

Review

Thermal activated (“thermal”) battery technology Part IIIb. Sulfur and oxide-based cathode materials[☆]

Patrick J. Masset^{a,*}, Ronald A. Guidotti^b

^a *Karl Winnacker Institut der Dechema e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany*

^b *Sierra Nevada Consulting, 1536 W. High Pointe Ct., Minden, NV 89423, USA*

Received 13 July 2007; received in revised form 1 November 2007; accepted 25 November 2007

Available online 1 February 2008

Abstract

This article presents an overview of cathode materials (except the pyrite FeS_2) used or envisaged in thermally activated (“thermal”) batteries. The physicochemical properties and electrochemical performance of different cathode families (oxides, sulfides) are reviewed, including discharge mechanisms, when known.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Thermal batteries; Molten salts; Cathode materials; CoS_2 ; NiS_2 ; CaCrO_4

Contents

1. Introduction	457
2. CoS_2	457
2.1. Basic properties	457
2.2. Electrochemical behavior	458
2.2.1. Discharge mechanism	458
2.2.2. Self-discharge	459
2.3. Comparison to FeS_2	459
3. Other sulfides	459
3.1. FeS	459
3.2. Nickel sulfides (NiS_2 and NiS)	460
3.3. Mixed sulfides	460
3.4. Other transition-metal sulfides	460
4. Transition-metal halides	461
5. Oxides	462
5.1. Chromates	462
5.1.1. Basic properties	462
5.1.2. Discharge mechanism	462
5.1.3. Earlier oxides	463
5.2. Other transition-metal oxides	463
5.2.1. Manganese oxides	463
5.2.2. Ag_2CrO_4	463
5.2.3. CrO_2	463
5.2.4. Chromium(V) oxides	463

[☆] Many Sandia reports are available at: <http://www.osti.gov/bridge>.

* Corresponding author. Tel.: +49 697 564 362; fax: +49 697 564 388.

E-mail address: masset@dechema.de (P.J. Masset).

5.2.5. Mixed transition-metal oxides	464
6. Conclusions	464
References	465

1. Introduction

Thermally activated (“thermal”) batteries are mainly used for military purposes that require a high level of reliability and whose performance is not compromised after lengthy storage times. Applications and the electrochemistry of such power sources were described in detail in the first part of this review dedicated to thermal batteries [1]. The properties of molten salts (high- and low-temperature electrolytes) were thoroughly reviewed in the second part of this review [2]. The third part of this review of thermal batteries is devoted to the cathode materials. It was shared into two parts the first one deals with the pyrite FeS_2 exclusively [3] whereas others systems are detailed in this document. Thermal batteries are complex chemical systems that include electrochemical, chemical and physical properties that should be well mastered to understand the global functioning of these systems. To reach the high level of confidence required by such electrical generators, the physicochemical properties of the cathode materials must be well assessed and understood. The main physicochemical properties required for the cathode materials to be used in thermal batteries are highlighted below:

- Redox potential: it should have a discharge potential compatible with the electrochemical window of the electrolyte in order to avoid its oxidation.
- Ability to provide a fixed discharge plateau: it should undergo multiphase discharge and not intercalation.
- High thermal stability: to minimize thermal decomposition and associated possible chemical reactions caused by the decomposition products (e.g., S_2 in the case of FeS_2 reacting with the anode or pyrotechnic source in the battery). These products can also results in increased self-discharge.
- Electronically conductive: to minimize the resistance of the cathode.
- Low solubility of the cathode materials in the molten electrolyte: to minimize self-discharge reactions with attendant loss in capacity.
- Low solubility of discharge products in the molten electrolyte: to minimize possible self-discharge reactions.
- Stable towards moisture and/or oxygen: to prevent the production of oxides at the cathode surface. (This gives rise to a voltage peak at the beginning of discharge).
- Ability to be wetted by electrolyte: to minimize the contact resistance at the electrolyte (separator)/electrode interface.
- Low equivalent weigh: for higher C mol^{-1} .
- Good discharge kinetics (high exchange-current density): for high rate capability.
- Reasonable costs.
- Being environmentally friendly (“green”) is an additional desirable attribute.

Beginning of the 1950s, the first thermal cells tested consisted in $\text{Mg(C)}/\text{LiCl-KCl}/\text{FeO}_x$, Ni electrochemical cell using iron oxide as cathode electrode [4,5]. Selis and McGinnis [6–8] have discussed the behavior of a soluble oxidant (potassium chromate) in the thermal cell system $\text{Mg}/\text{LiCl-KCl-K}_2\text{CrO}_4/\text{Ni}$. These systems were the premise of the future chromate-based systems but were not more detailed.

In this paper, the properties and performances of sulfide (other than FeS_2) and oxide cathode materials are reviewed. Their properties are analyzed with regard to their use as cathode material in thermal batteries. The most important properties for thermal-battery applications are highlighted.

