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THERMAL BATTERIES: A TECHNOLOGY REVIEW AND FUTURE DIRECTIONS

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ABSTRACT

Thermally activated ("thermal") batteries have been used for ordnance applications (e.g., proximity fuzes) since World War II and, subsequent to that, in nuclear weapons. This technology was developed by the Germans as a power source for their V2 rockets. It was obtained by the Allies by interrogation of captured German scientists after the war (1). The technology developed rapidly from the initial primitive systems used by the Germans to one based on $Ca/CaCrO_4$. This system was used very successfully into the late 1970s, when it was replaced by the Li-alloy/FeS_2 electrochemical system. This paper describes the predominant electrochemical couples that have been used in thermal batteries over the years. Major emphasis is placed on the chemistry and electrochemistry of the $Ca/CaCrO_4$ and Li-alloy/FeS_2 systems. The reason for this is to give the reader a better appreciation for the advances in thermal-battery technology for which these two systems are directly responsible. Improvements to date in the current Li-alloy/FeS_2 and related systems are discussed and areas for possible future research and development involving anodes, cathodes, electrolytes, and insulations are outlined. New areas where thermal-battery technology has potential applications are also examined.

KEYWORDS: Thermal Batteries, Characterization, High Temperature

1. INTRODUCTION

1.1 History Thermally activated ("thermal") batteries were conceived by the Germans during WW II and were used in the V2 rockets (1). Dr. Georg Otto Erb is credited with developing the molten-salt battery that used the heat of the rocket to keep the salt liquid during its mission. The technology was brought back to the United States in 1946 and was immediately adapted to replace the troublesome liquid-based systems that had previously been used in artillery proximity fuzes.

1.2 General Characteristics Thermal batteries are used as the primary power sources for the nuclear weapons that are designed by Sandia National Laboratories for the Department of Energy (DOE). They are also used for many applications for the Department of Defense, such as power sources for missiles and proximity fuzes in ordnance devices. Thermal batteries have the inherent advantages of being very reliable, rugged, and robust. Being hermetically sealed, they can remain in storage for 25 years or more without degradation. As long as the hermeticity of the case is maintained, the shelf life is almost indefinite.

Thermal batteries are high-temperature power sources that typically operate between 350° and 550°C. They use a molten, ionically conducting electrolyte as a separator between the anode and cathode. The liquid electrolyte is immobilized by a powdered metal oxide or ceramic that retains the electrolyte in place by capillary action. The deformation characteristics of the separator at operating temperatures are influenced by temperature, applied pressure, and electrolyte composition, and binder content (2). These properties also influence the interfacial resistances between the separator and the anode and cathode.

Until the electrolyte becomes molten, the battery is essentially inert. Once activated, however, power can be delivered at extremely high rates–in excess of 1,500 mA/cm^2 for times on the order of seconds. At sufficiently low current densities (e.g., <50 mA/cm^2), lifetimes can be easily extended to an hour or more.

To thermally activate the battery, each cell incorporates a pyrotechnic pellet. The desired battery voltage is obtained by stacking the required number of cells, based on the open-circuit of the particular electrochemical couple. The pyrotechnic pellets are ignited by a fuse strip in contact with each pellet, or by an igniter (electroexplosive device) firing through a hole in the center of the stack. Activation times range from under 40 milliseconds for small pulse batteries to hundreds of milliseconds for the larger power batteries.

2. PREVIOUS TECHNOLOGY

2.1 Cup-and-Cover Technology The various electrochemical couples used in thermal batteries over the years were almost exclusively based on the LiCl-KCl eutectic electrolyte which melts at 352°C. A number of the earlier thermal batteries used glass tape impregnated with molten electrolyte as the separator. The earliest technology used the so-called "cup and cover" approach, where each cell was encased in a metal cup The cells are interconnected with metal strips. The heat source for this technology was "heat paper," which is a mixture of $BaCrO_4$ and Zr powder, blended with ceramic fibers and formed into a paper. This material is very dangerous, being very sensitive to static and shock.

