10^{-5} \text{ cm s}^{-1}$, respectively. Motion by displacement appears to be more important for particles larger than $5 \mu\text{m}$.

(2) Black mossy zinc was found to grow at open circuit in concentration gradients formed in zinc cells at *ca.* $1 \times 10^{-5} \text{ cm s}^{-1}$ causing short circuits. This correlates with other reports of shorting of commercially purchased Ag/Zn cells at open circuit rather than at closed circuit, and of the observed presence of mossy zinc at dendrites in Ag/Zn cells.

(3) The charge passed before onset of zinc dendrite growth was found to be related to the amount of zincate ion present in the pore and to the current density. Typically, some 100 - 800 mC could be passed across a $1 \text{ cm} \times 2 \times 10^{-3} \text{ cm}$ pore opening at current densities corresponding to 50 - 125 mA cm^{-2} , respectively.

(4) During the cycling of a single-pore nickel electrode (150 cycles), a decrease in the discharge slope occurred after the 40th cycle, remaining the same thereafter. Exfoliation of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ layer on the polished Ni pore wall was observed during the post mortem. This preliminary information suggests that such exfoliation is related to the deterioration in performance.

During the last quarter of 1979, reaction profiles will be collected and the influence of cycling determined on the reaction profile, capacity, and morphology. The work for 1980 is suggested by the new findings itemized (2) - (4) above. Thus, it is important that conditions for open-circuit shorting by mossy zinc be determined in a series of experiments with controlled concentrations (item (2)), that the mechanism of closed-circuit dendrite shorting be further quantified by varying pore size and $\text{Zn}(\text{OH})_4^{2-}$ concentration (item (3)), and that the mode of nickel electrode failure suggested by the preliminary results (item (4)) be verified. Additionally, zinc studies should be made in acid media just as they were in alkaline during 1979 in preparation for Zn/ Cl_2 and Zn/ Br_2 applications. It is anticipated that shape change observations made during the cycling will be useful in interpreting causes for this harmful effect.

Finally, in 1980, we propose to cycle commercially available Ni/Zn cells to destruction and to perform post mortems to relate the research findings with actual hardware development.

To assist in the development and production of hardware Ni/Zn cells, technical backlogs are required for problem areas that are now anticipated with the Ni and Zn electrodes. These are outlined as follows.

(1) More detailed information is needed on the causes of Zn dendrite

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

Linfield Research Institute, McMinnville, OR 97128 (U.S.A.)

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