2. CoS_2

2.1. Basic properties

Papadakis et al. developed a $\text{Li-Al}/\text{CoS}_2$ rechargeable battery for military applications using the LiCl-LiBr-LiF electrolyte because of the inherent limitations with the FeS_2 cathode [9–11]. However, the pioneering work in the study of the electrochemistry of the disulfides of Fe, Ni, and Co was done at Argonne National Laboratory (ANL) in the late 1970s and early 1980s [12]. CoS_2 can be synthesized by an aqueous route from sulfate precursors by reaction with alkaline polysulfides (e.g., Na_2S_2) and by reaction of similar precursors at high-temperature with H_2S [13,14].

CoS_2 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 $\sim 100^\circ\text{C}$ higher than for FeS_2 and allows long-term application. During the thermal decomposition of CoS_2 sulfur is released (see the Co–S phase diagram from [15] presented in Fig. 1) in the molten phase according to Eq. (1).



CoS_2 seems to be less sensitive to oxygen compared to FeS_2 by the formation of oxidized species on its surface and induces a potential peak at the beginning of the discharge process (see Co–S–O diagram stability presented in Fig. 2). Selected values of the thermodynamic properties of cobalt sulfides from Kubaschewski et al. [16] are reported in Tables 1–3.

Thermal batteries that last for 2 h or more were envisaged. However, because of its limited high-temperature stability, lifetimes of only slightly more than 1 h were the longest that could be realized with $\text{Li-Si}/\text{FeS}_2$ thermal batteries [17,18].

Table 1
Selected values of the thermodynamic properties of cobalt sulfides [16]

Compound	<i>T</i> (K)	ΔH_f° (kJ mol ^{−1})	S_f° (J K ^{−1} mol ^{−1})	C_p (<i>T</i>) (J K ^{−1} mol ^{−1})
CoS _{0.89}	298	−94.6	51.5	40.25 + 15.52 × 10 ^{−3} <i>T</i> (K)
Co ₃ S ₄	298	−359.0	184.1	143.3 + 76.57 × 10 ^{−3} <i>T</i> (K)
CoS ₂	298	−152.1	69.0	60.67 + 25.31 × 10 ^{−3} <i>T</i> (K)

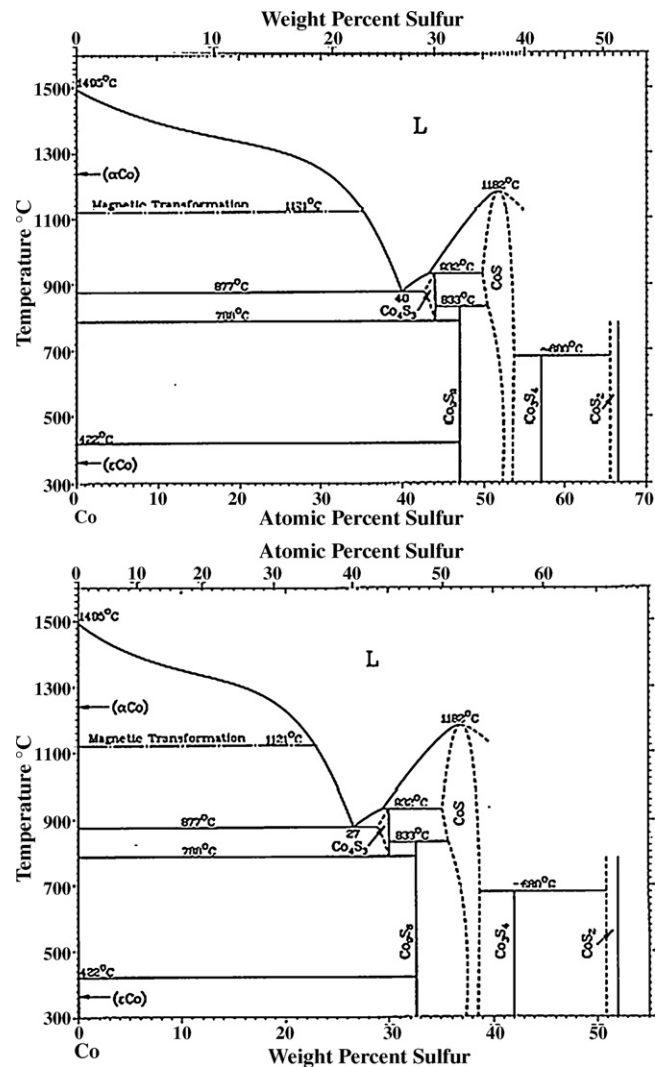


Fig. 1. Co–S phase diagram (from [15]).