2.2 Pellet Technology The cup-and-cover approach was not very satisfactory and led to the development of the pellet technology in the early 1960s (3). Here, the electrolyte was immobilized by powdered kaolin clay. The clay was abundant and cheap but a large amount–35 to 50 w/o–was required for effective electrolyte immobilization. In the last 1960s, Bush evaluated a number of ceramic materials as binders for the electrolyte (4). Fumed silicas were found to be much more efficient binders, requiring as little as 9 w/o of material.

The pellet technology was also applied to the pyrotechnic source used in thermal batteries. Through a joint effort with Unidynamics and Sandia, new pelletized heat sources were developed based on Fe and $KClO_4$ (5). These materials maintain their dimensional stability after ignition, produce very little gas, and are much safer than $Zr/BaCrO_4$ heat paper. What is more important, the ratios of Fe to $KClO_4$ could be adjusted to control the heat output of the pyrotechnic. The development of the pellet technology was a quantum leap in advancing thermal-battery technology.

2.3 Electrochemical Couples A number of electrochemical systems were evaluated for use in thermal batteries. The earlier technologies will only be briefly described in this section; the bulk of the discussion will focus on the more mature $Ca/CaCrO_4$ and Li/FeS_2 technologies.

2.3.1 Ca or Mg/WO₃ The WO_3-based couple was used primarily in fuzing applications. in the early 1950s (6). This technology used glass tape impregnated with electrolyte for the separator. There is a dearth of information in the open literature concerning the electrochemistry of the WO_3 couples used in thermal batteries. The WO_3-based technology was one of the earliest but was made obsolete by the introduction of the $Ca/CaCrO_4$ system in the mid-1950s.

2.3.2 Ca or Mg/V₂O₅ Another early technology that was used in thermal batteries was based on V_2O_5 (6). The use of V_2O_5 is complicated by its relatively high solubility in the molten electrolyte–in excess of 17 w/o. At such high concentrations, it can oxidize chloride to chlorine. As for the WO_3 system, almost nothing has been published concerning the electrochemistry of V_2O_5 in thermal batteries.

2.3.2 Ca/CaCrO₄ The $Ca/CaCrO_4$ couple was the mainstay technology for thermal batteries from the early 1960s until late into the 1970s. This couple has an open-circuit voltage over 3 V. The battery depends upon a delicate balancing of chemical reactions and electrochemical reactions for proper functioning.

2.3.2.1 Anode Reactions In a $Ca/CaCrO_4$ battery, the Ca anode is in direct physical contact with the $CaCrO_4$ material dissolved in the LiCl-KCl melt (soluble to 34 w/o at 600°C). Upon activation of the battery, a complex series of chemical reactions occurs to form a separator layer (reaction barrier) adjacent to the anode. This limits self-discharge reactions.

The use of Ca with the LiCl-KCl electrolyte results in the formation of a liquid Ca-Li alloy, which can lead to intercell shorting if not controlled. The Ca reacts with the Li^+ in a displacement reaction, as shown in eqn. 1.

$$Ca + 2Li^{+} \dashrightarrow CaLi_{2(liq)} + Ca^{+2} \qquad [1]$$

The $CaLi_2$ immediately reacts with the dissolved chromate to form a Cr(V) species (7):

$$3CaLi_{2(liq)} + 4Cl^{-} + 17Ca^{+2} + 12CrO_4^{-2} \dashrightarrow 4Ca_5(CrO_4)_3Cl_{(sol)} + 6Li^{+} \qquad [2]$$

This dark green Cr(V) compound can react further in the presence of excess Ca^{+2} to form a second Cr(V) compound, Ca_2CrO_4Cl, which is purple in color. The discharge is complicated by a competing double-salt reaction between the $CaCl_2$ and the KCl to form solid $KCaCl_3$. These constitute the separator layer in the battery. The unreacted $CaLi_2$ material continues to function as an anode with ionic transference across the separator during electrochemical discharge. The $CaLi_2$ discharges through several stages: $CaLi_2 \dashrightarrow CaLi \dashrightarrow Ca$. The Ca then reacts with the bulk Li^+ again (eqn. 1) to regenerate the $CaLi_2$ alloy anode.

