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DISCHARGE CHARACTERISTICS OF LITHIUM-BORON ALLOY ANODE IN MOLTEN SALT THERMAL CELLS

R. Szwarc and R. D. Walton
Thermal Battery Development

March 31, 1980

General Electric Company
Neutron Devices Department
P. O. Box 11508
St. Petersburg, Florida 33733

Prepared for the
U. S. Department of Energy
Albuquerque Operations Office
Under Contract No. DE-AC04-76DP00656

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ABSTRACT

Thermal cells comprised of Li-B anodes, LiCl-KCl eutectic electrolyte and one of three depolarizers, $CaCrO_4$, Li_2CrO_4 or FeS_2 have been investigated. These cells require a separator layer to obviate direct redox reactions between the anode and the cathode. The separator developed for these cells is an electrolyte layer immobilized with MgO. MgO is inert with respect to the anode as well as other cell components. Of the three systems investigated, the Li-B/FeS_2 combination is most promising for primary thermal batteries, particularly for long life power designs.

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INTRODUCTION

Thermal batteries are primary, reserve electrochemical power sources which contain fused salt electrolytes which are solid, and therefore nonconductive at normal ambient temperatures. When power is required, a pyrotechnic heat source is ignited, either by percussion primer or electric squib, which raises the internal temperature beyond the melting point of the electrolyte, thus making it conductive and permitting battery operation. As a result of the electrolyte being nonconductive at ambient temperature, self discharge does not take place, which is realized in shelf life in excess of 20 years.

The most common electrochemical system employed in thermal batteries used for weapons application is based on the system: Ca/LiCl-KCl, SiO_2, $CaCrO_4$/Fe. The cell is composed of an anode, calcium on an iron or steel substrate, a catholyte layer, a pressed powder pellet of blended electrolyte (E), depolarizer (D), binder (B) and an Fe cathode, where E is the eutectic mixture of LiCl-KCl, D is $CaCrO_4$ and B is SiO_2. While this system has been very successful, it is beset by a number of problems limiting its application, particularly for long life batteries. These limitations are due to the formation of a nonconductive $KCaCl_3$ double salt layer at the anode interface[1], a low melting alloy Li_2Ca which is responsible for noise and/or short circuits, and exothermic reactions between calcium and $CaCrO_4$. To overcome these difficulties, new systems, based on lithium compound anodes have been investigated in recent years.

Lithium aluminum compounds of varying compositions have been employed for primary and secondary battery applications.[2-9] Another compound, lithium-silicon, has been applied for secondary battery applications[10,11] and particularly for utility load leveling applications, [12] and more recently, it has been tested for primary battery applications.[13, 14] Lithium-foam metal matrix anodes have also been reported for thermal battery applications.[3, 5] Cells employing lithium compound anodes have been coupled primarily with FeS or FeS_2 depolarizer. In one study, however, lithium-aluminum anodes were discharged in cells employing a variety of depolarizers including $CaCrO_4$ and FeS_2.[7] In this study, we compared the discharge characteristics of a new alloy, Li-B, versus $CaCrO_4$, Li_2CrO_4 and FeS_2 depolarizers.

The system lithium-boron is the least known of the alkali-boron systems.[15] While a great number of phases with varying Li-B ratios have been reported, precise chemical formulas of these phases have not been possible to obtain due to difficulties in chemical analysis and to the presence of impurities. Earlier studies were limited to the boron rich phases,[16] the first documentation of a lithium rich, lithium monoboride was published recently. [17] This product was prepared by reacting lithium and boron in an inert environment at 800°C forming a dark-brown powder.[17] Metallic lithium-boron alloys were first reported by Wang,[18] and more recently the preparation and characterization lithium-boron alloys with a composition range of 50-90 at.% were reported by Dalleck et al.[19] James and DeVries investigated the structure and anodic discharge behavior of lithium-boron alloys in the LiCl-KCl eutectic melt.[20, 21] The lithium-boron alloy has been described as an Li_7B_6 phase which is a high-melting porous solid, filled with nearly pure lithium which at battery operating temperature is liquid.[19, 21]

The application of this anode to pelletized thermal cells of the system LiB/LiCl-KCl, $CaCrO_4Fe$[22, 23] requires the utilization of a separator to prevent direct redox reaction between lithium and calcium chromate while at the same time permitting ionic transport through it.

EXPERIMENTAL

Figure 1 depicts schematically the single cells employed in this investigation. The cells consist of a separator layer sandwiched between a DEB pellet and the anode. The anode is prepared by successively pressing the Li-B ingot* between Castathane** sheets in a hydraulic press. The foils so produced are 3 to 20 mils in thickness and are mechanically attached to a stainless steel backing which acts as the current collector. The DEB and EB pellets are made by hydraulically pressing the powders in a hardened steel die cavity. The separator composition is 50 wt% each of the LiCl-KCl eutectic and the MgO binder. The DEB compositions employed are given in Table 1.

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*Li-B alloy provided by S. Dalleck of the Naval Surface Weapons Center, Silver Springs, Md.

