LITHIUM/METAL SULFIDE BATTERY DEVELOPMENT

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The objective of this project is to develop lithium–aluminum/metal sulfide batteries for electric vehicle propulsion and for stationary energy storage with the overall goal of conserving petroleum. Ultimate performance goals for the electric vehicle battery are a specific energy of 130 W h/kg, a peak specific power of 160 W/kg, and a lifetime of 1000 cycles. Goals for a stationary energy storage demonstration of a 100 MW h battery are a peak power of 25 MW and a 3000-cycle lifetime. Cost goals (1977 dollars) are $35 - 40/kW h for the electric vehicle battery and $25 - 45/kW h for stationary energy storage. Approximately one-half of this effort is at ANL, with the other half subcontracted to industrial firms. The ANL effort is concerned mainly with basic research and development and cell and battery testing; the subcontractors are involved primarily with the development, design, and fabrication of cells and batteries.

The development of the electric vehicle battery is scheduled to proceed through three phases designated Mark I, II, and III. The objectives of these phases are as follows — Mark I, to evaluate the technical feasibility of the system; Mark II, to develop potentially low-cost materials and fabrication methods; Mark III, to develop a high-performance battery for passenger cars.

(1) In 1978 and 1979, a major effort was devoted to the Mark I phase of the project. A significant advance was made in the development of a multiplate Mark IA cell having a specific energy of 100 W h/kg at the 4 h rate, compared with a value of 50 W h/kg for previous bicells. A 40 kW h battery consisting of two modules was fabricated by Eagle–Picher Industries and delivered to ANL for testing. An attempt to operate the battery was unsuccessful, however, due to a short circuit in one of the modules.

(2) Tests of 40 Li–Al/FeS bicells at ANL from mid-1978 to mid-1979 indicated an average specific energy of 52 W h/kg at the 6 h rate over an average of 289 cycles. Tests of 83 Mark IA-type multiplate cells during the same period showed an average specific energy of 99 W h/kg at the 4 h rate over an average of 110 cycles. A 6-V module consisting of five Mark IA-type cells was operated successfully through 70 cycles in laboratory tests and an in-vehicle test in which the module was connected in series with a 144 V lead–acid battery.

(3) Preliminary safety and vibration tests were conducted on the Mark IA cells. Cells subjected to a simulated 30 mph crash into a barrier while at operating temperature (450 °C) were ruptured, allowing a small amount of the molten LiCl–KCl electrolyte to escape. There was no evidence of com-

bustion or noxious fumes. The 6-V module was subjected to a vibration test equivalent to 2.3 years of in-vehicle service with no observable ill effects.

(4) Late in 1978, cost and design studies on a Mark II battery were conducted by Gould Inc., Eagle–Picher Industries, Inc., and Rockwell International, and development work was initiated at Gould early in 1979.

(5) The electrode separator is a key component of lithium/metal sulfide cells. A major cost reduction would result from the use of boron nitride felt, rather than fabric, as separators. The Carborundum Co. has developed a satisfactory felt and ANL has evolved cell designs that will accommodate felt separators. Another possible low-cost alternative to fabric separators is the use of powder beds. Cells having powder separators (*e.g.*, MgO, Y_2O_3, AlN, Si_3N_4) have been operated successfully at ANL and Rockwell International.

(6) Two other significant advances in the materials work are the discovery of an agent ($LiAlCl_4$) that greatly enhances the wetting of boron nitride separators by the LiCl–KCl electrolyte and the development of an iron–5 wt.% molybdenum alloy (ANL-5-0) that is much more corrosion-resistant than iron in FeS electrodes.

(7) A satisfactory reference electrode (Ni/Ni_3S_2) for lithium/metal sulfide cells has been developed. Such an electrode is essential for diagnostic studies of practical battery cells, as well as for basic electrochemical research.

(8) Two types of modeling studies have been initiated. One is a mathematical expression of cell performance (energy, power, cycle life) as a function of cell design parameters. The other is a classical electrochemical modeling study of the electrode reactions and other processes occurring within the cell.

(9) During the last quarter of 1979 and in 1980, the major effort will be directed toward the Mark II electric vehicle battery. Experience from the Mark IA battery has shown that improvements are needed in three major areas: (1) battery hardware, (2) thermal insulation for the battery case, and (3) loss of cell capacity during cycling. Work in the first two areas will be performed primarily by industrial contractors; the third will be a joint effort of ANL and contractors. The conceptual plant design studies on stationary energy storage will be completed in the last quarter of 1979. A modest effort on the development of stationary energy storage cells is expected to continue in 1980.