2.3.2.2 Cathode Reactions At the cathode, the $CaCrO_4$ dissolved in the molten LiCl-KCl reacts in a non-stoichiometric manner with the iron current collector upon activation to form an Fe-rich lithium-chromium ferrite $[Li(Cr_{1-y}Fe_y)O_2]$ and a Cr-rich lithium-iron chromite $[Li_{0.5}(Fe_{2.5-x}Cr_x)O_4]$ (8). Both of these materials are good electronic conductors at thermal-battery operating temperatures. Consequently, once a film of material has formed on the iron current collector, further reaction ceases, due to cathodic protection of the Fe substrate

The electrochemical discharge sequence that occurs at the cathode involves the generation of the same Cr(V) compounds that are formed chemically at the anode, through a Cr(V)-chromate intermediate (9). The process involves a one-electron reduction first, followed then by a two-electron transfer (10):

$$CrO_4^{-2} + e^- \text{---->} CrO_4^{-3} \qquad [3a]$$

$$3CrO_4^{-3} + Cl^- + 5Ca^{+2} \text{---->} Ca_5(CrO_4)_3Cl_{(sol)} \qquad [3b]$$

$$Ca_5(CrO_4)_3Cl_{(sol)} + 3Li^+ + 6e^- \text{---->} 3LiCrO_{2(sol)} + 5Ca^{+2} + Cl^- + 6O^{-2} \qquad [3c]$$

2.3.2.3 Problem Areas The performance of the Ca/$CaCrO_4$ electrochemical system tended to be somewhat unpredictable. Changes in lots of Ca or $CaCrO_4$ catholyte could lead to unexpected changes in performance. It was sometimes necessary to match a given batch of Ca with a particular batch of catholyte, in an empirical fashion, for proper performance. A detailed study of the chemical and physical properties of various sheet-Ca materials showed little correlation of battery performance to surface chemistry, metallic impurities, melting point, phase and texture (11). Only the bulk nitrogen content appeared to directly influence battery performance.

The source of $CaCrO_4$ as well as the methods used for processing of the various catholyte mixes also affected the battery performance (12). The heat treatment of the $CaCrO_4$ influenced its average particle size and, consequently, its rate of dissolution in the molten LiCl-KCl to replace chromate that has been electrochemically consumed (13).

2.3.3 Li or Li-alloy/FeS_2 The advent of the FeS_2-based electrochemical system was a welcome improvement to the previous Ca/$CaCrO_4$ system. It had few of the inherent problems of chemical side reactions and variability of the Ca/$CaCrO_4$ system and was much more predictable. The FeS_2 was readily obtained from processing pyrite and was inexpensive, relatively to chemically synthesized $CaCrO_4$. In addition, it had improved power and lifetimes over the Ca/$CaCrO_4$ system, with none of the deleterious consequences of $CaCrO_4$ which contains the Cr(VI) carcinogen.

There were several disadvantages inherent to the FeS_2-based system, however. First, a true separator pellet was required, rather than the one formed chemically *in situ* in the Ca/$CaCrO_4$ system, to prevent direct reaction of the anode with the cathode. Consequently, more piece parts were needed for a battery. Second, the open-circuit voltage of the Li/FeS_2 couple is only about 2 V, which is over a volt less than for the Ca/$CaCrO_4$ couple. As a result, more cells were required for a given battery voltage and these cells had to be thinner than those for Ca/$CaCrO_4$ batteries for the same battery volume (height).

2.3.3.1 Anode Reactions The reactions that take place in the Li-alloy/FeS_2 battery depend upon the composition of the anode material and which elements are used as alloying agents. The most common alloys used are Li-Si and Li-Al alloys.

The discharge stages for Li-Si alloy anodes are: $Li_{22}Si_5$ ---> $Li_{13}Si_4$ ---> Li_7Si_3 ---> $Li_{12}Si_7$ (14). Sandia prefers to use the $Li_{13}Si_4$--->Li_7Si_3 transition (44 w/o Li) for DOE applications. This has a potential about 157 mV more positive than pure Li at 415°C. Although the alloy with a higher Li content ($Li_{22}Si_5$) would produce a higher emf (44 mV vs. Li), it is too reactive to be suitable for processing in a dry-room environment, even at 3% RH.