**Trademark, Upjohn Co.

Table 1. Catholyte Layer DE or DEB Compositions given in Weight Percent

D/E 70/30	D = $CaCrO_4$, E = LiCl-KCl eutectic*
D/E/B 35/55/10	D = $CaCrO_4$, B = SiO_2
D/E/B 30/55/15	D = Li_2CrO_4
D/E/B 50/35/15	D = Li_2CrO_4
D/E 80/20	D = FeS_2
D/E/B^x 64/16/20	D = FeS_2, B^x = 10 wt% SiO_2, 90 wt% E

*45 wt% LiCl and 55 wt% KCl

SEPARATOR DEVELOPMENT

Lithium reacts directly with silica and calcium chromate, hence, cells in which the lithium alloy anode rests directly against the DEB layer have short activated lives and poor coulombic efficiency. To improve both, a separator must be employed to physically separate the anode from the cathode. An effective separator must be ionically conducting and chemically inert to all the cell components. Two concepts were considered for the separators: (1) a refractory powder compact composed of the electrolyte and binder and (2) separator pads fabricated from BN or Y_2O_3 fiber pads* impregnated with electrolyte. Originally, six refractory oxide binders were considered which, based on published thermodynamic data, were known to be inert to lithium. The choice of the candidate was based upon its ability to gell or immobilize the electrolyte which would otherwise flow when subjected to the battery operation temperature, some 200°C above the eutectic melting point.

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*The separator pads were provided by Professor Robert Walker, Department of Chemical Engineering, University of Florida, Gainesville, Florida. Y_2O_3 was provided by the Zircar Co., Florida, N. Y. and the BN by Carborundum Co., Niagara Falls, N.Y.

The oxides investigated were: finely divided Al_2O_3 (specific area 100 m^2/g), $LiAlO_2$, Y_2O_3, $CaZrO_3$, ZrO_2, CaO and MgO. Of these, only MgO was found to be an effective gelling agent. MgO is not as effective an immobilization agent as SiO_2, consequently the binder content is higher, 50 wt% for the former, as compared to 7 to 15 wt% for the latter. As a result of the high MgO content, the cell's internal resistance is increased, as will be discussed below.

TESTER AND DATA ACQUISITION SYSTEM

The tester described earlier[26] was modified by the addition of a Hewlett-Packard 9872A data acquisition system. This system incorporates a multiprogrammer which interfaces the tester with the computer, enabling the computer to read the voltage outputs from the cell during the cell discharge. Two plug-in voltage monitoring cards in the multiprogrammer convert dc input voltage to equivalent 12-bit complement digital words for computer reading. Using software specifically developed for this tester, the computer automatically monitors the discharge as soon as the cell voltage reading becomes positive. Data is read and stored in the computer memory for preset voltage increments. By choosing voltage rather than time increments, sufficient data is stored during the initial and final portions of the discharge, when rapid voltage changes are taking place, producing good resolution of the shape of the discharge curve without overloading the computer memory capacity. The computer is programmed to sense and record the peak voltage and time to peak. It simultaneously computes the normalized cell capacity in coulombs per gram of anode and the normalized power density in watt-seconds per gram of anode.

REFERENCE ELECTRODES

The reference electrode selected for this study, the Ag/AgCl has been successfully employed for single cell studies of thermal cells at Sandia Laboratories.[27] Physically, the reference electrode consists of a pure silver wire inserted into a thin walled, 50-mil o.d., Pyrex capillary, containing a 15% molar solid solution of AgCl in LiCl-KCl eutectic. The reference electrode is inserted into a slot between two EB pellets as shown in Figure 1. The anode-reference voltage is read by means of a high impedance voltage card, the anode to cathode voltage is also measured directly, and the cathode to reference voltage is obtained as follows:

$$V_{cathode/reference} = V_{anode/reference} - V_{cell}$$

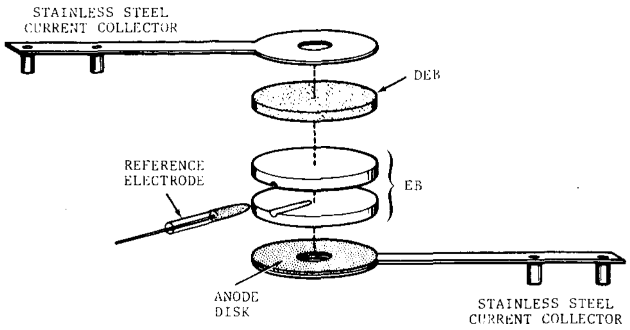


Figure 1. Single Cell Incorporating Reference Anode

RESULTS AND DISCUSSION

A striking contrast of the discharge characteristics of Li-B anodes is their ability to deliver between 50 and 90 percent theoretical coulombic capacity even at high current densities. Figures 2 to 4 depict the delivered cell capacity as a function of anode weight illustrating that for anode limited cells, the capacity is a function of the anode weight. The solid line represents the calculated theoretical capacity, 7700 C/g anode.[20] For chromate depolarizer cells, the capacity appears to decline for heavier anodes, as shown in Figure 2. This is due to the decreasing effectiveness of the separator as a result of chromate diffusion through the separator and consequent direct chemical reduction of the depolarizer by lithium. This effect becomes more pronounced for longer discharge times. The separator's diminished effectiveness is due to the partial solubility of the chromates in the electrolyte. Cells incorporating FeS_2 as depolarizer (Figure 4) do not show diminished cell capacity at long discharge times because

FeS_2 is insoluble in the electrolyte and, as can be seen in Figure 5, FeS_2 does not penetrate through the separator. Nevertheless, some reduction in coulombic capacity is evident even for FeS_2 as shown in Figure 4. The diminished capacity of the three cells depicted in Figure 4, which fell below 50 percent theoretical, is due to the reaction between Li and SiO_2 employed as a binder in the EB layer of those particular cells. Two other cells shown in Figure 4, exhibit low capacity. These cells were discharged at high current densities i.e., 0.5 and 1.0 A/cm^2. Reference electrode discharges (Figure 6) show that at high current density, the cell became cathode rather than anode limited, hence, the anode material was not completely consumed. This limitation is at least in part due to high internal cell resistance as discussed below. Other cell discharges depicted in Figure 4, on the other hand, were slightly higher than the calculated theoretical maximum, indicating that perhaps more lithium is available for the electrochemical processes than was estimated in reference 20. The discharge characteristics for cells incorporating each of the three depolarizers investigated are shown in Figure 7 for low current density and in Figure 8 for high current density. Despite the loss of about 0.5 V/cell, the FeS_2 cells produce higher power density than either chromates. This is due to the absence of side reactions, resistive products and to the more effective isolation of the anode from the cathode.