Recent publications

1 J. A. Smaga, F. C. Mrazek, K. M. Myles and J. E. Battles, Materials requirements in LiAl/LiCl–KCl/FeS_x secondary batteries, in J. J. Hoffman and G. A. Whitlow, (eds.), *Materials Considerations in Liquid Metals Systems in Power Generation*, NACE, Houston, TX, 1978, pp. 52 - 64.

2 J. E. Battles, J. A. Smaga and K. M. Myles, Materials requirements for high performance secondary batteries, *Metall. Trans.*, *9A* (1978) 183.

3 P. A. Nelson *et al.*, Development of lithium/metal sulfide batteries at Argonne National Laboratory: summary report for 1977, *ANL-78-20, March 1978.*

4 P. A. Nelson *et al.*, High-performance batteries for stationary energy storage and electric-vehicle propulsion, progress report for the period October - December 1977, *ANL-78-21, March 1978.*

5 L. Burris and P. A. Nelson, Advanced batteries for vehicle propulsion, *SAE Earthmoving Industry Conf., Peoria, IL, April 10 - 12, 1978, Technical Paper 780458.*

6 C. A. Melendres and C. C. Sy, Structure and cyclic discharge behavior of LiAl electrodes, *J. Electrochem. Soc., 125* (1978) 727.

7 P. A. Nelson *et al.*, High-performance batteries for stationary energy storage and electric-vehicle propulsion, progress report, January - March 1978, *ANL-78-45, July 1978.*

8 E. C. Gay, W. E. Miller, R. F. Malecha and R. C. Elliott, Review of industrial participation in the ANL lithium/iron sulfide battery development program, *Proc. 13th IECEC, San Diego, CA, Aug. 20 - 25, 1978,* Vol. 1, p. 690.

9 F. J. Martino, T. D. Kaun, H. Shimotake and E. C. Gay, Advances in the development of lithium–aluminum/metal sulfide cells for electric-vehicle batteries, *Proc. 13th IECEC, San Diego, CA, Aug. 20 - 25, 1978,* Vol. 1, p. 709.

10 P. A. Nelson, A. A. Chilenskas and R. K. Steunenberg, Lithium–iron sulfide batteries for electric vehicles, *Proc. 5th Int. Elect. Vehicles Symp., Philadelphia, PA, Oct. 2 - 5, 1978, Paper No. 783104 (E), EVC (1978).*

11 D. R. Vissers, K. E. Anderson, C. K. Ho and H. Shimotake, Effects of the LiCl–KCl electrolyte composition on the performance characteristics of the Li–Al/FeS cells, *Extended Abstracts Electrochem. Soc. Meeting, Pittsburgh, PA, Oct. 15 - 20, 1978,* Vol. 78-2, 1978, p. 97.

12 R. C. Elliott, W. E. Miller and E. C. Gay, Computer aided design of lithium/metal sulfide cells, *Extended Abstracts Electrochem. Soc. Meeting, Pittsburgh, PA, Oct. 15 - 20, 1978,* Vol. 78-2, 1978, p. 104.

13 R. B. Swaroop, C. W. Boquist and J. E. Battles, Development of electrode separators for lithium–aluminum/metal sulfide batteries, *Extended Abstracts Electrochem. Soc. Meeting, Pittsburgh, PA, Oct. 15 - 20, 1978,* Vol. 78-2, 1978, p. 145.

14 R. B. Swaroop, J. A. Smaga and J. E. Battles, Materials for high-performance lithium–aluminum/iron sulfide secondary batteries, *Proc. V. Inter-American Conf. on Materials Technology, Sao Paulo, Brazil, Nov. 5 - 10, 1978,* p. 137.

15 P. A. Nelson *et al.*, High-performance batteries for electric-vehicle propulsion and stationary energy storage, progress report, Oct. 1977 - Sept. 1978, *ANL-78-94,* November 1978.

16 J. P. Mathers, C. W. Boquist and T. W. Olszanski, Powder electrode separators for high temperature lithium–aluminum/iron sulfide batteries, *J. Electrochem. Soc., 125* (1978) 1913.

17 R. B. Swaroop, J. A. Smaga and J. E. Battles, Development and evaluation of materials for high-temperature lithium/sulfur rechargeable batteries, *Proc. Solar Energy Storage Workshop, Panjab Univ., Chandigarh, India, March, 1979.*

18 C. C. Sy, Z. Tomczuk and M. F. Roche, Evaluation of secondary magnesium cells with molten-salt electrolytes, *Extended Abstracts Electrochem. Soc. Meeting, Boston, MA, May 5 - 11, 1978,* Vol. 79-1, p. 938.

19 L. Redey and D. R. Vissers, Reference electrode development for the lithium/metal sulfide battery system, *Extended Abstracts Electrochem. Soc. Meeting, Boston, MA, May 5 - 11, 1978,* Vol 79-1, p. 941.