Table 2
Solubility of Li₂S in various molten salts [19]

Electrolyte composition (m/o)	Temperature (°C)	Li ₂ S solubility (ppm)
65 LiCl/35 KCl	400	1100
55 LiCl/45 KCl (eut.)	400	650
66 LiCl/34 KCl	500	1800
54 LiCl–46 KCl	500	840
22 LiF–31 LiCl–47 LiBr	466	6840
22 LiF–31 LiCl–47 LiBr	500	8700

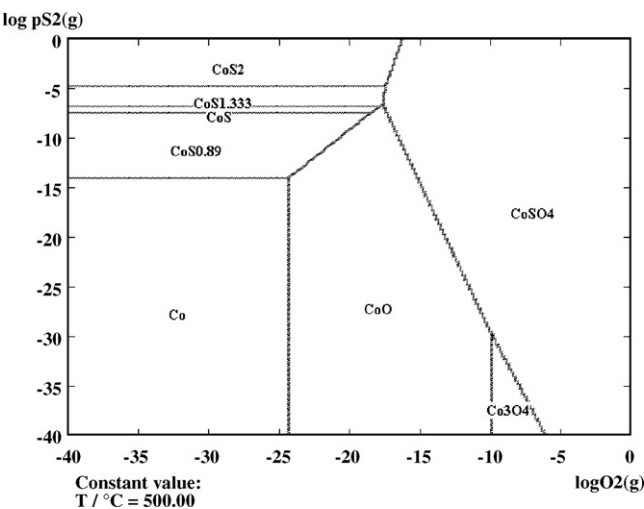
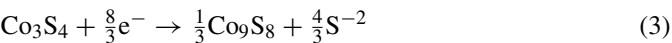
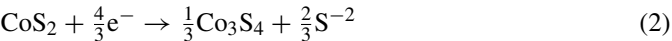


Fig. 2. Predominance diagram of the Co–S–O system at 500 °C.

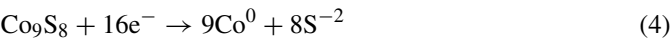
2.2. Electrochemical behavior

2.2.1. Discharge mechanism

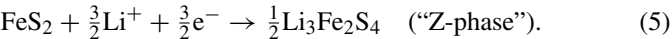
The discharge reaction for CoS₂ is differs from that for FeS₂, in that lithiated intermediates are not formed (Eqs. (2)–(4)).



and



There are 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 of 1206 A·s g^{−1} (Eq. (5)).



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.

Table 3
Expression of the solubilities of sulfur-containing species (Li₂S, FeS₂, FeS_{1.14}) versus the temperature in the LiCl–KCl eutectic

	ln X _{M_xS_y} (mol. fract.)	References
Li ₂ S	(11.077) − (6.1046) × 10 ³ <i>T</i> (K)	[20–25]
FeS ₂	(10.753) − (11.882) × 10 ³ <i>T</i> (K)	[26]
FeS _{1.14}	(6.4477) − (7.6622) × 10 ³ <i>T</i> (K)	[26]

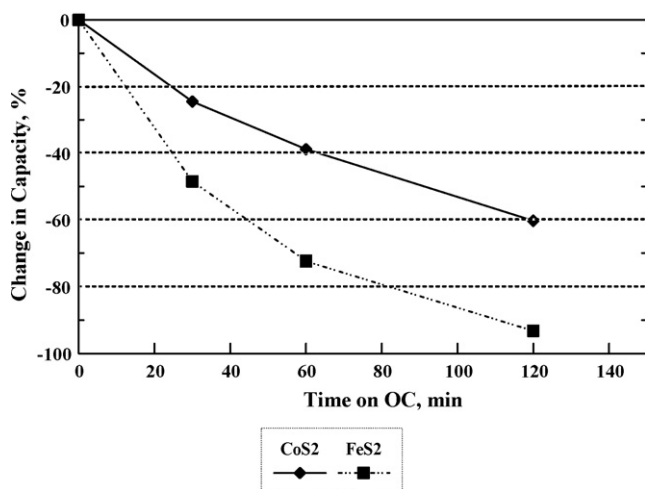


Fig. 3. Loss in capacity of Li-Si (25% electrolyte)/LiCl-LiBr-LiF/MS₂ cells as a function of time on open circuit prior to discharging at 550 °C and 125 mA cm⁻².

2.2.2. Self-discharge

While direct solubility measurements have not been reported for CoS₂ in molten salts, the loss in capacity upon standing on open circuit prior to discharge has been studied at Sandia National Laboratories (SNL). Fig. 3 compares the response of FeS₂ and CoS₂ cathodes in the all-Li LiCl-LiBr-LiF electrolyte at 550 °C during discharge at 125 mA cm⁻². This is the electrolyte in which the greatest self-discharge was observed for the FeS₂ cathode. The loss of capacity for the cell with the CoS₂ cathode was only half of that for the FeS₂ cell after 60 min on open circuit. This reduced self-discharge is important for this electrolyte, as one typically would pair CoS₂ with the all-Li electrolyte because of its very high ionic conductivity and the high electronic conductivity of CoS₂ to maximize the rate capabilities.

2.3. Comparison to FeS₂

The Li-Si/CoS₂ couple was much better suited for long-life thermal batteries than is Li-Si/FeS₂. The major disadvantages of CoS₂ relative to FeS₂ are its higher cost—it must be synthesized in the laboratory. Pyrite is available for several dollars per pound, while thermal-battery grade CoS₂ costs more than \$1.50 per gram. In addition, it has a lower emf (by 100 mV per cell) than FeS₂. However, while the initial potential of an FeS₂ cell may be higher than that for the corresponding CoS₂ cell, the higher impedance of the discharge phases in the former case begins to dominate the discharge process so that the emf of the CoS₂ cell will be higher later in discharge (e.g., after 1 equiv. Li per mole of sulfide) [1].

