

Thermally activated (“thermal”) battery technology Part I: An overview

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Abstract

Thermally activated (“thermal”) batteries are primary batteries that use molten salts as electrolytes and employ an internal pyrotechnic (heat) source to bring the battery stack to operating temperatures. They are primarily used for military applications, such as missiles and ordnance, and in nuclear weapons. This paper discusses the development history and presents a general overview of this technology.

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1. History

Thermal batteries were conceived and developed by German scientists during WW II and were used in the V2 rockets [1]. The batteries used exhaust heat from the rocket to keep the electrolyte molten in the battery during the missile’s mission. Dr. Georg Otto Erb is credited with developing this technology. After interrogation of German scientists after the war, the technology was brought back to the United States in 1946. A troublesome and sometimes unreliable liquid-based Pb/fluoroboric acid reserve system had been used in artillery proximity fuses. The new technology was immediately adapted to replace the previous batteries because of intrinsic advantages. In 1947, Catalyst Research Corp. (CRC) studied various electrolyte systems and finally decided on LiCl–KCl eutectic that melts at 352 °C. In 1952, Eagle Picher (Joplin, MO) also started in the business. (EaglePicher Technologies is the largest US manufacturer of thermal batteries today.) In 1954, Sandia National Laboratories (SNL) (Albuquerque, NM) started to develop thermal batteries for the Atomic Energy Commission (AEC), now the Department of Energy (DOE) weapons’ programs.

2. Thermal-battery uses

Thermal batteries are used for many military applications, primarily as power sources for guided missiles (Tow, Patriot, Sidewinder, Cruise, etc.) and proximity fuzes in ordnance devices. They serve to provide power for radar and electronic guidance as well as the guidance-fin motors. In ordnance applications (e.g., 55 mm artillery shells), thermal batteries provide power to the proximity fuses as well as for arming and safeing functions. Some torpedoes and guided bombs depend on thermal batteries for a power source. Thermal batteries have also been used in the past for extended space flights to power critical electronics packages years into flight (e.g., Galileo). Some of the largest thermal batteries are used to provide emergency backup power for the hydraulics systems in select military aircraft.

Thermal batteries are also used as the primary power sources for the radar and electronics packages for nuclear weapons. Almost universally, such batteries are right circular cylinders of varying sizes. However, some unusual shapes have been designed over the years (e.g., half moon). A number of typical batteries developed at SNL are illustrated in Fig. 1. The smallest batteries are generally short-lived (<10 s), high-rate (e.g., >1 A cm⁻²) units that can be used for cutting reefing lines on parachutes or for firing another thermal battery. The power batteries operate in the tens of milliamperes per sq. cm for longer periods of time (e.g., 30 min). The so-called long-life batteries

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Fig. 1. Photograph of the wide variety in sizes of Li–Si/FeS₂ thermal batteries developed at Sandia (a 12-in. ruler is shown for size comparison).

are designed to operate for more than 1 h [2]. By utilizing a vacuum-foil insulation, discharge times of over 2 h have been demonstrated [3].

3. General characteristics

Thermal batteries have the inherent advantages of being very reliable, rugged, and robust. They are able to operate in the high-spin (e.g., 16,000 rpm) and setback environment of artillery shells. In addition, they are able to survive the high shock (16,000 × g) experienced in an earth-penetrator weapon. They

are hermetically sealed and can remain in weapons systems for 25 years or more over a wide range of storage temperatures (typically, –55 to +75 °C) without degradation. A sectional view of a typical thermal Li–Si/FeS₂ thermal battery is shown in Fig. 2.

The main degradation process involves moisture and oxygen reacting with the anodes. The shelf life of the batteries is almost indefinite as long as hermeticity is maintained. Once activated, the batteries will function until the electrochemistry is exhausted or until the electrolyte freezes or solids precipitate at the anode-separator interface due to high Li⁺ concentration gradients that move the electrolyte composition off eutectic. The latter short-

