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L. D. Hansen

R. H. Hart

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Authors

L. D. Hansen, R. H. Hart, D. M. Chen, and H. F. Gibbard

High-temperature battery calorimeter

L. D. Hansen

Thermochemical Institute, Brigham Young University, Provo, Utah 84602

R. H. Hart

Post Office Box 934, Hart Scientific, Provo, Utah 84601

D. M. Chen and H. F. Gibbard

Gould Laboratories, 40 Gould Center, Rolling Meadows, Illinois 60008

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A battery calorimeter was built for the measurement of thermal energy generation of high-temperature lithium-aluminum/iron sulfide battery cells, which are under development for electric vehicle propulsion and other energy storage applications. The calorimeter was designed with a temperature range of 400°–500°C, a detection limit of 1 mW, and an upper limit of heat flow of 50 W. The results of measurements on 200-Ah LiAl/FeS cells were in excellent agreement with the predictions of thermodynamic calculations based on precise measurements of the total cell polarization and the temperature coefficient of the emf. Details of the construction and operation principles of this calorimeter are given.

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INTRODUCTION

High-temperature lithium-aluminum/iron sulfide batteries are under development for electric vehicle propulsion and other energy storage applications. Owing to their high specific energy (more than 100 Wh/kg) and operating temperature (400°–500°C), thermal management is an important aspect of design of these batteries. The rate of thermal energy generation under various operating conditions is essential information for thermal modeling and temperature control. Therefore, a high-temperature calorimeter was constructed to study the rate of thermal energy generation of engineering-scale LiAl/FeS cells.

The requirements on such a calorimeter are severe. The operating temperature must be 400°–500°C, the calorimeter must be capable of measuring up to 50 W of heat, and electrical connections to the cell must carry up to 40 A. Also, the cell must be clamped by constrained plates in order to eliminate the shape change of cell electrodes as it is heated, cooled, and operated. The dimensions of the cell under study are approximately 21 × 13.3 × 3.2 cm.

The purpose of this paper is to present the details of construction and principles of operation of this high-temperature calorimeter and its use in the measurement of the thermal energy generated by LiAl/FeS cells.

I. CONSTRUCTION AND OPERATION PRINCIPLE OF THE CALORIMETER

A. Description of calorimeter

A schematic diagram of the calorimeter construction is shown in Fig. 1. The calorimeter conceptually consists

of three closely fitting chambers. The outermost chamber, designated as chamber C, is a stainless-steel box approximately 55 × 34 × 45 cm lined with 10 cm of thermal insulation material (Duraboard, product of Carborundum). The outside wall of this chamber is in contact with room air which acts as the final heat sink for all heat generated either by the battery or by the heating elements within the calorimeter. The middle chamber (chamber B) is a constant temperature oven which also provides the structural support for the innermost chamber and for clamping the battery in place. The innermost chamber, chamber A, encloses the battery and contains the control and measurement elements.

The nickel sensors and heaters are all identical parts made by Thermal Circuits of Salem, Massachusetts. These parts consist of 0.025-mm nickel foil, with a room-temperature resistance of 40 Ω, embedded in 0.50 mm of a high-temperature, mica-filled binder. The units are approximately 10 × 15 cm in size, so that two units connected in series for sensors and in parallel for heaters were used at each of the locations indicated in Fig. 1. At the operating temperature of 400°–450°C the resistance of each unit is approximately 140 Ω. Type E thermocouples (Omega Engineering, Inc., Stamford, Connecticut) were placed between each pair of Ni heater and sensor units so that the temperature at each location in the calorimeter could be determined independently during heating and testing.