The superiority of the CoS₂ to FeS₂ was demonstrated using a number of electrolytes in single-cell and battery screening tests [27]. The performance of the two cathodes is compared in Fig. 4 at 400 °C and 125 mA cm⁻² using the LiBr-KBr-LiCl eutectic electrolyte (The cells were pulsed to 250 mA cm⁻² for 5 s every minute to obtain polarization information.) The potential of the Li-Si/FeS₂ cell was initially higher at the start of discharge, but

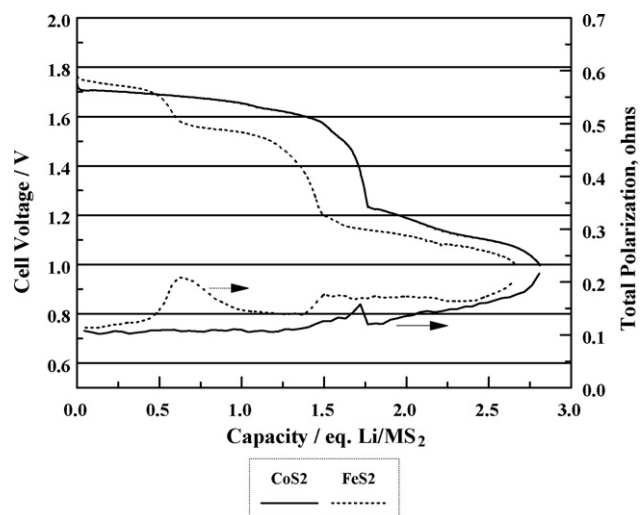


Fig. 4. Discharge at 400 °C and 125 mA cm⁻² of Li-Si (25% electrolyte)/FeS₂ and Li-Si/CoS₂ cells made with LiBr-KBr-LiCl eutectic electrolyte.

dropped below that of the Li-Si/CoS₂ cell after about 0.5 equiv. Li per mole of sulfide has been extracted. There were two major voltage transitions noted for the FeS₂ cathode during discharge, at ~0.5 and 1.5 equiv. Li per mole FeS₂. The CoS₂ cathode exhibited only one voltage transition near 1.75 equiv. Li per mole over the same depth of discharge. Overall, more capacity was extracted from CoS₂ than from FeS₂ to a 1 V cutoff. Note that there are two peaks in the total polarization for the FeS₂ cell at the voltage transitions and that they are greater in magnitude than that for the CoS₂ cell. This reflects the higher resistivity of the discharge phases for the Li-Fe-S system as noted above.

3. Other sulfides

3.1. FeS

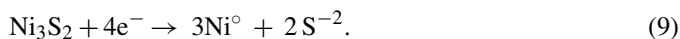
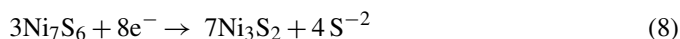
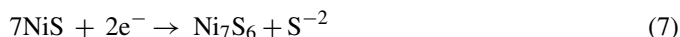
FeS was studied extensively by ANL for use in secondary high-temperature batteries for vehicle applications as part of the U.S. Advanced Battery Consortium (USABC) with the automobile industry [28–33]. The solubility product constant, K_{sp} , of FeS in LiCl-KCl eutectic electrolyte was calculated to be only 2.3×10^{-12} on an ion-fraction basis, which is very low [24]. Others have reported solubilities of FeS of from 7×10^{-10} to 2×10^{-9} mole fractions between 400 and 500 °C, respectively, for a Li₂S-saturated melt [26]. The electrical conductivity of porous FeS electrodes has been reported to be 7 S cm^{-1} [34]. During discharge some J-phase material forms along with elemental Fe. The J-phase is converted to the X-phase that, in turn, transforms to Fe and Li₂S. The J-phase formation can be repressed by using a Li-rich electrolyte. The decrease in the electrode resistance during discharge is due to the formation of Fe. However, this is countered by the formation of insulating Li₂S.

While FeS may have applicability for use in secondary batteries, it is of little interest for primary use, in spite of its extremely high thermal stability (mp = 1090 °C). Its greatest detriment is its lower emf relative to FeS₂. FeS forms the basis for the lower-voltage plateau during discharge of FeS₂ cathodes. This loss of ~0.5 V per cell is not acceptable.

3.2. Nickel sulfides (NiS₂ and NiS)

The thermal stability of NiS₂ is intermediate between that of FeS₂ and CoS₂, as is its emf in a cell. The thermogravimetric analysis (TGA) results are shown in Fig. 5 for sulfides synthesized in house at SNL by an aqueous process along with reference data for natural pyrite [35,36]. Like the other disulfides, the product of thermal decomposition is the monosulfide (stoichiometric NiS) and S₂ vapor.

In addition to studying FeS₂ and CoS₂, ANL also examined the electrochemistry of NiS₂ [12]. The discharge mechanism for this material is shown in Eqs. (6)–(9).



Much of the initial ANL work involved the monosulfide [37,38] but emphasis shifted later to NiS₂.