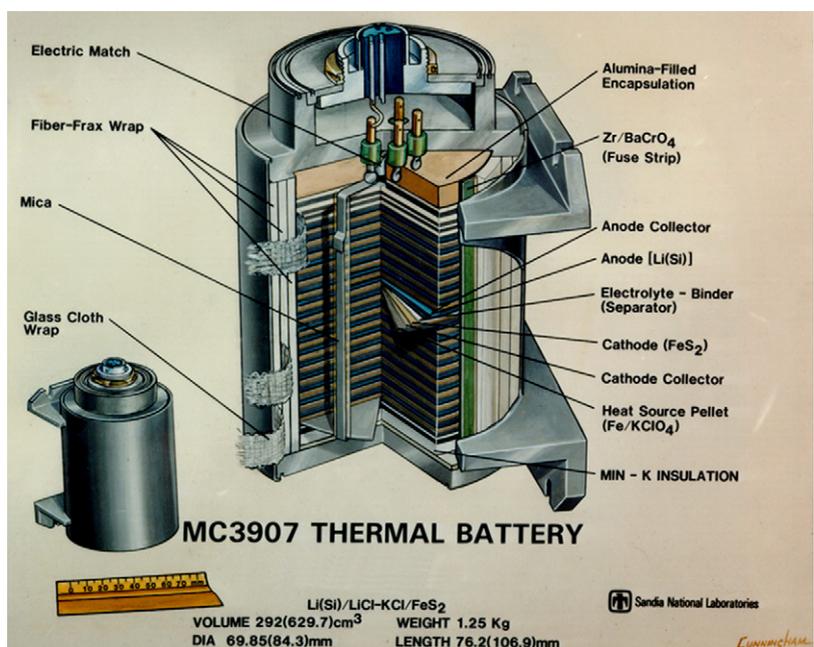


Fig. 2. Section view of a Li–Si/FeS₂ thermal battery.

ens the life of the battery and is most likely to occur under high-rate discharge conditions. Freezing of electrolyte is generally the limiting factor for the lifetimes that can be realized. Once the battery is activated, it immediately starts to cool, so the amount of insulation present will dictate the rate of heat loss. The best commercial insulation available is a composite material (Microtherm[®] and Min-K[®]) developed for use with radioisotope thermoelectric generators (RTGs). This is used for battery lifetimes of generally 30 min or more. Thermal batteries tend to be application specific, so that a given form factor is generally not used for new applications. This, and the high labor costs associated with them, tends to make them somewhat expensive.

Thermal batteries are high-temperature power sources typically operating between 350 and 550 °C that use an ionically conducting molten salt in the separator between the anode and cathode. Consequently, they will generate heat during operation, which can be detrimental to nearby electronic packages. In addition, the heat released may be detrimental for the IR signature for furtive missions. Typically, the cell parts are pressed from powdered mixtures. The liquid electrolyte is held in place in the separator pellet by the capillary action of special types of MgO powder. The electrolytes used typically melt between 319 and 436 °C, with the LiCl–KCl eutectic that melts at 352 °C being the most common. The mechanical properties of the separator pellets at operating temperatures are important to minimize pellet deformation and electrolyte extrusion. These characteristics are influenced by temperature, applied pressure, electrolyte composition, and binder content [4]. These properties also influence the interfacial resistances between the separator and the anode and cathode.

Until the electrolyte becomes molten, the battery is inert. Once activated, however, power can be delivered at extremely high rates because of the high intrinsic ionic conductivity of molten salts. For example, the conductivity of LiCl–KCl eutectic at 400 and 500 °C is 1270 and 1850 mS cm⁻¹, respectively, which is several orders of magnitude greater than typical Li-ion electrolytes. The power densities of thermal batteries tend to be somewhat modest, however, due to the high hardware overhead associated with them, especially the pyrotechnic weight. Typical values for several modern thermal batteries are compared to other battery technologies in Table 1. To bring the battery

stack to operating temperatures requires the use of pyrotechnic (“heat”) pellets – typically a blend of Fe and KClO₄ – in each cell. The pyrotechnic pellets are ignited by a Zr/BaCrO₄ fuse strip (“heat paper”) in contact with each pellet, or directly by an igniter (electroexplosive device) firing through a hole in the center of the stack. Activation times range from under 40 ms for small pulse batteries to hundreds of milliseconds for the larger power batteries.

4. Early technology

4.1. Cup-and-cover technology

The various electrochemical couples used in thermal batteries over the years were almost exclusively based on the LiCl–KCl eutectic. 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 were interconnected with metal strips. The heat source for this technology was the same material Zr/BaCrO₄ heat paper used for the fuse strips. This material is very dangerous, being quite sensitive to static and shock.