The limiting current density attained for $CaCrO_4$ cells is approximately 500 mA/cm^2. Reference electrode work reveals that this is due, at least in part, to cathodic polarization (Figure 9), or more specifically to diffusion polarization. It has been demonstrated that the cell's limiting current can be increased from 500 to 1000 mA/cm^2 by substituting Li_2CrO_4 for $CaCrO_4$. This could be due to the greater solubility of Li_2CrO_4 in the electrolyte. This advantage of Li_2CrO_4 is somewhat offset by the need for higher binder content in the DEB pellet, which contributes to the cell's internal resistance. This increased binder content is due to the need for undissolved chromates help immobilize the electrolyte.

Text continued on page 13.

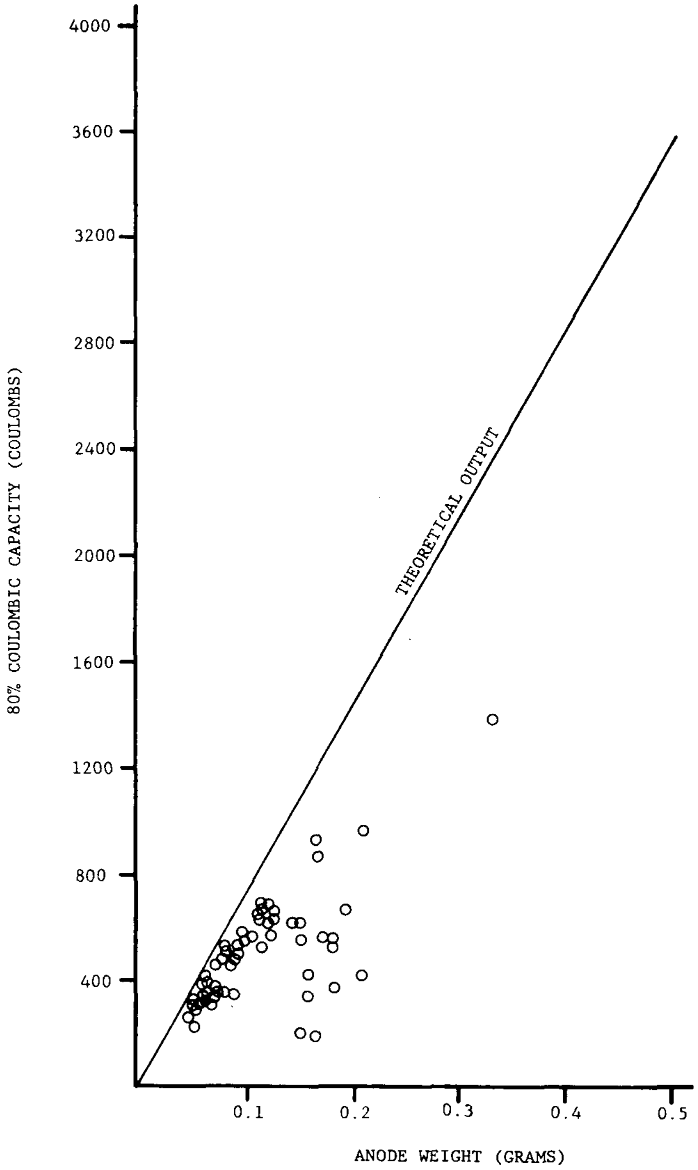


Figure 2. Coulombic Capacity Versus Anode Weight, Calcium Chromate

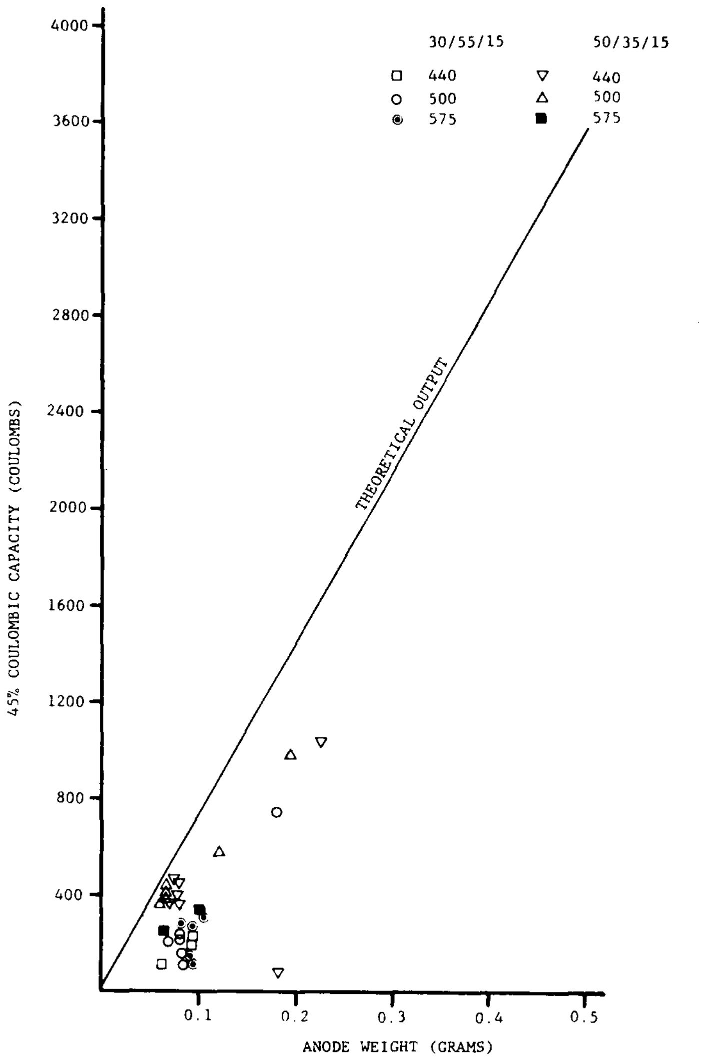


Figure 3. Coulombic Capacity Versus Anode Weight, Lithium Chromate

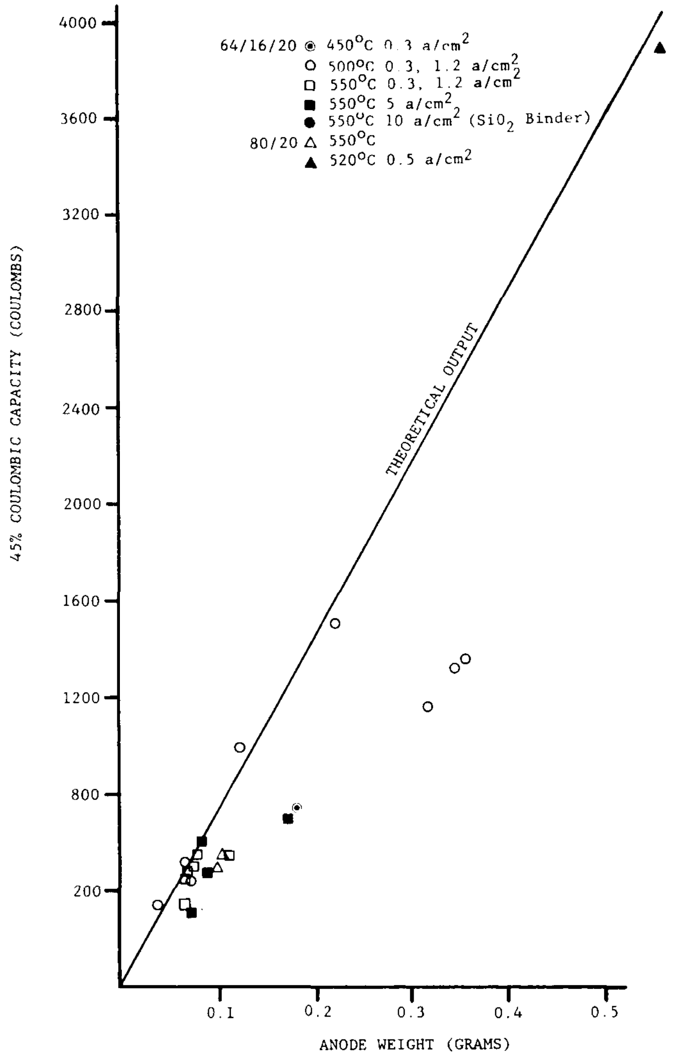
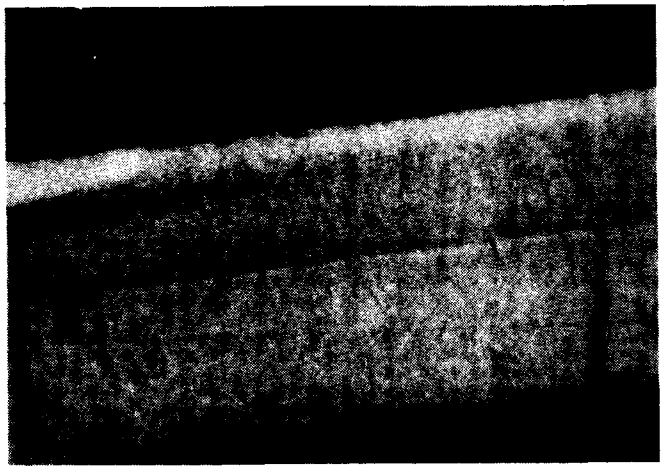
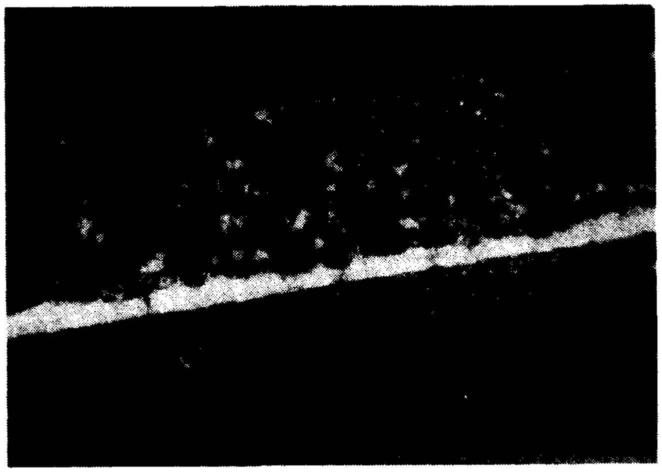


