It should be noted that two insulation systems demonstrated to date have exceeded the goals of the program. The Pegged Multi-Foil system has a measured conductivity of 0.0017 W/m K (100×10^{-5} BTU/h ft °F) between 450 °C (840 °F) and 24 °C (75 °F), a density of 177 kg/m^3 (11 lb/ft^3), and a compression of 10%. The second system which exceeded the goals of the program is a Linde Multi-Foil insulation with discrete load-carrying support areas. It had a measured thermal conductivity of 203×10^{-5} W/m K (117×10^{-5} BTU/h ft °F), a density of 192 kg/m^3 (12 lb/ft^3) and a compression of 9%. A third promising insulation is a continuous support, load-bearing board system, but to-date, the thermal conductivity and density are slightly above the goal of the program. The best load-bearing board insulation system developed to-date has a conductivity of 388×10^{-5} W/m K (224×10^{-5} BTU/h ft °F), a density of 352 kg/m^3 (22 lb/ft^3) and a compression of 9%.

It is believed that the new insulation systems need further development in order fully to qualify for the above application. Questions that remain to be answered include long-term stability, handleability, and cost-effective manufacturing. The proposed follow-on program for 1980 is directed at: (1) advanced development of attractive insulation candidates; (2) evaluation of insulation and enclosure design through fabrication and testing of enclosure test units; (3) cost estimation of insulation and enclosure manufacturing.

Recent publications

1 Insulation development for high-temperature batteries for electric vehicles application, 1979 Annual Report.

CALCIUM/METAL SULFIDE BATTERY DEVELOPMENT

Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439 (U.S.A.)

The objective of this program is to develop inexpensive high-performance calcium alloy/iron disulfide secondary cells for electric-vehicle propulsion. This program was initiated in 1979, and is an outgrowth of an earlier program (Advanced Battery Research) in which various calcium alloys and transition metal sulfides were shown to be reversible toward calcium ions in molten-salt electrolytes. The ultimate goal of this program is to develop a calcium alloy/iron disulfide cell having the following characteristics: specific energy, 160 W h/kg; energy density, 525 W h/l; peak power, 200 W/kg; energy efficiency, 75%; lifetime, 1000 cycles; materials cost (1979 dollars) $15/kW h in mass production.

Four interdependent research areas are included in the program. They are electrolyte development, negative electrode development, positive electrode development, and engineering-scale cell development. The experiments in these areas include a variety of chemistry studies, cyclic voltammetry studies, cycling tests on cells ranging in capacity from 4 to 300 A h, and post-test examinations of cells using metallographic, X-ray, and microprobe techniques.

Cyclic voltammetry at low scan rates (0.02 to 0.5 mV/s) was used to study the electrochemistry of FeS_2, CoS_2 and NiS_2 electrodes in two candidate electrolytes for calcium cells: LiCl (54 mol%)–KCl (39 mol%)–$CaCl_2$ (7 mol%), mp 340 °C and LiCl (29 mol%)–NaCl (20 mol%)–$CaCl_2$ (35 mol%)–$BaCl_2$ (16 mol%), mp 390 °C. The current peaks were larger and better resolved in the quaternary electrolyte, reflecting a higher utilization of the electrode material. The areas of the current peaks corresponded to approximately 90% utilization of the electrode materials, and the peak areas remained constant during repeated scans. Because of its superior characteristics in these voltammetry tests, the quaternary electrolyte was selected for use in the calcium-alloy/iron disulfide cells.

Cells of about 4 A h capacity were operated to study the performance of the iron disulfide electrode in the quaternary electrolyte. In these tests (and in the above voltammetry studies) calcium–aluminum alloys were used as reference and counter electrodes. A capacity density of 0.86 A h/cm^2 (70% utilization) at 40 mA/cm^2 current density was achieved by an $Fe_{0.93}Co_{0.07}S_2$ electrode in these tests, and the capacity density remained high at high current densities (*e.g.* 0.64 A h/cm^2 at 160 mA/cm^2). This excellent performance led to the selection of the Fe(Co)S_2 electrode for engineering-scale tests. In similar tests of calcium silicide negative electrodes, a capacity density of 0.37 A h/cm^2 (50% utilization) was achieved at a current density of 80 mA/cm^2. This electrode was also selected for engineering-scale tests. However, further research is needed to improve this negative electrode; its achieved capacity density is only half that of the Fe(Co)S_2 electrode.

In the most recent engineering-scale tests, two 30 A h Ca–Si/Fe(Co)S_2 cells have been operated for up to 75 cycles at 460 - 485 °C. These cells are prismatic (13.5 × 13.5 × 3.5 cm) bicells having 1.5 cm thick positive electrodes sandwiched between two 0.75 cm thick negative electrodes. The current collectors are honeycomb structures of iron in the negative electrodes and molybdenum in the positive electrodes; the electrode separators are BN fabric. The maximum achieved specific energy was 86 W h/kg at the 24 h rate, 70 W h/kg at the 10 h rate, and 50 W h/kg at the 5 h rate. The cells have exhibited coulombic efficiencies of 95 - 99% and a capacity density of about 0.4 A h/cm^2. The cycling tests are being continued to determine the cycle-life characteristics of the Ca–Si/FeS_2 system.

In the coming year, the research in the program will focus on making significant improvements in the specific energy and power capabilities of the engineering-scale cells through the use of thinner electrodes and more compact cell designs. Electrode studies will focus on improving the performance of the calcium silicide electrode, which has limited the engineering-scale cells to a capacity density of about 0.4 A h/cm^2. It is expected that a calcium cell capable of meeting the program goals will be identified by the end of 1980.

Recent publications

1 P. A. Nelson *et al.*, High-performance batteries for electric-vehicle propulsion and stationary energy storage, progress report for the period October 1977 - September 1978, *ANL-78-94, November, 1978.*

2 P. A. Nelson *et al.*, High-performance batteries for electric-vehicle propulsion and stationary energy storage, progress report for the period October 1978 - March 1979, *ANL-79-39, May, 1979.*

3 C. C. Sy, Z. Tomczuk and M. F. Roche, Evaluation of secondary magnesium cell with molten-salt electrolytes, *Extended Abstracts, Electrochem. Soc. Meeting, Boston, MA, May 6 - 11, 1979, Vol. 79-1*, 1979, pp. 938 - 940.

4 S. K. Preto and M. F. Roche, Electrochemistry of FeS_2, CoS_2, and NiS_2 electrodes in calcium cells, *156th meeting of the Electrochem. Soc., Los Angeles, CA, October 14 - 19, 1978.*