4.2. Pellet technology

The cup-and-cover approach was not very satisfactory, requiring many parts per cell, and led to the development of the pellet technology in the early 1960s [5]. Initially, the electrolyte was immobilized by powdered kaolin clay, which was abundant and cheap. However, a large concentration – 35–50 w/o – was required for effective electrolyte immobilization. In the last 1960s, Bush evaluated a number of ceramic materials as binders for the electrolyte [6]. Fumed silicas were 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 SNL, new pelletized heat sources were developed based on Fe and KClO₄ [7]. These materials maintain their dimensional stability after ignition, produce very little gas, and are much safer than Zr/BaCrO₄ heat paper. In addition, the ratios of Fe to KClO₄ can be easily adjusted to control the heat output. The development of an all-pellet thermal battery at SNL was a quantum leap in advancing thermal-battery technology.

5. Electrochemistry

5.1. Ca or Mg/WO₃

The Ca/WO₃ and Mg/WO₃ couples were used primarily in fuzing applications in the early 1950s [7]. In this technology, glass tape impregnated with electrolyte was used for the separator. There is almost no information in the open literature concerning the electrochemistry of the WO₃ as used in thermal batteries. This technology was one of the earliest but was replaced by the Ca/CaCrO₄ system in the mid-1950s.

Table 1
Specific power and specific energy of representative thermal batteries compared to other battery technologies

Battery type	Specific power (W kg ⁻¹)	Specific energy (Wh kg ⁻¹)	Nominal voltage (V)
Pulse thermal (Li–Si/FeS ₂)	8000	3	1.95
Long-life thermal (Li–Si/FeS ₂)	18	22	1.95
Li/SO ₂	100	220	2.95
Li/SOCl ₂	145	500	3.60
Ni/Cd	175	55	1.25
Pb/acid	90	30	2.15
Zn/AgO	400	300	1.60

5.2. Ca or Mg/V₂O₅

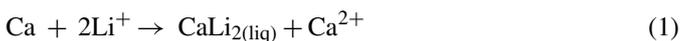
The Ca/V₂O₅ and Mg/V₂O₅ were also used in early thermal batteries in the 1950s [7]. The high solubility of V₂O₅ – more than 17 w/o – complicated its use, as it can lead to chloride oxidation in the melt. As for the WO₃ system, almost nothing has been published concerning the electrochemistry of V₂O₅ in thermal batteries.

5.3. Ca/CaCrO₄

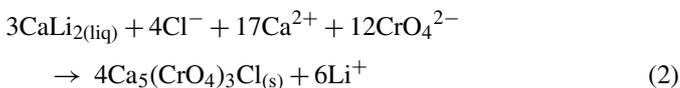
From the early 1960s until into the 1970s, the Ca/CaCrO₄ couple, with an emf of over 3 V, was the primary technology for thermal batteries. The CaCrO₄ replaced K₂CrO₄ that had been used earlier. However, there is a delicate balance that must be maintained between the chemical reactions and electrochemistry during discharge for the battery to function properly. The discharge reactions are quite complex and involve many intermediates that are critical for battery operation.

5.3.1. Anode reactions

There is no separator present in the Ca/CaCrO₄ battery as it is constructed. Thus, the Ca anode is in direct physical contact with the CaCrO₄ cathode material that is 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. First, the Ca reacts with the Li⁺ to form a liquid alloy in a displacement reaction, as shown in Eq. (1). (Uncontrolled, this can lead to intercell shorting.)



The CaLi₂ then immediately reacts with the dissolved chromate to form a dark green Cr(V) compound [8], as shown in Eq. (2).



The Ca₅(CrO₄)₃Cl can react further in the presence of excess Ca²⁺ under certain temperature conditions, as shown in Eq. (3), to form a second Cr(V) compound, Ca₂CrO₄Cl that is purple in color.



The discharge is complicated by a competing double-salt reaction between the CaCl₂ and the KCl to form solid KCaCl₃. These Cr(V) compounds constitute the separator layer (reaction barrier) in the battery to minimize self-discharge. The unreacted CaLi₂ material continues to function as an anode with ionic transference across the separator during electrochemical discharge.

