

SODIUM/ALKALI NITRATE AND CALCIUM/METAL SULFIDE CELL RESEARCH

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The objective of this project is to determine the technical feasibility of new electrochemical couples for advanced secondary batteries of high specific energy, specific power, and cycle life. The current emphasis is on sodium/alkali nitrate cells; research on calcium/iron disulfide cells has been concluded.

The sodium/alkali nitrate cells employ a molten sodium negative electrode, the β'' -alumina electrolyte, and a molten alkali nitrate positive electrode having a nickel current collector. The molten alkali nitrates employed to date are NaNO_3 (m.p. 307 °C), LiNO_3 (m.p. 256 °C), and the NaNO_3 - LiNO_3 eutectic (m.p. 196 °C). Cell operating temperatures range from 250 to 350 °C, depending on the composition of the positive electrode.

Potentiometric titrations and X-ray diffraction analyses have been conducted to determine the reactions in $\text{Na}/\beta''/\text{NaNO}_3$ (345 °C) and $\text{Na}/\beta''/\text{LiNO}_3$ (275 °C) cells. The electromotive force for the Na/NaNO_3 cell was 1.55 V, and the cell discharge product was Na_3NO_3 (or $\text{Na}_2\text{O}\cdot\text{NaNO}_2$), which is a golden yellow solid at cell temperature. The overall cell reaction is $2\text{Na} + \text{NaNO}_3 \rightarrow \text{Na}_3\text{NO}_3$; the theoretical specific energy of this reaction is 630 W h/kg. The Na/LiNO_3 cell had two voltage plateaus at 2.25 V and 1.45 V, each representing 50 percent of the total capacity. The cell discharge products were molten NaNO_2 , and the two solids, Li_2O and Na_3NO_3 . From these products, the overall cell reaction is $4\text{Na} + 2\text{LiNO}_3 \rightarrow \text{Li}_2\text{O} + \text{NaNO}_2 + \text{Na}_3\text{NO}_3$. The theoretical specific energy of this reaction is 860 W h/kg.

A variety of small cells (1- to 3-A h theoretical capacity) have been operated to explore the interactions between the nitrates, the current collector, and the β'' -alumina (Al_2O_3 -8.85 wt.% Na_2O -0.75 wt.% Li_2O). For example, cells with the NaNO_3 electrode have operated at 330 °C for up to 500 h (20 cycles) with an electrode utilization of 60 percent. In these cells, the nickel current collector was heavily oxidized, forming a thick, black coating on the nickel. This coating is thought to be NaNiO_2 , a compound identified by X-ray diffraction analysis of the black solid produced by reacting NiO with NaNO_3 at 330 °C.

Cells with the LiNO_3 - NaNO_3 eutectic have been operated at 260 °C for up to 700 h (14 cycles) with an electrode utilization of 25 percent. In these cells, a thin, adherent oxide layer (approximately 25 μm) formed on the nickel current collector. Cells with the LiNO_3 electrode have generally failed within 50 h through fracture of the β'' tube; ion microprobe profiles of the fracture zones indicated a doubling of the Li:Na ratio. In LiNO_3 melts, the oxidation of nickel is apparently quite slow; no film is visible on the nickel surface.

Cyclic voltammetry studies are in progress to aid in interpreting the reactions of the alkali nitrate electrodes and the nickel current collector. In these studies, the effects of state of discharge on the reactions are being determined by adding the discharge products (alkali nitrite plus Na_2O) to the alkali nitrate and repeating the voltammetry study. The cathodic processes for NaNO_3 include an ohmic peak, which begins at 1.65 V versus Na and is followed by a plateau current that is independent of sweep rate and potential. The anodic analogs of the ohmic peak and plateau current are relatively small in pure NaNO_3 , but are approximately equal to their cathodic counterparts in the half-discharged melt (' Na_2NO_3 '). The ohmic peak is attributed to the reaction of a film (perhaps NaNiO_2) on the nickel surface and the plateau current to the reaction of the melt, which appears to be chemically coupled to the reaction of the film. In the presence of LiNO_3 , the ohmic peaks shift to a higher potential (centered at 2.3 V versus Na in $\text{NaNO}_3 + 10 \text{ mol}\% \text{ LiNO}_3$ and at 2.6 V versus Na in pure LiNO_3) and the plateau currents are absent. Studies of the effect of state of discharge on the LiNO_3 reactions are in progress.

Research on calcium/metal sulfide cells has been concluded. The cell developed in this program employs $\text{CaAl}_{1.2}\text{Si}_{0.4}$ alloy negative electrodes, FeS_2 positive electrodes, and a quaternary electrolyte ($\text{LiCl}-\text{NaCl}-\text{CaCl}_2-\text{BaCl}_2$, m.p. 383°C). The electrodes are separated by BN felt, and the current collectors are iron in the negative electrode and molybdenum in the positive electrode. A small cell ($13.5 \text{ cm} \times 13.5 \text{ cm} \times 1.5 \text{ cm}$; 65 A h) of this type yielded 70 W h/kg at the 4-h rate, a peak specific power of 100 W/kg, and a cycle life of 300 cycles. Based on this performance, 350-A h multiplate cells will yield 120 W h/kg and 170 W/kg. The major problem with the small cells tested to date has been their declining coulombic efficiency, which appears to be due to contamination of the separator by finely divided positive electrode materials (less than $10 \mu\text{m}$ diameter after extended cycling). This coulombic efficiency problem limits the cell life to about a half year of accelerated testing or 300 cycles.

In 1983, cyclic voltammetry and X-ray diffraction will be employed to identify the reactions and phases in NaNO_3 , LiNO_3 , and $\text{NaNO}-\text{LiNO}_3$ electrodes having nickel or iron current collectors. The measurements will extend over the range of melt compositions from full charge to full discharge. In addition, the effects of nickel and iron oxides on the electrode reactions will be determined. The expected result is a nitrate electrode and a current collector for a high-performance sodium cell that operates at about 200°C .

Recent publications

- 1 D. L. Barney, M. F. Roche, S. K. Preto *et al.*, Calcium/metal sulfide battery development program, Progress Report for October 1979 - September 1980, ANL-81-14, Argonne National Laboratory, March 1981.
- 2 S. K. Preto, L. E. Ross, N. C. Otto *et al.*, Proc. 16th Intsoc. Energy Conversion and Eng. Conf., Am. Soc. of Mech. Eng., 1981, pp. 765 - 768.