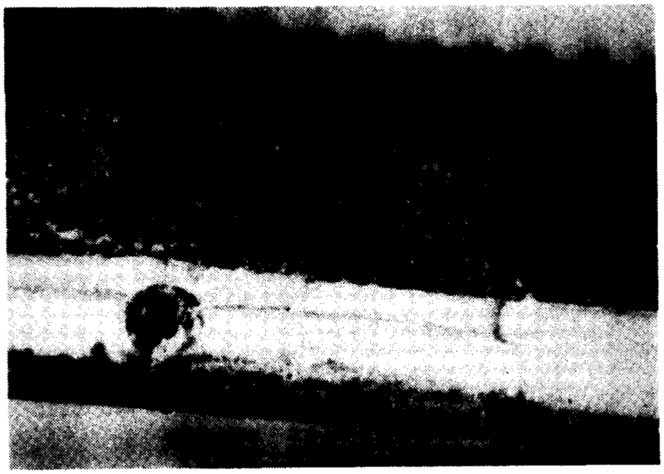
Figure 4. Coulombic Capacity Versus Anode Weight, Iron Disulfide



Li_2CrO_4 Depolarizer



FeS_2 Depolarizer



FeS_2 Depolarizer

Figure 5. Cross Section of Discharged Cells Showing the Catholyte and Separator Layers and the Anode, Magnification 10X

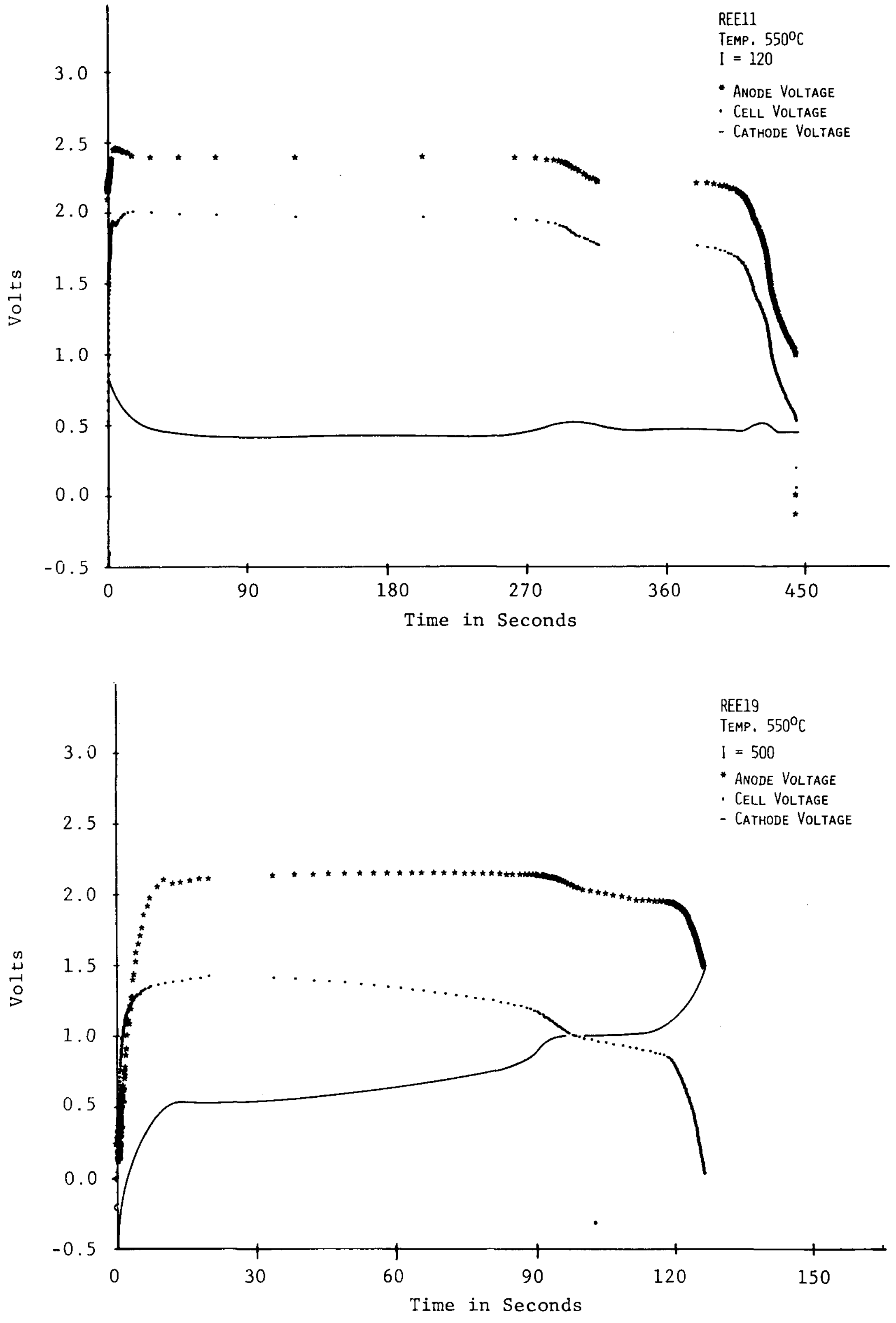


Figure 6. Cathodic Polarization Occurs at High Current Densities in Li-B/FeS$_2$ Cells

