- The cell reaction of FeS to J-phase and J- to X-phase during discharge has been noted in calorimetric measurements for cells containing LiCl–KCl–LiF electrolyte.
- The effect of varying electrolyte composition on cell heat generation was investigated. For cells containing no potassium ion, in which the formation of J-phase is impossible, the endothermic effect associated with the J-to-X transition is not observed.

The primary objective for 1983 is to determine the rate of thermal energy generation by cells at various rates of discharge and operating temperatures. Emphasis of this third phase of the project will be placed on cells containing LiAl and Li_4Si negative electrodes and iron disulfide positive electrodes. The results obtained for all cells to date will be processed to yield intensive properties useful for general design purposes.

Recent publications

1 D. M. Chen, H. F. Gibbard, R. M. Hart and L. D. Hansen, Calorimetric measurements of LiAl/FeS batteries up to 450 °C, *36th Calorimetry Conference, Washington, DC, October 7, 1981.*

2 C. C. Chen, T. W. Olszanski and H. F. Gibbard, Thermal behavior of an experimental 2.5-kW h lithium/iron sulfide battery, *Electrochemical Society Fall Meeting, Denver, CO, October 11 - 16, 1981, Extended Abstract No. 48.*

3 H. F. Gibbard and D. M. Chen, Generation of thermal energy in high-temperature lithium/iron sulfide cells, *Electrochemical Society Fall Meeting, Denver, CO, October 11 - 16, 1981, Extended Abstract No. 49.*

4 H. F. Gibbard, D. M. Chen, C. C. Chen and T. W. Olszanski, Thermal properties of LiAl/FeS batteries, *16th Intsoc. Energy Conversion and Eng. Conf., August 9 - 14, 1981,* Am. Soc. Mech. Eng., Vol. I, Paper Number 819362.

5 L. D. Hansen, R. H. Hart, D. M. Chen and H. F. Gibbard, High-temperature battery calorimeter, *Rev. Sci. Instrum., 53* (1982) 45 - 48.

PHYSICAL CHEMISTRY OF MOLTEN SALT BATTERIES

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The objectives are to provide experimental measurements of composition profiles in porous LiAl electrodes and molten LiCl–KCl electrolytes and to provide experimental data useful for the optimal design and operation of Li/FeS batteries.

Current-induced composition gradients were produced by electrolysis of LiCl–KCl melt in Y_2O_3 matrices between 1.0-cm-diameter solid and porous Li/Al electrodes with 0.2- to 0.3-cm separation, current 200 mA

cm^{-2}, followed by quenching. Composition profiles in the Y_2O_3 separators were measured by SEM/EDAX with 50 μm distance resolution and with 8 percent relative uncertainty in composition. The spatial distribution of LiCl and KCl in the electrolyte within porous Li/Al anodes was obtained from SEM/EDAX measurements of K/Cl ratios along several paths perpendicular to the anode/separator interface and at differing distances from the cell axis. Auger spectroscopy was initiated in the electrolyte contained within a porous anode.

The following conclusions were drawn:

- Composition profiles produced by electrolysis have overall gradients in Li/K ratio of 40 to 50 percent across the separator. The profiles are steepest near the electrodes.
- Precipitation of LiCl occurred during electrolysis in the porous anodes of two cells at locations near the anode/separator interface and on the paths closest to the cell axis.
- SEM/EDAX measurements of the local distribution of LiCl and KCl in the quenched electrolyte of a porous Li/Al anode demonstrated anodic and cathodic regions in the anode and suggest a complementary method for studying the current distribution in a porous electrode.
- Electrolyte compositions richer in LiCl than the initial melt were found in the majority (70 percent) of the areas examined. These areas were located within 0.3 cm of the cell axis.
- Electrolyte compositions richer in KCl than the initial melt, probably due to local cathodic reactions, were found near the walls of the cell.
- No simple one-dimensional profile would represent the electrolyte composition in a porous anode probably because of inhomogeneities.
- Auger spectroscopy confirmed LiCl precipitation in the anode by direct observation of lithium and chlorine in regions without potassium.

Recent publications

1 J. Braunstein, S. Cantor and C. E. Vallet, Current-induced composition gradients in molten LiCl–KCl battery electrolytes, *Proc. 16th Intsoc. Energy Conversion Eng. Conf., 1*, Am. Soc. Mech. Eng., 1981, p. 759.

2 C. E. Vallet, D. E. Heatherly and J. Braunstein, Composition gradients in electrolyzed LiCl–KCl melts, *Proc. Symposium on Transport Processes in Electrochemical Systems*, The Electrochemical Society, in press.

3 C. E. Vallet, D. E. Heatherly and J. Braunstein, Composition gradients in electrolyzed LiCl–KCl melts, submitted to the *J. Electrochem. Soc.*