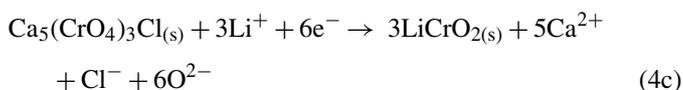
The CaLi₂ discharges through several stages: CaLi₂ → CaLi → Ca. The Ca then reacts with the bulk Li⁺ again Eq. (1) to regenerate the CaLi₂ alloy anode.

5.3.2. Cathode reactions

The chemical reactions that occur at the cathode upon battery activation involve CaCrO₄ dissolved in the molten

LiCl–KCl and the iron current collector to form an Fe-rich lithium–chromium ferrite [Li_{0.5}(Fe_{2.5-x}Cr_x)O₄] and a Cr-rich lithium-iron chromite [Li(Cr_{1-y}Fe_y)O₂] [9]. 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 that these materials provide.

The electrochemical discharge sequence that occurs at the cathode involves the generation of the same Ca₅(CrO₄)₃Cl compound that is formed chemically at the anode, through a Cr(V)-chromate intermediate Eq. (2) [10]. This material then becomes the active cathode. The discharge process involves a one-electron reduction first, followed then by a two-electron transfer [11]:



The discharge products form dendrites that extend well into the electrolyte. Since these materials are electronically conductive, the Cr(VI) in the adjacent vicinity is gradually depleted, causing the electrolyte color to change from canary yellow to white. During extended discharge times, these conductive dendrites can result in cell shorting.

5.3.3. Problem areas

The performance of the Ca/CaCrO₄ electrochemical system tended to be somewhat unpredictable, with changes in performance attributed to changes in lots of Ca or CaCrO₄ catholyte. Detailed study of the chemical and physical properties of various sheet-Ca materials, for example, showed some correlation in performance only with the bulk nitrogen content [12].

Battery performance was also influenced by the source of CaCrO₄ as well as the methods used for processing of the various catholyte mixes made with it [13]. The heat treatment of the CaCrO₄ influenced performance, as it affected its average particle size. This, in turn, influenced its rate of dissolution in the molten LiCl–KCl electrolyte and, consequently, its electrochemical characteristics [14].

During discharge, the chemical reactions associated with the self-discharge reactions between the dissolved CaCrO₄ and the anode resulting in the generation of heat. This helped to keep the battery temperatures higher than they normally would have been. There had to be a delicate balance maintained between the chemical and electrochemical reactions for the battery to function as intended. In spite of the intrinsic problems with the Ca/CaCrO₄ batteries, they were able to be successfully engineered for a wide variety of weapons applications in a range of sizes for many years. A good example of this is the small so-called “mailbox” battery developed at Sandia. This battery contained two 500 V parallel stacks in a very small volume, as shown in Fig. 3. This was quite a technical achievement and involved a good deal of engineering and assembly skills. Thou-

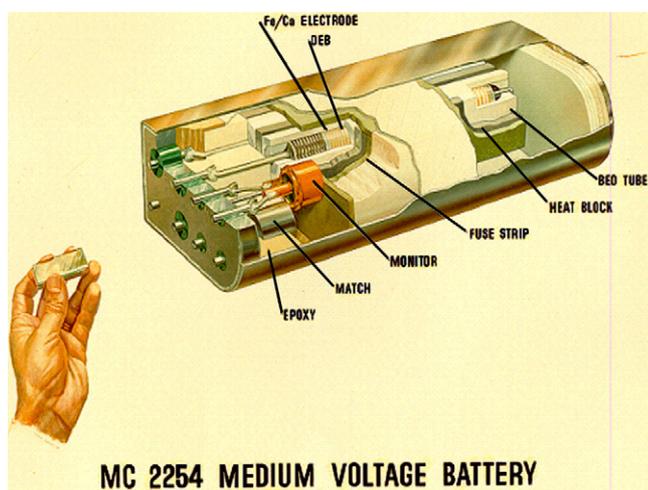


Fig. 3. An older, small Ca/CaCrO₄ thermal battery with two 500 V parallel stacks.

sands of these units were built and used successfully in a number of weapons.