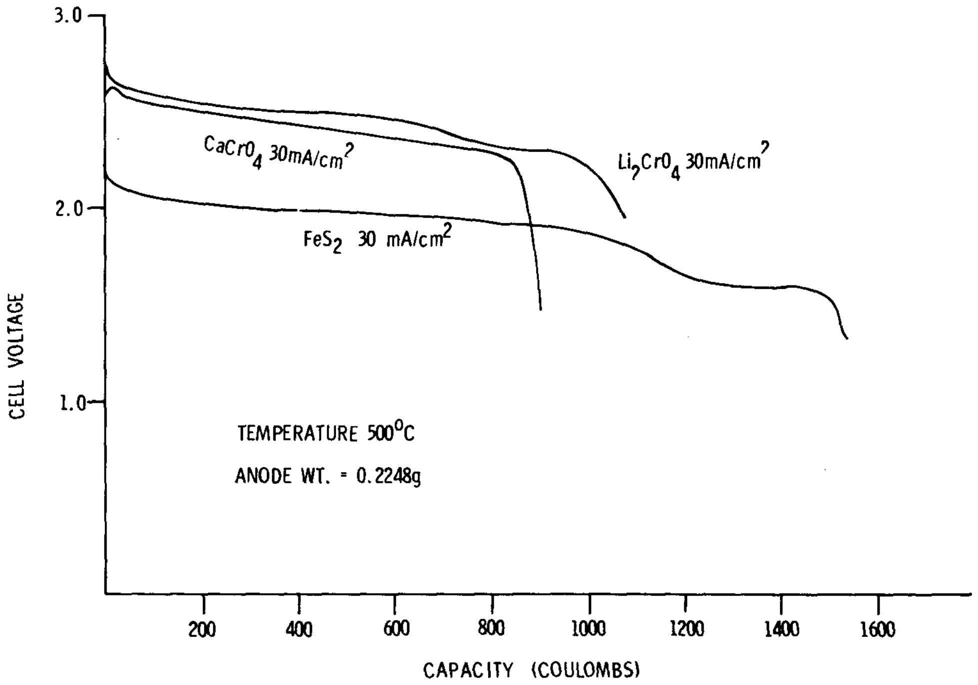


Figure 7. Cell Voltage as a Function of Capacity, Low Current Density

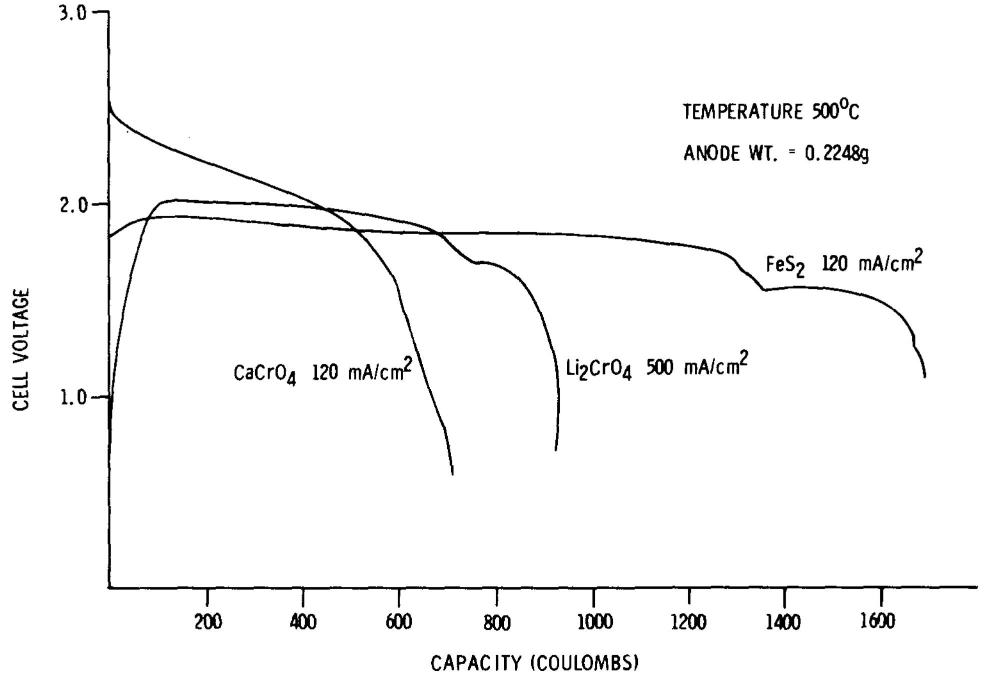


Figure 8. Cell Voltage as a Function of Capacity, High Current Densities

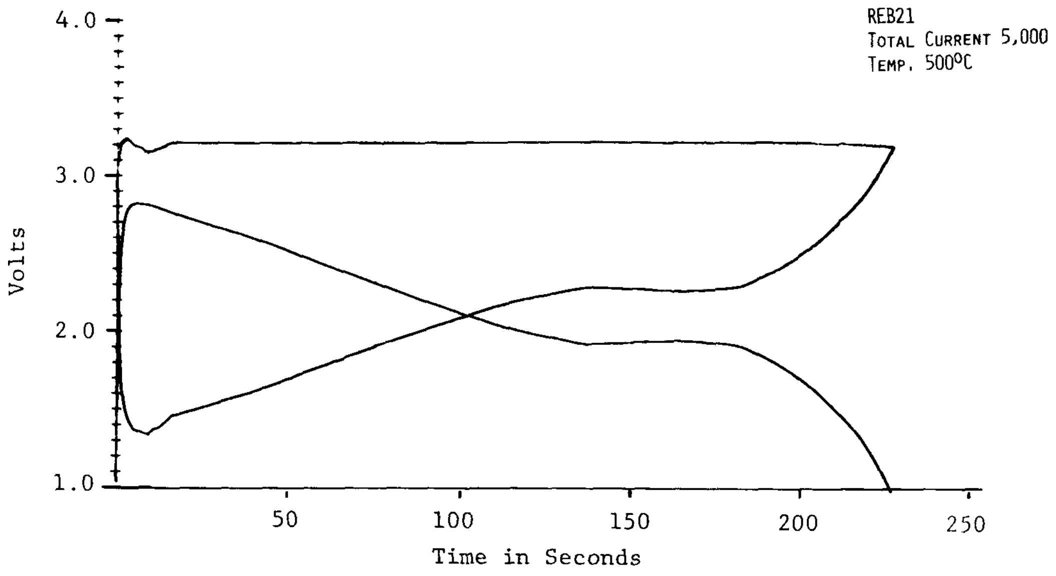


Figure 9. Cathodic Polarization in Li-B/$CaCrO_4$ Cells

Electrode polarization studies of Li-B/$CaCrO_4$ cells by means of a current interruption method reveals an interesting phenomena shown in Figure 10. During discharge, the cell's resistance remains constant, about 0.2 to 0.4 Ω for more than half of its activated life. For discharge at 30 mA/cm^2, the resistance rapidly increases to a maximum, dropping again at the end of life. At 120 mA/cm^2 the internal resistance increases at a later stage of life. This phenomena may be due to the formation of intermediate insoluble products such as those discussed by Laitinen and co-workers;[27, 28] which later undergo disproportionation. They report that the electrochemical reduction of the chromate ion, CrO_4^{2-}, in LiCl-KCl eutectic melt proceeds via a series of steps resulting in the intermediate solid product Li_3CrO_4, which later undergoes disproportionation yielding $LiCrO_2$, another solid product. These reactions and the products are sensitive to the presence in the melt of various divalent metal ions such as Mg++ and/or to the presence of moisture in the melt.[27]