The several layers in each of the two halves of chambers A and B on each side of the battery are fastened together with #8-32 stainless-steel screws 1.5 cm long, which are staggered in location so that no continuous heat flow path exists through them from chamber A to B. The sides and ends of chamber A are covered with

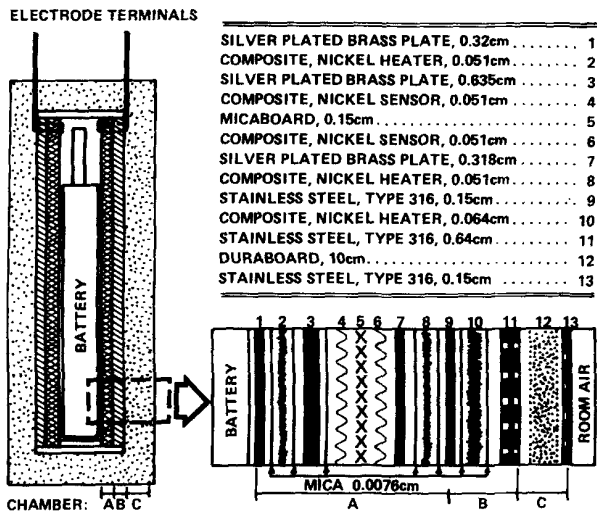


FIG. 1. Construction of high-temperature battery calorimeter.

silver-plated brass plates fastened to part 3 (see Fig. 1) with #6-32 stainless-steel screws. The sides and ends of chamber B are similarly covered with stainless-steel plates.

All electrical connections to the calorimeter heaters and sensors are made with Ni ribbon wire insulated with two layers of high-temperature glass sleeving. All such wires are thermally connected to an appropriate temperature-regulated surface by Ni tabs built into the ends of the sensor or heater units. The lead wires are then brought out to a terminal block constructed of mica and stainless steel which is mounted on the outside of chamber B.

The calorimeter is assembled by clamping the two halves of chambers A and B on the battery with four 0.635-cm stainless-steel bolts torqued to 4.6 Newton meters (40 in.-lb) on the periphery of the 0.64-cm plate (part 11) which forms the outermost part of chamber B. The battery terminals are then connected to two 1.91 × 0.48 × 14 cm silver-plated brass bars mounted on the top inside of chamber A. Electrical insulation and thermal contact between these bars and part 1 is provided by a 0.08-mm thick mica sheet. Each bar is held in place by three 0.790 × 4.5 cm stainless-steel bolts. These bolts form an electrical connection to another pair of bars of the same size on the outside of chamber B. A pair of 0.64 × 20 cm silver-plated brass rods attached to the outer bars extend vertically outside of chamber C to provide electrical connections to the battery. Two silver wires are attached at the battery terminals and two at the outside of chamber B so that the heat generated by I^2R heating in the battery leads can be measured and subtracted from the total measured heat. A platinum resistance thermometer is also placed at the battery terminal connection so that the absolute temperature of the battery can be monitored. The assembled chambers A and B with a battery cell inside are then placed inside chamber C. The lid of chamber C is fitted down over the electrode terminals.

The heater at location 2 in Fig. 1 is used to control the temperature sensed by the sensor at location 4 by a Hart Scientific model 3702 controller. The controller contains an analog multiplier which is used to obtain the product of the current and voltage and hence, the power supplied to the heater. The current, voltage, and their product can be displayed on a strip chart recorder from terminals on the controller.

The heater at location 8 in Fig. 1 is connected to a Hart Scientific model 3701 controller which controls the temperature at the sensor location 6.

Power to the outermost heater, at location 10, is supplied by a manually adjusted constant voltage power supply.

B. Theory of operation

The calorimeter is an isothermal type instrument in which a constant rate of heat loss from chamber A is balanced by a constant combined power input from the battery and the control heater at location 2. The calorimetric measurement is made in chamber A by monitoring the power input from the heater at location 2. A constant rate of heat loss from the area immediately around the battery is maintained by controlling the temperatures at sensors 4 and 6 (Fig. 1) to be constant but different so that T_4 is greater than T_6 . This fixes the rate of heat flux across the micaboard at location 5, as long as the thermal conductance K_5 between the two sensors also remains constant. Given the condition that the temperature at location 4 remains constant, a thermal balance equation for the calorimeter can be written as follows:

$$P_B + P_c = K_5(T_4 - T_6), \quad (1)$$

where P_B is the heat generation rate from the battery and P_c is the power output from the control heater. The right hand side of Eq. (1) is equal to a constant, C , under a given set of conditions so we can rewrite Eq. (1) as

$$P_B = C - P_c. \quad (2)$$

It is readily apparent from Eq. (2) that changes in P_c are exactly equal to, but opposite in sign to, changes in P_B . Monitoring the power input, P_c , thus yields P_B if a base line is obtained when $P_B = 0$.