The discharge reaction for the $Li_{13}Si_4$---->Li_7Si_3 transition is shown in eqn. 4; this corresponds to a capacity of 1,747 A-s/g of alloy.

$$Li_{13}Si_4 \dashrightarrow 4/3Li_7Si_3 + 11/3\ Li^+ + 11/3\ e^- \qquad [4]$$

The discharge sequence for Li-Al is considerably different, since the only phases present in the system are the solid-solution and LiAl which contains 20 w/o Li. Thus, only a single anode transition is possible: LiAl (ß-Al) ----> Al (α-Al). The discharge reaction for nonstoichiometric LiAl is shown in eqn. 5:

$$Li_{0.47}Al_{0.53} \dashrightarrow Li_{0.0578}Al_{0.53} + 0.4111\ Li^+ + 0.4111\ e^- \qquad [5]$$

This corresponds to a capacity of 2,259 A-s/g, which is higher than that for the Li-Si transition of eqn. 7. However, the Li-Si alloy has the capability of multiple transitions and can generally deliver power at a higher rate. In addition, the emf of the 44 w/o Li-Si alloy is about 140 mV more negative than that of LiAl (297 mV vs. Li).

Pure-Li anodes have also been used in thermal batteries. Catalyst Research Corp. developed an anode of pure Li immobilized with 80 w/o powdered iron (15). The so-call "LAN" anode was successfully used in a variety of batteries (16).

2.3.3.2 Cathode Reactions The cathode reactions that occur during the discharge of FeS_2 in high-temperature rechargeable batteries have been extensively studied by the workers at Argonne National Laboratory (ANL) (17). The sequence of phases that form during the discharge of FeS_2 in molten LiCl-KCl is shown in eqn. 6:

$$FeS_2 \dashrightarrow Li_3Fe_2S_4 \dashrightarrow Li_{2-x}Fe_{1-x}S_2\ (x\sim0.2) + Fe_{1-x}S \dashrightarrow Li_2FeS_2 \dashrightarrow Li_2S + Fe \qquad [6]$$

Li(Si)/FeS_2 thermal batteries designed at Sandia use only the first cathode transition:

$$FeS_2 + 3/2\ Li^+ + 3/2\ e^- \dashrightarrow 1/2\ Li_3Fe_2S_4 \qquad [7]$$

This is equivalent to 1,206 A-s/g. What is generally not realized is the oxidation state of Fe in FeS_2 is not +4 but +2 (18,19). The species actually undergoing reduction in eqn. 6 is the polysulfide, S_2^{-2}.

Besides being a readily available inexpensive material, FeS_2 has several additional advantages. It is a very good extrinsic semiconductor, with an energy gap at room temperature of about 0.92 eV (20, 21). Both *n* and *p* types have been reported. The electrical conductivity at 20°C has been reported to range from 0.03-333 S/cm, depending on the source and types and amounts of impurities (22).

2.3.3.3 Problem Areas In spite of its inherent advantages as a cathode material for thermal batteries, FeS_2 has several properties that limit its use: only moderate thermal stability, a voltage transient upon battery activation, and significant solubility in molten salts.

FeS_2 begins to decompose at temperatures above 550°C to form FeS and sulfur vapor. The fugitive sulfur can then react very exothermically with the Li-alloy anodes in the battery to generate more heat that leads to even more decomposition of FeS_2. Ultimately, a thermal-runaway condition occurs which can destroy the battery.

The use of FeS_2 as a cathode material also causes a large voltage transient ("spike") of 0.2 V or more per cell upon activation of a thermal battery. This is unacceptable for applications where strict voltage control is critical. This phenomenon is related to the impact of temperature, electroactive impurities (e.g., oxides, sulfates), elemental sulfur from FeS_2 decomposition, and the activity of the Li^+ not being fixed in the cathode (23, 24).