Resistance measurements of DEB and EB pellets were performed using an alternating current technique by Delnick.[30] The resistance values he found from these measurements (Figure 11) show that EB pellets containing 50 wt% MgO are roughly twice as resistive as the DEB pellets. To increase the value of the

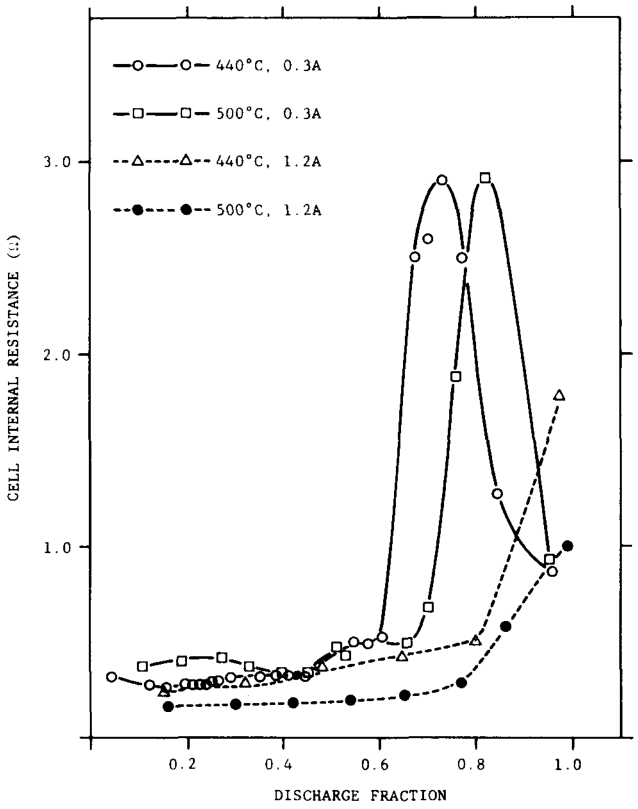


Figure 10. Single Cell Internal Resistance as a Function of Cell Life for 30 mA/cm^2 and mA/cm^2 at 440 and 500°C

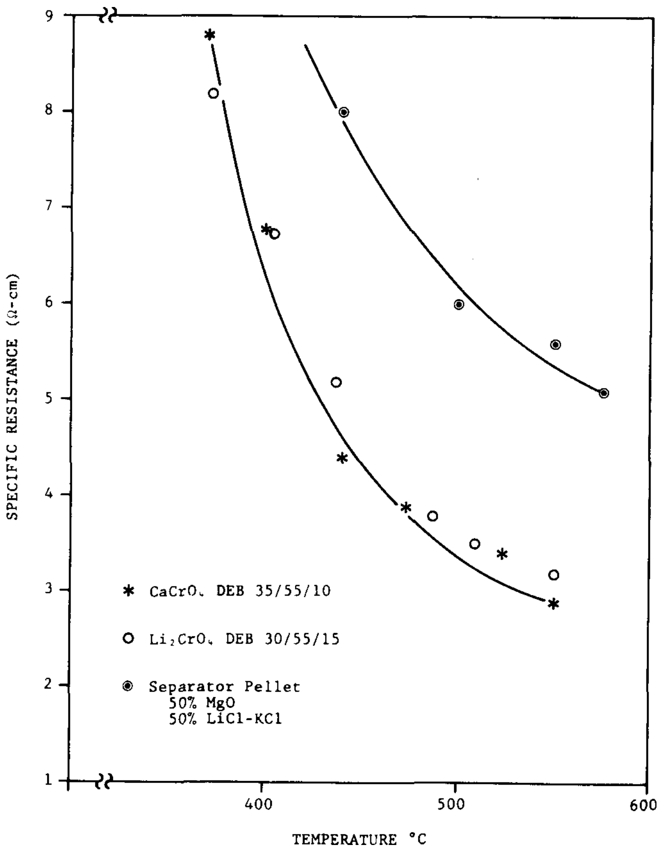


Figure 11. DEB and Separator Pellet Resistance Versus Temperature

limiting current density of Li-B/FeS_2 cells, it was found necessary to decrease the cell's internal resistance. This was accomplished with two layer pellets incorporating a very thin separator layer 20- to 30-mils thick. These thin separator layers could be employed only because FeS_2 is insoluble in the melt. The resulting cells could be discharged at current densities of up to 1 A/cm^2 without apparent loss in coulombic efficiency. In Figure 5b the cross section of such a discharged cell demonstrates that no FeS_2 penetrated the separater layer. This is fortunate since battery designs are often volume limited and the nonproductive inert separator layer should be minimized.