The purpose of chamber B is to maintain a constant temperature heat sink around chamber A. Chamber C serves to maintain the rate of heat loss to the room air at a small and approximately constant value.

C. Operation of the calorimeter

Chambers A and B are purged with argon gas through a 0.16-cm stainless-steel tube inserted alongside one of the battery terminals. The purpose of the argon is to prevent corrosion of the calorimeter parts at high temperature. During operation of the calorimeter the argon is left running at about 0.5 dm³/min to maintain the inert atmosphere. The model 3702 controller is set to control the temperature of the battery at the desired

point. Then the model 3701 controller is adjusted to some lower temperature such that the power output of the 3702 controller is a bit higher than the maximum power output expected in the battery. The outermost heater in chamber B controlled by an oven temperature controller is manually adjusted to a temperature about 10 °C below that of the battery. The calorimeter is allowed to stabilize for more than 24 h and measurements are begun. The measurement is the change in power of the innermost heater which occurs when the battery is being charged or discharged. In other words, the rate of thermal energy generation of the battery cell during charge or discharge is compensated by the power change of the heater at location 2. The power signal from the 3702 controller was recorded on a strip chart recorder (Hewlett-Packard model 1700B) during the measurements described in the following.

II. MEASUREMENT OF THERMAL ENERGY GENERATION IN LiAl/FeS CELLS

The rate of thermal energy generation \dot{q} may be calculated¹ by using the thermodynamic Eq. (3)

$$\dot{q} = I \left[-T \left(\frac{\partial E}{\partial T} \right)_{P,\xi} + \eta \right], \quad (3)$$

where I is current, taken positive for discharge; $\partial E/\partial T$ is the temperature derivative of the cell potential; P is pressure; ξ represents the progress of the cell reaction; and η is the cell polarization. Equation (3) is valid provided that the cell is a thermodynamically reversible electrochemical system. This has not been shown previously for the LiAl/FeS system. Therefore, we directly measured P_B [see Eq. (1)] using the high-temperature calorimeter and compared the results with thermodynamic calculations of \dot{q} . If the calorimeter is functioning properly, $P_B = \dot{q}$.

The cells under study were five-plate prismatic cells with three lithium-aluminum negative electrodes, two iron sulfide positive electrodes, molten LiCl-KCl-LiF

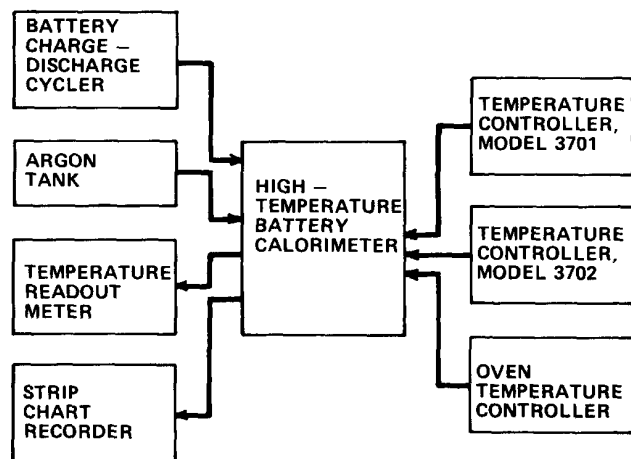


FIG. 2. Block diagram for high-temperature battery calorimeter and associated hardware.

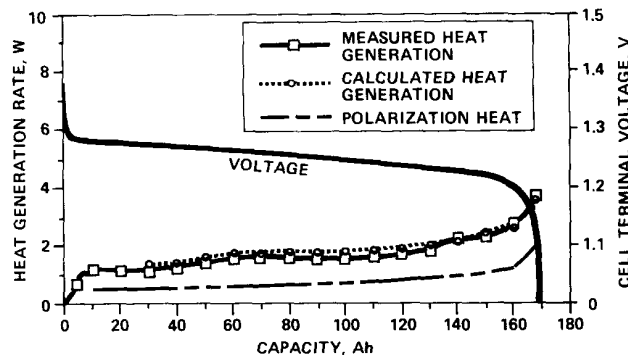


FIG. 3. Thermal energy generation rate and cell terminal voltage of a LiAl/FeS cell during 10 A discharge at 410 °C.