5.4. Li or Li-alloy/FeS₂

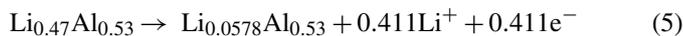
The intrinsic difficulties of engineering a thermal battery based on the Ca/CaCrO₄ electrochemistry was obviated with the introduction of Li and Li-alloy/FeS₂ couples. These were “clean” systems with well-characterized and very predictable and reproducible reactions, in contrast to the Ca/CaCrO₄ system. The FeS₂ was readily obtained from processing pyrite, which is a plentiful and inexpensive materials compared to chemically synthesized CaCrO₄. It was also “greener”, in that it did not involve Cr(VI), a known carcinogen. Pyrite is a good semiconductor – both n and p types being reported – with electrical conductivities at room temperature ranging from 0.03 to 333 S cm⁻¹ [15]. It has an energy band gap at room temperature of about 0.92 eV [16,17]. This makes it perfect for use in thermal batteries, as it has a higher electrical conductivity at elevated temperatures. This gives rise to improved power and lifetimes over the Ca/CaCrO₄ system.

In spite of all of these benefits, there were several disadvantages inherent to the FeS₂-based system. First, a true separator pellet was required, rather than the one formed chemically *in situ* as in the Ca/CaCrO₄ system. This was necessary to prevent direct reaction of the anode with the cathode. Consequently, more piece parts were now needed for the battery. Second, the open-circuit voltage of the Li/FeS₂ couple is lower than that of the Ca/CaCrO₄ couple—a nominal 2 V versus 3 V. As a result, more cells were required for a given battery voltage and these cells had to be thinner than those for Ca/CaCrO₄ batteries for the stack to fit into the same battery volume (height).

5.4.1. Anode reactions

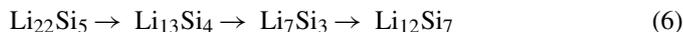
The most common alloys used as anodes are and Li–Al alloys. The discharge sequence for the Li–Al anode involves the solid-solution and LiAl which contains 20 w/o Li. Thus, only a single anode transition is possible: LiAl (β-Al) to Al (α-Al). The dis-

charge reaction for nonstoichiometric LiAl is shown in Eq. (5):



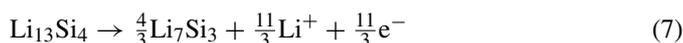
This corresponds to a capacity of 2259 A s g⁻¹.

The discharge stages for alloy anodes are shown in Eq. (6) [18]:



The preference is to use the Li₁₃Si₄ → Li₇Si₃ transition (44 w/o Li) for most applications, as this is the highest Li content that can readily be handled with minimum oxidation under dry-room conditions (<3% RH). This alloy has a potential about 157 mV more positive than pure Li at 415 °C.

The discharge reaction for the Li₁₃Si₄ → Li₇Si₃ transition is shown in Eq. (7); this corresponds to a capacity of 1747 A s g⁻¹ of alloy.

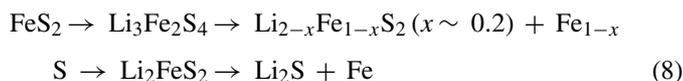


This is lower than the capacity of the Li–Al anode material Eq. (5). However, the alloy has the capability of multiple transitions and can generally deliver power at a higher rate. In addition, the emf of the 44 w/o alloy is about 140 mV more negative than that of LiAl (297 mV versus Li) under comparable discharge conditions.

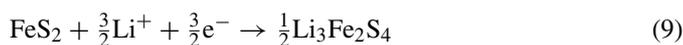
Pure-Li anodes have also been used in thermal batteries but only when properly immobilized with iron powder (typically 80 w/o) as a binder [19]. This type of anode (“LAN”) was developed by Catalyst Research Corp., and was successfully used in a variety of batteries [20].

5.4.2. Cathode reactions

The discharge reactions that occur when a FeS₂ cathode is used in high-temperature batteries have been extensively studied by Argonne National Laboratory (ANL) for rechargeable applications [21]. The phases that form during the discharge of FeS₂ in molten LiCl–KCl are shown in Eq. (8):



Li–Si/FeS₂ thermal batteries are designed to use only the first cathode transition because of rigid voltage requirements associated with the use of such batteries:



This transition is equivalent to 1206 A s g⁻¹ of FeS₂. The species actually undergoing reduction in Eq. (8) is the polysulfide, S₂²⁻, i.e., the oxidation state of Fe in FeS₂ is 2+ and not 4+ [22,23]. This is illustrated in Eq. (10):

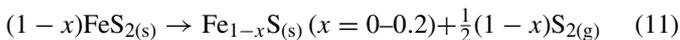


5.4.3. Problem areas

While the pyrite cathode does not have all of the technical problems associated with the CaCrO₄ cathode, it still has some slight problems of its own. These include: only moderate ther-

mal stability, a voltage transient upon battery activation, and significant solubility in molten salts.