In addition to supporting higher current density, the Li-B anode thermal cells are able to operate over a wider temperature range, 400 to 600°C for chromate depolarizer and 400 to 550°C for FeS_2. The lower limit is, of course, due to lower conductivity; the upper limit for the case of the chromates is due to electrolyte leakage. In the case of FeS_2, it is due to its thermal decomposition. This wider temperature range is very helpful for battery design optimization since thermal batteries must often perform over a wide range of ambient temperatures, as great as 150°C. Thermal batteries employing the Ca/$CaCrO_4$ system cannot usually be optimized for the entire ambient temperature range.

The general shape of the Li-B anode discharge is shown in Figure 12. The discharge is always characterized by a series of two or three flat plateaus separated by a break of about 0.2 volts. The capacity corresponding to each plateau is found to vary with discharges. DeVries et al[21] maintain that the number of breaks is a function of the initial anode composition.

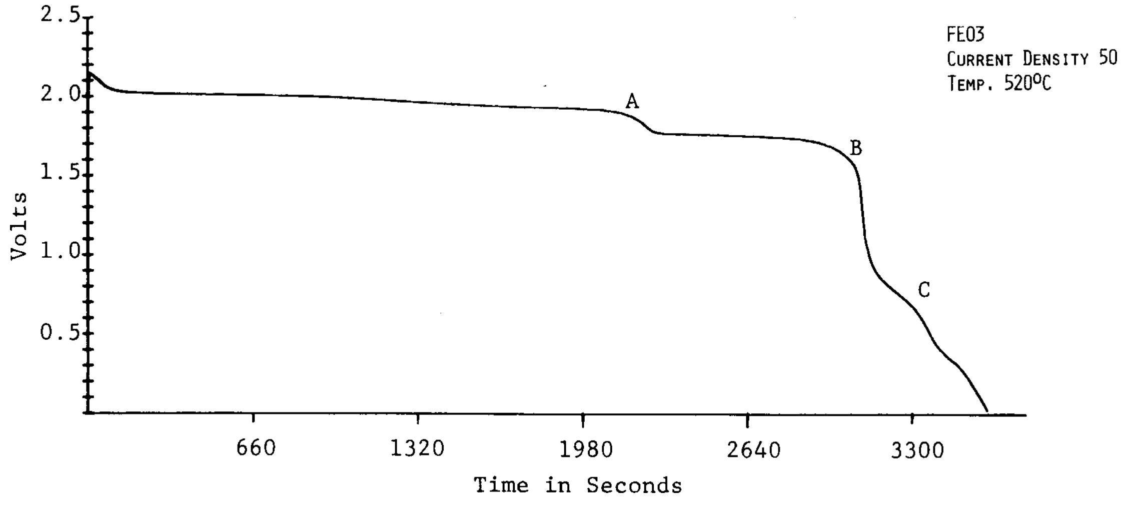


Figure 12. Anode Discharge Curve for Li-B/FeS_2 Cell

The initial part of the discharge corresponding to the first two plateaus behave as though a liquid of nearly pure lithium is being discharged from the anode surface and lithium-filled cavities.[21] These conclusions are based on their reference electrode results which show that the measured open cell voltages are very close to values corresponding to free lithium. No definite explanation was suggested for the drop in voltage between plateaus A and B.[21] The cavities in the alloy described in[21] were demonstrated by micrographs published by Dalleck et al.[19] The last break C, in Figure 12 corresponds to lithium being discharged from Li_2B to form Li_7B_6. No evidence has been found of oxidized boron, hence, boron is not thought to be an active participant in the anodic process.

CONCLUSIONS

Li-B alloys appear to be most promising as anodes for primary reserve thermal batteries. The attractive features are as follows:

1. Li-B alloys can be prepared in compositions in excess of 80 at.% Li (72 wt%), higher active metal content than any other lithium compound anodes or foamed metal anodes.
2. Because the anode retains liquid lithium at battery operating temperature, the anode is not polarized even at very high current density.
3. The alloy is soft and malleable; can be formed into thin foils which are very suitable for anodes. The mechanical characteristics are superior to other lithium compounds which are brittle. This is particularly important since thermal batteries must be designed to withstand severe mechanical shock.

Of the three systems investigated, the LiB/FeS_2 is the most promising, particularly for long life power batteries. It has the advantage of being a more forgiving and predictable system.

ACKNOWLEDGMENTS

The authors wish to acknowledge S. Dalleck and B. F. Larrick of the Naval Surface Weapons Center (NSWC) for providing the Li-B alloy used in this investigation, R. East of the General Electric Company for providing the software used for the single cell tester, S. C. Levy, D. M. Bush and F. M. Delnick of Sandia Laboratories for providing the AgCl/LiCl-KCl reference electrode, FeS_2 and for making resistance measurements. This work was supported by the U. S. Navy, NSWC under Contract No. N60921-77-PO-W0068.

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