(62.7, 28.2, 9.1 mol %; melting point, 397 °C) electrolyte, and boron nitride nonwoven separators. Each cell weighed 2.5 kg and had a theoretical capacity of 200 Ah based on FeS content. The normal operating temperature is 400 °–500 °C.

The experimental setup for the measurement of thermal energy generation is shown as a block diagram in Fig. 2. A LiAl/FeS cell was embedded in the high-temperature calorimeter with a pair of power cables connected to the battery charge-discharge cycler (Model CDC-50-10, PROPEL Inc., South Plainfield, New Jersey). In addition, two voltage leads were connected between the cell terminals and the battery cycler for sensing the cell voltage. The charge and discharge cutoff voltages were 1.55 and 1.0 V, respectively. The temperatures at various locations in the calorimeter were monitored. The cell terminal voltages and rates of thermal energy generation during the charge and discharge of cells were recorded on a strip chart recorder. Other details of the calorimeter operation are given in Sec. C above.

In a typical experiment a LiAl/FeS cell was heated to 410 °C and maintained at that temperature. Two testing charge-discharge cycles of the cell indicated that the cell had excellent coulombic efficiency (more than 98%). After a 20-A constant-current charge to the cutoff voltage of 1.55 V, the cell was put on open-circuit stand for more than 24 h. The calorimeter stabilized thermally so that a constant base line was obtained which varied less than 0.001 W within one hour. The cell was then discharged at a current of 10 A at 410 °C. Figure 3 shows the cell terminal voltage and heat generation rate. The measured heat generation rates, corrected for I^2R heating in the battery leads as previously mentioned, are shown by the squares and solid curve. The dashed curve and circles represent the thermodynamic prediction of heat generation rate based on measurements of the cell polarization and temperature coefficient of the emf.^{2,3} The agreement is seen to be excellent. The polarization heat $I\eta$ is also shown in Fig. 3. It lies below and nearly parallel to the curve of total heat. The calculated heat generation in Fig. 3 at the beginning of discharge is not shown because the rapid change of the cell potential with state of charge makes it very difficult to obtain accurate values of $\partial E/\partial T$.

III. DISCUSSION

Although the calorimeter functioned as designed and provided valuable results on LiAl/FeS cells up to 420 °C, initial tests revealed the need for several modifications, which will be incorporated in future calorimeters of this design.

The electrical resistance of the stainless-steel bolts used in the current leads is too high. Adequate correction for the I^2R heating due to the passage of current through these bolts can be made at currents below 40 A. However, at higher currents an undetermined fraction of the resistive heat escapes through the calorimeter top and is not detected by the nickel sensor at location 4. This problem would be avoided by replacing the bolts with others of lower resistance.

At temperatures above 400 °C, some of the nickel heaters failed after 15 days of operation. Thus, more robust heaters are needed. Because of the high-current lead resistance and heater failure, the 50 W design limit was not achieved.

While the cell terminals were well protected from oxidation by the flow of argon gas, the silver-plated brass plates were badly oxidized. The corrosion of these plates did not impair operation of the calorimeter. However, for operation over longer periods of time or at higher tem-

peratures a more corrosion resistant material, such as nickel, must be used.

In conclusion, an isothermal calorimeter containing a 200-Ah LiAl/FeS cell has been successfully operated at 420 °C. The calorimeter has a base line stability of 1 mW. The data obtained in the calorimeter measurements were in excellent agreement with thermodynamic predictions. A new method of establishing a steady-state condition in an isothermal calorimeter was also demonstrated, i.e., the use of a constant ΔT across a path with a constant thermal conductivity.

ACKNOWLEDGMENTS

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³ H. F. Gibbard and D. M. Chen, "Generation of Thermal Energy in High-Temperature Lithium/Iron Sulfide Cells," Extended Abstracts of the Electrochemical Society Fall Meeting, Denver, Colorado, October, 1981.