FeS₂ begins to thermally decompose at temperatures above 550 °C to form a nonstoichiometric monosulfide (pyrrhotite) and sulfur vapor, as shown in Eq. (11):



Any fugitive sulfur can react very exothermically with the Li-alloy anodes in the battery. This reduces the battery capacity as well as generating more heat. This, in turn, leads to even more thermal decomposition of FeS₂, which can destroy the battery if thermal runaway occurs.

A large voltage transient (“spike”) occurs upon activation of a thermal battery if the FeS₂ contains impurities such as oxides, sulfates, and elemental sulfur or if the activity of Li is not fixed in the cathode. This interferes with maintaining strict voltage control. This is readily remedied by lithiation, however [24,25]. Common lithiation agents are Li₂O or Li₂S, added in small quantities of 1–2 w/o. The chemistry of the Li-alloy/FeS₂ system is well understood, which is in marked contrast to the Ca/CaCrO₄ system [26]. This allows good science to be brought to bear on production, materials, and performance issues. This contrasts with the Ca/CaCrO₄ system, where similar solution efforts tended to be empirical in nature because the chemistry was so poorly defined and understood.

While FeS₂ has a finite solubility in molten salts, it is not nearly as great as for CaCrO₄. This only becomes an issue if the battery sits on open circuit for a prolonged time or if the battery is discharged under a very light load (e.g., <20 mA cm⁻²). The solution species arising from FeS₂ dissolution can diffuse into the separator and react with anodic species (that originate from some dissolution of the anode) to form elemental Fe and Li₂S [27,28]. This can cause a loss in capacity of the battery.

5.5. Li or Li-alloy/CoS₂

Papadakis et al. developed a Li–Al/CoS₂ rechargeable battery for military applications using the LiCl–LiBr–LiF electrolyte because of the inherent limitations with the FeS₂ cathode [29–31]. CoS₂ has a lower solubility in molten electrolytes and a much higher electronic conductivity, which permits a higher rate of discharge. Most importantly, it has a much higher thermal stability, starting to decompose only above 650 °C, which is ~100 °C higher than for FeS₂.

There was a need in the 1990s at Sandia for a thermal battery to last for 2 h or more. However, because of its limited high-temperature stability, lifetimes of only slightly more than 1 h were the longest that could be realized with Li–Si/FeS₂ thermal batteries [32,33]. The Li–Si/CoS₂ couple was much better suited for this application. The only disadvantages of CoS₂ relative to FeS₂ are its higher cost – it must be synthesized in the laboratory – and its lower emf (by 100 mV per cell).

The superiority of the CoS₂ to FeS₂ was demonstrated using a number of electrolytes in single-cell and battery screening tests [34]. The performance of the two cathodes is compared in Fig. 4 at 500 °C and 125 mA cm⁻² using the LiCl–KCl eutectic electrolyte. (The cells were pulsed to 250 mA cm⁻² for 5 s

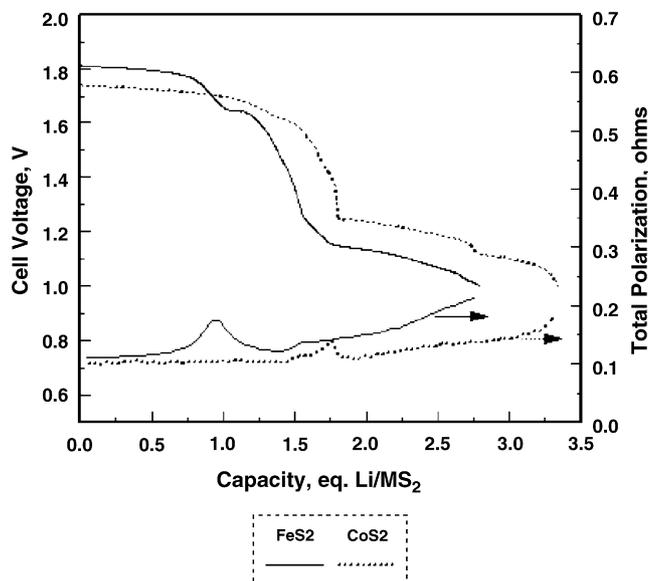


Fig. 4. Comparison of discharge of Li–Si/MS₂ couples in LiCl–KCl eutectic electrolyte in single cells at 500 °C and 125 mA cm⁻².