Fortunately, the voltage-transient problem is ready remedied by lithiation, which involves the addition of a small amount (1-2 w/o) of Li_2O or Li_2S to the catholyte during processing. The kinetics of the lithiation reactions are fast enough for most applications that lithiation occurs during activation of the battery. For small fast-rise pulse batteries, it is necessary to prefuse the catholyte under an inert gas to lithiate it before use in the battery (25). The chemistry of the lithiation process has been thoroughly studied and is fairly well understood (26). The ease with which good science can be brought to bear with problems in the Li-alloy/FeS_2 system is in marked contrast to the Ca/$CaCrO_4$ system that depended on poorly understood empirical solutions to problems.

The solubility of FeS_2 in molten salts only becomes a problem when the battery is under a very light load or on open circuit. Under these conditions, the solubilized FeS_2 diffuses into the separator where it reacts with soluble Li-containing species that originate at the anode. The result is the formation of elemental Fe and Li_2S in a band in the separator and a loss of capacity of active material (27, 28).

2.3.3.4 Electrolyte Effects The majority of the thermal batteries have generally used the LiCl-KCl eutectic as the electrolyte. Since this is a multi-cation electrolyte, it is subjected to severe Li^+ concentration gradients at the anode interface under high-rate conditions (29). In contrast, the use of the all-Li LiCl-LiBr-LiF minimum-melting electrolyte avoids these difficulties. Even though it has a higher melting point (436°C) than that of the LiCl-KCl eutectic (352°C), it is ideally suited for pulse-power batteries, where lifetimes can be of the order of seconds or less, because of its higher ionic conductivity.

The properties of a number of separator materials that have been optimized for thermal-battery applications are summarized in Table 1 for a temperature of 500°C.

Table 1. Properties of Separator Materials Optimized for Use in Thermal Batteries (30, 31)

Electrolyte	w/o MgO	Melting Point, °C	Conductivity, S/cm
CsBr-LiBr-KBr eut.	30	238	0.30
LiBr-KBr-LiF eut. (SNL)	25	313	1.25
LiCl-LiBr-KBr eut. (ANL)	30	321	0.86
LiCl-KCl eut.	35	352	1.00
LiCl-LiBr-LiF min. melting	35	436	1.89

For batteries with lifetimes of an hour or more, it would be advantageous to use an electrolyte that has a much greater liquidus range. The CsBr-LiBr-KBr eutectic melts at 238°C but has too low a conductivity to be usable. The ANL-developed LiCl-LiBr-KBr eutectic has a reasonably low melting point and good conductivity but not quite as good as those for the Sandia-developed LiBr-KBr-LiF eutectic.

The relative effect of various electrolytes on the electrochemical performance of Li(Si)/FeS_2 cells and batteries is summarized in greater detail in ref. 32.

2.3.5 Li-alloy CoS_2 Because of its limited high-temperature stability, the longest lifetime that can be reasonably attained in a $Li(Si)/FeS_2$ thermal battery is somewhat over an hour (33, 34). The need at Sandia to develop a thermal battery with a lifetime of two hours or more could not be met with this technology. Fortunately, researchers at Westinghouse had been developing the $LiAl/CoS_2$ for high-temperature rechargeable military applications (35-37). The advantages of CoS_2 relative to FeS_2 are its higher rate capability, very low solubility in molten salts, and, most importantly, its higher thermal stability–up to 650°C, about 100°C higher than that for FeS_2. The major disadvantage of CoS_2 is its higher cost–it must be synthesized in the laboratory–and its lower emf (by 100 mV/cell).

2.3.5.1 Cathode Reactions The discharge sequence for CoS_2 is completely different from that for FeS_2, in that lithiated materials are not formed: CoS_2 ----> Co_3S_4 ----> Co_9S_8. The first discharge step is shown in eqn. 8:

$$CoS_2 + 4/3\ e^- \text{---->} 1/3\ Co_3S_4 + 2/3\ S^{-2} \qquad [8]$$

There are thus 1.33 equivalents per mole of CoS_2 during the first discharge step, compared to 1.50 for FeS_2. The capacity for this reaction is 1,045 A-s/g.