The electrochemical performance of NiS₂ in LiCl–KCl eutectic electrolyte is compared to that of synthetic FeS₂ and CoS₂ in Fig. 6. The FeS₂ catholyte was not lithiated, giving rise to the initial voltage spike at the start of discharge. As expected, the voltage response for the cell with the NiS₂ cathode was intermediate between that of the CoS₂ and FeS₂ cells. Overall, however, the performance of the NiS₂ cathode was similar to that of the CoS₂ counterpart. Since the costs of the NiS₂ precursor agents are much less than those for CoS₂, the similar electrochemical performance is incentive to seriously consider the use of NiS₂ for applications where CoS₂ might have been used. However, more data are needed at higher current densities and a wider temperature range to validate this assumption.

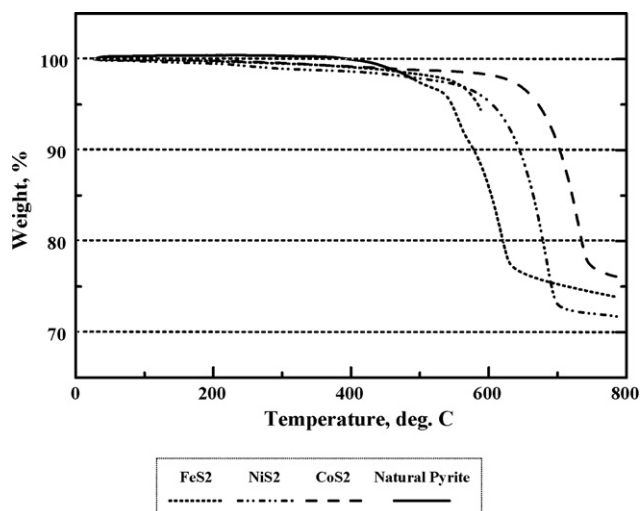


Fig. 5. TGA traces for synthetic FeS₂, CoS₂, and NiS₂ under argon (heating rate of 10 °C min⁻¹).

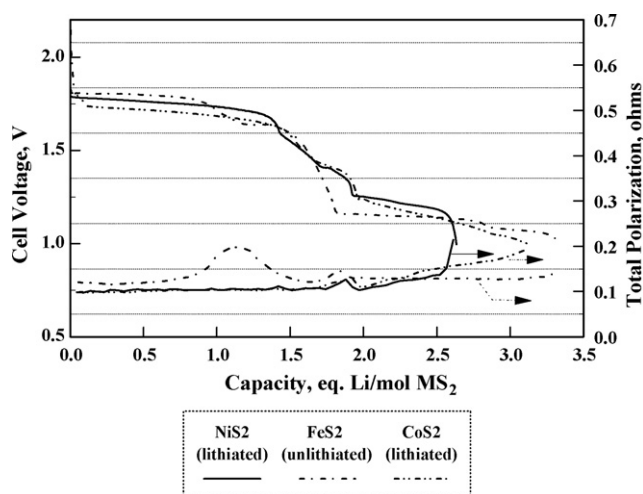


Fig. 6. Discharge of Li–Si (25% electrolyte)/MS₂ cells at 500 °C and 125 mA cm⁻² in LiBr–KBr–LiCl eutectic electrolyte. All catholytes made with synthetic disulfides (pyrite catholyte unlithiated).

3.3. Mixed sulfides

A number of mixed sulfides have been examined for possible use as thermal-battery cathodes. Dallek reported a higher voltage for the mixed sulfide Fe_{0.2}Co_{0.8}S₂ than for each of the end members of the series [39]. However, this appeared to be anomalous and could not be verified in related work at SNL [35]. There does not appear to be any reason to pursue this approach given that there are alternative transition-metal cathodes that show better promise.

3.4. Other transition-metal sulfides

There are a number of transition-metal sulfides that have the necessary properties to be considered candidates for use as thermal-battery cathodes. Some of these have already been used for ambient-temperature systems with nonaqueous electrolytes [40]. CuS, for example, has been used in pacemakers [41]. There were great plans at one time by Moli Energy to produce large quantities of Li/MoS₂ cells rechargeable cells [42,43]. However, the use of MoS₂ would not be feasible as a thermal-battery cathode, as it undergoes intercalation by Li, resulting in a declining voltage during discharge. A number of polysulfides of Ni and Co were evaluated by researchers at Duracell in the 1980s [44,45]. BaNiS₂ has been studied with a Li–Al anode in LiCl–KCl eutectic for high-rate applications [46]. It did not require the use of conductive additives and performed well at discharge rates of up to 1 A cm⁻² in a rechargeable mode. It has a somewhat lower emf than FeS₂ under the same discharge conditions.

Other materials, such as Sb₂S₃ and Bi₂S₃ have possibilities. However, the formation of low-melting Bi^o (mp = 271 °C) during discharge disqualifies Bi₂S₃. In the case of Sb₂S₃, this would not be an issue, since Sb^o melts at 630.5 °C. Preliminary tests at SNL showed this material to have only about half the capacity of FeS₂. In addition, it suffers from poor electronic conductivity [47].