every minute to obtain polarization information.) The potential of the Li–Si/FeS₂ cell was initially higher at the start of discharge, but dropped below that of the Li–Si/CoS₂ cell after about 1 equivalents Li/mol of sulfide has been extracted. There were two major voltage transitions noted for the FeS₂ cathode during discharge, at ~0.8 and 1.5 equivalents Li/mol FeS₂. The CoS₂ cathode exhibited three voltage transitions over the same depth of discharge. Overall, more capacity was extracted from CoS₂ than from FeS₂ to a 1 V cutoff.

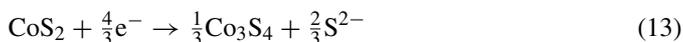
The total polarization (impedance) of the Li–Si/CoS₂ cell was lower than that for the Li–Si/FeS₂ cell and was more consistent throughout discharge. There were peaks in the polarization for the FeS₂ cathode associated with the observed voltage transitions. These polarization peaks are due to changes in the resistance of the cathode phases that form during discharge. The resistivity of the first discharge phase, Li₂Fe₂S₄, is much higher than that for FeS₂ [35]. Only a single peak in the polarization was evident for the CoS₂ cathode (at the second voltage transition).

5.5.1. Cathode reactions

The discharge sequence for CoS₂ is completely different from that for FeS₂ Eq. (8), in that lithiated materials are not formed:



The first discharge step is shown in Eq. (13):



There are thus 1.33 equivalents of Li per mole of CoS₂ during the first discharge step, compared to 1.50 for FeS₂. The capacity for this reaction is 1045 A s g⁻¹, which is lower than the first-stage discharge for FeS₂ Eq. (9).¹

¹ It should be noted that while there some self-discharge associated with the use of CoS₂ due to solubilization of it or its discharge products in the molten salt, it is not nearly as great as for the case of FeS₂.

The initial favorable results obtained with CoS_2 using the LiCl-KCl eutectic were extended to similar single-cell tests with the lower-melting LiBr-KBr-LiF and LiBr-KBr-LiCl eutectics that melt at 324.5 and 321 °C, respectively. These electrolytes have a greater Li^+ content and a higher ionic conductivity relative to LiCl-KCl and are better suited for a long-life battery because of the larger liquidus region that is possible. This results in a longer upper-voltage discharge plateau. Similar trends in relative performance were found with these electrolytes, confirming the results obtained with the LiCl-KCl eutectic electrolyte. Based on the favorable results of single-cell tests, follow-on battery tests were conducted, with the ultimate result that a 2 h, Li-Si/CoS_2 thermal battery was successfully tested [36].

The Li-Si/CoS_2 technology is much more expensive than that based on Li-Si/FeS_2 , but there are certain difficult battery designs that cannot be built or requirements that cannot be met with the standard FeS_2 chemistry. Under those conditions, CoS_2 may be the only reliable choice for successful battery operation.

6. Technology improvements

There are a number of areas in which extensive research has been done, and continues to be conducted, to improve the performance of thermal batteries. Improved thermal insulations such as aerogels [37] and vacuum multifoils [38] have received some attention for use in long-life thermal batteries. Areas dealing with strictly electrochemistry include the development of improved electrolytes and the use of higher voltage cathodes. These needs have arisen because of anticipated new uses for thermal batteries (e.g., borehole power supplies). These will be the subjects of future articles.

7. Summary and conclusions

This paper provides an overview of the history of thermally activated batteries, invented during WW II by German scientists. The various uses and characteristics of such electrochemical devices are described along with the various chemistries that have been examined over the years. A detailed description of the mechanisms of discharge of the earlier Ca/CaCrO_4 thermal batteries is provided along with those associated with the current Li-alloy/FeS_2 and Li-alloy/CoS_2 chemistries. The use of CoS_2 is preferred over FeS_2 for high-power and high-rate application because of the higher electrical conductivity and greater thermal stability of CoS_2 .

Acknowledgments

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