Sandia subsequently successfully incorporated the Westinghouse technology into a nominal two-hour, $Li(Si)/CoS_2$ thermal battery, using the low-melting, LiBr-KBr-LiF eutectic electrolyte developed at Sandia specifically for such an application (38).

In related single-cell and battery tests, the superiority of the CoS_2 to FeS_2 was demonstrated using a number of electrolytes (39). Single-cell resistances are shown in Figures 1-3 for the LiCl-KCl eutectic, the low-melting LiBr-KBr-LiF eutectic, and the all-Li LiCl-LiBr-LiF minimum-melting electrolyte, respectively. The cells were discharged under a steady-state current of 190 mA/cm^2 with 1,130 mA/cm^2 pulses, 1 ms wide applied with a 10% duty cycle. The resistances of the CoS_2 cells were very consistent as a function of depth of discharge and were lower than those of the FeS_2 cells–especially later in life. The peak in the resistance of the FeS_2 cells is related to the higher resistance of the first discharge phase, $Li_3Fe_2S_4$ (40).

3. FUTURE THERMAL-BATTERY APPLICATIONS

3.1 Sonobuoys There is an effort currently underway to develop the existing thermal-battery technology for use in sonobuoys, to replace the Li/SO_2 cells currently used. Thermal batteries offer a number of potential advantages over the current technology. They can be stored for longer periods of time and they can provide very high rate capabilities. They avoid the personnel-related safety issues associated with Li/SO_2, as well.

Ideally, the U.S. Navy would like to have a thermal battery that would last up to four hours (or more). The best performance attained with today's technology is a little over two hours. The biggest challenge facing the use of thermal batteries for long-term sonobuoy use is thermal management. The batteries will need improved insulations and some type of auxiliary heating. The long lifetime requirement also involves high-power pulses spread throughout the mission of the battery. These can be as high as 100 A and 4 kW for up to 1 s.

3.2 Geothermal Borehole Batteries The batteries currently used for instrument power in geothermal boreholes are based on a $Li\text{-alloy}/SOCl_2$ technology. These cells are designed to operate up to 180°C, which is the melting point of pure Li. Since boreholes temperatures may exceed 300°C, the cells and associated electronics must be protected in an expensive dewar system. The use of a battery that can operate at 300°C or more in a borehole suggests that thermal-battery technology may be applicable. This temperature is above that for normal ambient-temperature Li batteries and below that for standard thermal-battery electrolytes.

The types of electrolyte–either solid or liquid–will determine, in large part, the performance and thermal window of a potential borehole battery. There are a number of solid ionic conductors that are potentially usable under these conditions. The β''-Al_2O_3 material, used in Na/S cells, is one possible candidate. It could be used with the Na/S couple or other suitable couples based on Na, to provide voltages of between 2.6 V and 4.2 V.

Low-melting electrolytes containing alkali-metal halides (such as Cs salts) are a possibility but these could only be used at low rates. Similarly, the alkali-metal tetrachloroaluminates which melt at between 86° and 256°C offer other possibilities. These have a much lower voltage-stability window (<2 V), however, and would require the use of solid electrolytes with high-activity anodes, to prevent reduction of Al^{+3} to Al.

Any approach selected would require the implementation of a pyrotechnic heat source to activate the battery so that power would be available to power instrumentation while lowering into the borehole. Once in place, the ambient heat would maintain the battery at operating temperature. Much needs to be done, however, to determine the relative rate capabilities of candidate systems over the temperature and load regimes envisioned for borehole power applications.

4. FUTURE RESEARCH AREAS

4.2 Anode Materials The area where there is the least chance of realizing significant improvements in thermal-battery technology is the anode. The emf of the current Li-Si alloy with 44 w/o Li is only 157 mV from pure Li at 415°C (14). The use of other Li alloys with higher emfs will be counterbalanced by the increased chemical reactivity toward oxygen and moisture due to the higher activity of Li. This is a consequence of the higher surface area of these powdered alloys compared to a disc of pure Li. The development of ternary alloys could rest in an improvement in the capacity of the alloys, but with little likelihood of realizing any significant improvement in emf. Consequently, alloy development would have a low priority in future research activities.