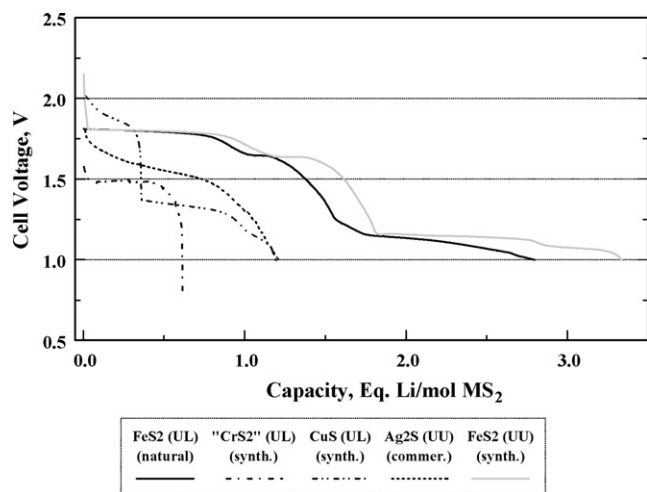


Fig. 7. Discharge of Li-Si (25% electrolyte)/MS_x cells in LiCl-KCl eutectic at 500 °C and 125 mA cm⁻². (UU: unfused, unlithiated catholyte; UL: unfused, lithiated).

There has been some previous work on the electrochemical study of CuS in LiCl-KCl eutectic [48]. This material does not have the high conductivity of FeS₂, however. A number of candidate materials have been tested in single cells at 500 °C and 125 mA cm⁻² at SNL using the LiCl-KCl eutectic electrolyte [47]. The voltage responses are shown in Fig. 7 and the corresponding total polarization (ohmic losses) are shown in Fig. 8. The "CrS₂", CuS, and FeS₂ were made by an aqueous route. (The X-ray diffraction pattern for "CrS₂" did not agree completely with the reference pattern).

The potential for the cells with the Ag₂S and "CrS₂" cathodes were less than those for the natural and synthetic FeS₂ and showed lower capacities than FeS₂. The ohmic losses for the Ag₂S cell were low, as one would expect, as Ag⁰ is formed during discharge. In contrast, the ohmic losses for the "CrS₂" cell were the highest of all of the cells (Fig. 8). While the potential for the CuS cell started higher than the FeS₂ cell, it quickly dropped off as the CuS → Cu₂S plateau transitioned into the lower-voltage Cu₂S → Cu⁰ plateau. (Similar results were

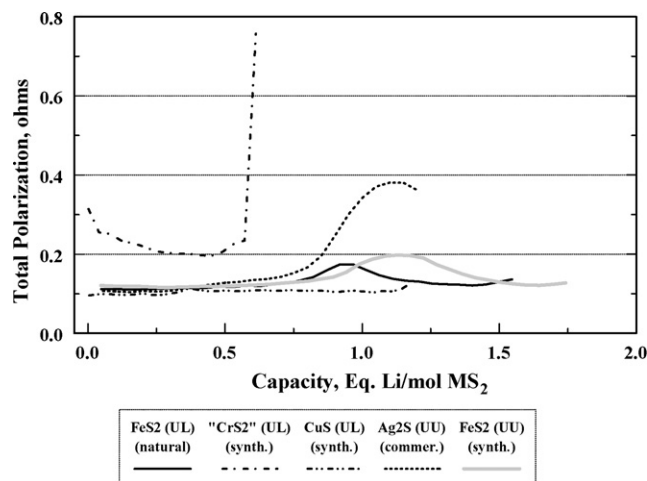


Fig. 8. Total polarization for the cells of Fig. 7.

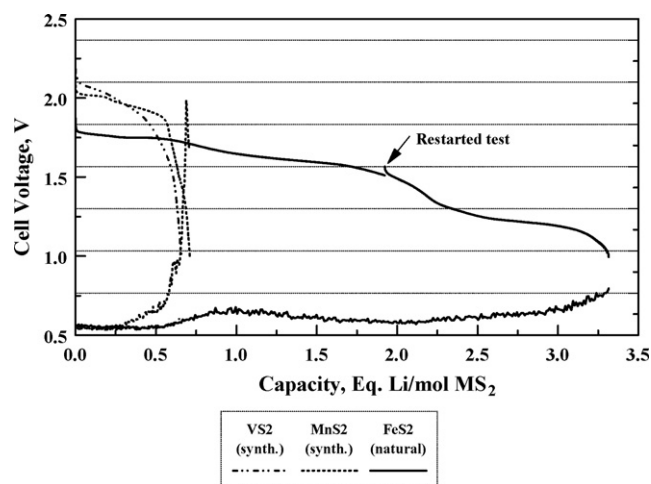


Fig. 9. Discharge of Li-Si (25% electrolyte)/MS₂ cells at 300 °C and 8 mA cm⁻² in CsBr-LiBr-KBr eutectic electrolyte.

obtained with chalcopyrite mineral, CuFeS₂.) The use of Cu compounds for cathodes in thermal batteries poses certain risks, as the elemental Cu can form dendrites that can grow through the separator, shorting the cell.

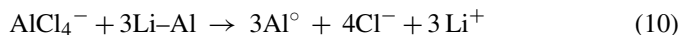
Additional chalcogenides were synthesized and tested at SNL but in a low-melting CsBr-LiBr-KBr eutectic electrolyte (mp = 238 °C). MnS₂ was synthesized by an aqueous route from MnSO₄ [49] and Na₂S₄, while VS₂ was made by heating VCl₂ with Na₂S₄ at 300 °C under Ar for 4 h. The electrochemical performance of these materials is shown in Fig. 9. The upper plateau voltages for the VS₂ and MnS₂ cathodes were considerable higher than that for FeS₂. However, the capacities were only about 1/4 as great, which translates into much lower specific energies and energy densities. Consequently, it is unlikely that these can be considered serious competitors to inexpensive, native pyrite as cathode materials for thermal batteries.

4. Transition-metal halides

A number of transition-metal halides have been examined for possible use as thermal-battery cathodes, such as NiCl₂ [50–53], FeCl₂ [54–56], and SbCl₃ [57] in conjunction with tetrachloroaluminate melts (e.g., NaAlCl₄). However, these studies involved the use of a liquid-Na anode and solid Na⁺ conductors, such as β''-Al₂O₃ rather than an immobilized molten salt as the separator.

A limited amount of work has been reported for the use of an immobilized NaAlCl₄ electrolyte with several transition-metal halides. Vaughn et al. used FeCl₃ in their cells, but tested them at temperatures where the electrolyte was solid [58]. Ryan et al. reported data for similar cells with CuCl₂, FeCl₂, and MoCl₅ cathodes and Li-Si and Li-Al anodes tested at 200 °C with the NaAlCl₄ electrolyte (mp = 152 °C) [59]. Erbacher reported similar data for the Li-Al/NaAlCl₄/CuCl₂ single cells [60]. However, what these researchers failed to realize is that molten NaAlCl₄ is not compatible with these high-activity, Li-alloy anodes under these tests conditions. The tetrachloraluminate

undergoes reduction, as shown in Eq. (10) for Li–Al.



Thus, the actual anode during these tests was mainly Al, which greatly reduces the cell emf to where it would not be practical for use in an actual thermal battery.

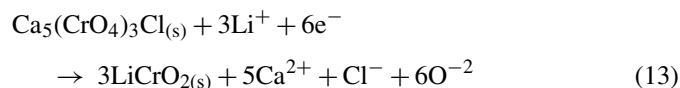
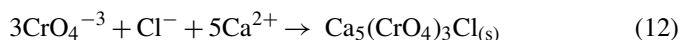
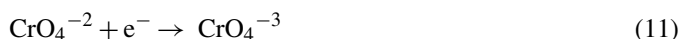
The use of transition-metal fluorides as thermal-battery cathodes has been reported by Briscoe et al. using fluoride-based electrolytes [61,62]. Cathodes of CuF_2 , AgF_2 , FeF_2 , CrF_3 , and FeF_3 were examined. The electrolytes chosen were a LiF–KF eutectic (mp = 492 °C) and the LiF–NaF–KF eutectic (mp = 454 °C). While open-circuit voltages over 3 V were obtained in many cases, discharge of the cells required much higher temperatures relative to the more-conventional thermal-battery electrolytes because of the much higher melting points of the fluoride electrolytes. The formation of LiF as a discharge product caused electrolyte solidification at the lower temperatures as the composition moved off eutectic. In addition, there were compatibility issues with the oxide binder in contact with the aggressive fluoride melts. These factors would very likely preclude the success use of such material in conventional thermal batteries.

5. Oxides

5.1. Chromates

5.1.1. Basic properties

The earlier, prominent thermal-battery technology was the Ca/CaCrO₄ system. The electrochemical discharge sequence that occurs at the CaCrO₄ cathode involves the generation of the same $\text{Ca}_5(\text{CrO}_4)_3\text{Cl}$ compound that is formed chemically at the anode, through a Cr(V)-chromate intermediate (see mechanism described by Eqs. (11)–(13)) [63]. This material then becomes the active cathode. The discharge process involves a one-electron reduction first, followed then by a two-electron transfer [64]:



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 [65]. 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 [66]. 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 [67].

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 is a delicate balance that must be 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.

Most transition-metal oxides generally do not have a high electronic conductivity, but in the case of the CaCrO₄ cathode, the actual functioning cathode is the electrolyte in which the CaCrO₄ is dissolved. The CaCrO₄ lowers the melting point of the LiCl–KCl eutectic to ~342 °C [68]. The conductivity of this solution is 0.596 S cm⁻¹ at ~390 °C, which is about half of that for pure LiCl–KCl eutectic [69]. The conductivity of the solid CaCrO₄, however, is quite poor. The battery becomes rate limited by how fast the solid CaCrO₄ can dissolve to replenish that consumed electrochemically during battery discharge. The rate capability of a Ca/CaCrO₄ thermal battery is only a fraction of a standard, modern Li-alloy/FeS₂ counterpart and its associated chemical reactions occurring during discharge and Cr(VI) carcinogenicity have made it obsolete.