The use of a Li-B alloy developed by the Naval Surface Warfare Center has potential, since it actually contains elemental Li in the pores of a Li-B structure (41, 42). This material can be rolled out much as Li foil. Unfortunately, the synthesis procedure is very difficult to carry out and obtain repeatable results. It has never been successfully developed beyond the laboratory stage.

4.2 Electrolytes A considerable amount of work has already been done in examination of improved electrolytes for thermal batteries. Many of these electrolytes contain bromide as a main constituent. This immediately reduces the voltage-stability window relatively to electrolytes based on chloride or fluoride. The decomposition voltages at 527°C for a number of the common metal halides are summarized in Table 2.

4.2.1 Iodide-Based Electrolytes A number of iodide-based electrolytes have much lower melting points than the corresponding bromide electrolytes, but at the expense of a reduced voltage-stability window. This has immediate ramifications when the use of higher-voltage cathodes is desired. In addition, use of iodide-based electrolytes would force electrolyte

Table 2. Thermodynamic Decomposition Voltages for Metal Halides at 527°C

Halide	Decomposition Voltage, V
LiF	5.593
KF	5.047
LiCl	3.553
KCl	3.731
LiBr	3.147
KBr	3.452
LiI	2.512
KI	2.969

preparation to be conducted in a glovebox (rather than fusing in dry-room air as is now done) because of the reaction with oxygen to generate elemental iodine. Consequently, the iodide-based electrolytes do not appear practical for the majority of thermal-battery applications.

4.2.2 Cs- and Rb-Based Electrolytes A number of the low-melting, metal-halide electrolytes that melt below 300°C contain Cs or Rb halides. Such systems suffer from low ionic conductivities associated with the massive Cs and Rb cations. In addition, Rb and Cs salts are very expensive, so that they do not appear to be viable candidates for improved electrolytes.

4.2.3 Other Electrolytes Other categories of electrolytes that have been examined in the past include nitrates, nitrites, perchlorates, and various organic-based compounds (e.g., thiocyanates). These suffer from either thermal decomposition reactions or a limited thermodynamic stability window when used with reactive anodes or high-voltage cathodes.

The truth is that there is very little likelihood of developing new, improved electrolytes for thermal batteries over what already is being used.

4.3 Cathode Materials The biggest payoff in improving thermal-battery technology will come in the area of better cathodes. The ideal cathode for thermal batteries will have the following properties: high emf, low solubility in molten salts, good electronic conductivity, low equivalent weight, good kinetics (rate), high capacity, multiphase discharge (non-intercalating), reaction products with similar properties, and reasonable cost.

The actual number of combinations of materials that can be considered for use as cathodes is limited to a select number of transition metals coupled with O, S, P, and various combinations of these. Typical suitable transition metals include: Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Mo, W, Sn, Pb, Sb, Ag, and Nb. Because of strict voltage-control requirements for DOE thermal batteries, materials that exhibit an intercalation reaction are generally unsuitable, because of the decline in voltage during discharge.

A large number of mixed oxides are currently being surveyed and synthesized at Sandia for evaluation as possible cathode materials. A similar series of mixed sulfides are also being examined. Open-circuit voltages of greater than 3 V are desired, to increase the energy density and the specific energy. More-energetic pyrotechnic sources would also reduce the height of the battery stack. This would allow fewer cells for a given battery-voltage requirement and would provide the design engineer with more options for future applications.

4.4 Improved Insulations Improved insulations will be necessary if the goal of a four-hour thermal battery is to be achieved. The best commercial insulation on the market today is a molded composite board containing silica, titania, and quartz fibers (Min-K® and Microtherm®). Vacuum/foil insulation is not likely to be practical for small thermal batteries, because of the significant heat losses associated with the ends of the batteries.

One area that looks promising involves aerogel insulations. These materials have the potential of having up to one-third the thermal conductivity of the best molded insulations. Their main disadvantage, however, it that they are transparent in the IR region between 3-7 µm, which covers the operating temperature range for thermal batteries. Consequently, thermal opacifiers such as carbon black must be added. A second disadvantage is that the aerogels are quite fragile and will require the use of some strengthening agents (e.g., ceramic or carbon fibers). This would undoubtedly increase heat losses by conduction, so that some tradeoff will be necessary between thermal properties and physical strength.

5. CONCLUSIONS

Great strides have been made in improving the crude thermal-battery technology developed by the Germans during WW II. The earliest systems were based on cup-and-cover design and used WO_3 or V_2O_5 cathodes, Mg or Ca anodes, and heat-paper pyrotechnic with molten LiCl-KCl eutectic impregnated in glass tape. This was followed by the $Ca/CaCrO_4$ system that incorporated pellet technology and a $Fe/KClO_4$ pyrotechnic. This system was replaced by the more reliable and predictable and better-performing Li-alloy/FeS_2 system that has now become the mainstay of the thermal-battery industry. The development of low-melting electrolytes, in conjunction with the more-thermally stable CoS_2 has resulted in the realization of a two-hour thermal battery.

There is great potential for extending the current thermal-battery technology through the development of improved cathodes with higher emfs, thermal stabilities, capacities, and kinetics. The simultaneous development of improved thermal insulations based or aerogels containing thermal opacifiers and strengthening agents increases the likelihood of achieving a four-hour thermal battery. Such a system would be ideally suited for sonobuoy and geothermal borehole applications to replace the current Li-ambient technology with its inherent limitations. These applications present a great technical challenge.

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Figure 1. Resistance vs. Time of Li(Si)/MS$_2$ Cells at 450°C with LiCl-KCl Electrolyte.

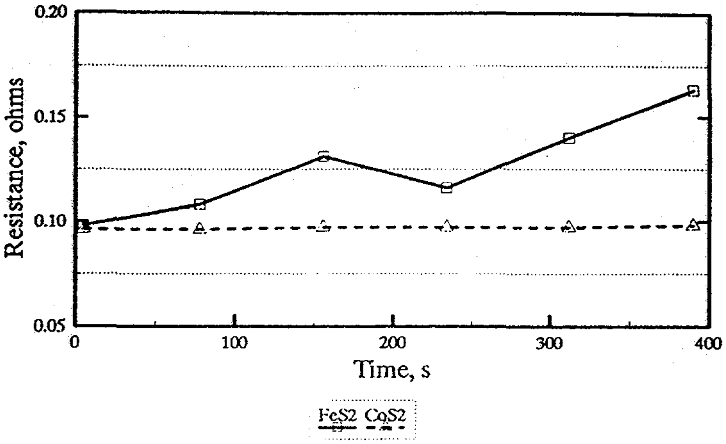

Figure 2. Resistance vs. Time of Li(Si)/MS$_2$ Cells at 450°C with LiBr-KBr-LiF Electrolyte.

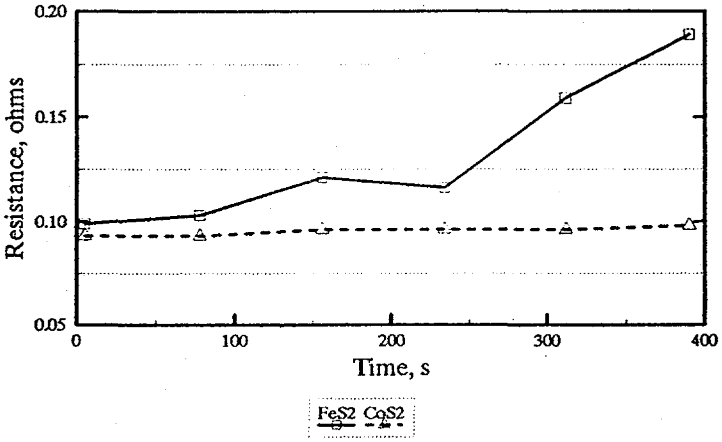

Figure 3. Resistance vs. Time of Li(Si)/MS$_2$ Cells at 450°C with LiCl-LiBr-LiF Electrolyte.