5.1.2. Discharge mechanism

During discharge, the chromate undergoes a one-electron reduction to form a Cr(V) compounds as shown in Eq. (14).

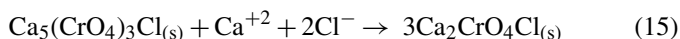


This reacts with Ca^{2+} and Cl^{-1} to form a dark-green-colored Cr(V) compound, as in Eq. (12):

This material is electronically conductive and undergoes a further reduction of the Cr(V) to Cr(III), as shown in Eq. (13).

These discharge products are dendritic in form and can extend well into the electrolyte from the current collector. The Cr(VI) in the immediate vicinity of this discharge product 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.

The initial discharge product of $\text{Ca}_5(\text{CrO}_4)_3\text{Cl}$ can react further in the presence of excess Ca^{+2} under certain temperature conditions, as shown in Eq. (15), to form a second Cr(V) compound, $\text{Ca}_2\text{CrO}_4\text{Cl}$ that is deep purple in color.



The discharge is complicated by a competing double-salt reaction between the CaCl_2 and the KCl present in the electrolyte to form solid KCaCl_3 .

These Cr(V) compounds constitute the separator layer (reaction barrier) in the battery to minimize self-discharge. These Cr(V) compounds form at the cathode electrochemically but similar reactions occur chemically at the Ca and CaLi₂ alloy upon battery activation. These materials constitute the separator

(barrier) for the battery – much as LiCl formation in Li/SOCl₂ cells – to minimize self-discharge. Without their formation, the very exothermic direct reaction of the anode with the dissolved cathode material would result in self-destruction of the battery. The complex chemistry and electrochemistry involved with the Ca/CaCrO₄ thermal battery made designing batteries with this technology very difficult, in that the chemical reactions need to be controlled to allow the battery to function properly. In spite of these challenges, thousands of such batteries were commercially produced over the years, until the 1970s, when the Li-alloy/FeS₂ technology was introduced.

5.1.3. Earlier oxides

The technology that preceded the CaCrO₄-based technology involved WO₃ and V₂O₅, which has similar issues with reactivity with the halide melts as well as poor conductivity.

5.2. Other transition-metal oxides

5.2.1. Manganese oxides

The possibility of using MnO₂ or other manganese oxides as cathodes for thermal batteries is appealing because they are seen as “green” in terms of environmental acceptability. However, the use of conductive additives is necessary with these materials. DSC screening tests with LiCl–KCl eutectic showed MnO₂ reacted exothermically upon electrolyte melting [70]. A slight reaction with the lower-melting CsBr–LiBr–KBr eutectic was noted between 350 and 450 °C. In contrast, LiMn₂O₄ was much more stable under the same conditions.

In single-cell tests with the CsBr–LiBr–KBr eutectic at 250 °C and 16 mA cm^{−2}, Li–Si/MnO₂ cells delivered longer life and had a much lower polarization compared to the Li–Si/LiMn₂O₄ cells under the same circumstances [71]. At 300 °C, however, both cathodes were comparable in capacity at this same discharge rate—almost 400 C g^{−1}. The Li–Si/LiMn₂O₄ cell exhibited a flat plateau voltage of 2.7 V under these conditions. The capacity was reduced to ~250 C g^{−1} when the current density was doubled for this couple. The performance of the MnO₂ cathode was somewhat better than that of the LiMn₂O₄ cathode under these conditions. A cathode based on MnO₂ still had a lower specific energy and energy density than a FeS₂ cathode because of the need to use graphite powder (20 w/o) as a conductive additive. While the manganese oxides exhibit higher potentials than FeS₂, the discharge capacities are lower. An initial 5-cell battery test with LiMn₂O₄ indicates some loss of capacity due to parasitic chemical reactions involving the electrolyte and cathode because of the high peak interfacial temperatures that result upon burning of the pyrotechnic heat source.

Unlike bromide-containing melts, both MnO₂ and LiMn₂O₄ are chemically compatible with molten nitrate electrolytes at temperatures well over 300 °C. The performance of the Li–Al/MnO₂ couple in LiNO₃–KNO₃ eutectic electrolytes has been reported [72]. Discharge rates near 8 mA cm^{−2} were possible at 150 °C and increased to over 30 mA cm^{−2} at 300 °C. Self-discharge became important above 300 °C due to breakdown of the protective passive film on the Li–Al anode.

More recently, MnO₂ and LiMn₂O₄ cathodes were examined by DSC for chemical compatibility with the low-melting tetramethylammonium imide (TMAIm) salt [73]. TMAIm is stable with LiMn₂O₄ to temperatures up to 300 °C. MnO₂, on the other hand is stable with TMAIm only up to 250 °C.

5.2.2. Ag₂CrO₄

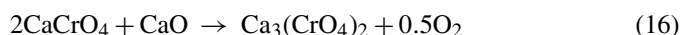
Ag₂CrO₄ was studied in the CsBr–LiBr–KBr eutectic in single cells using 10–20% graphite powder in the catholyte as a conductive additive [74]. The Li–Si/CsBr–LiBr–KBr/Ag₂CrO₄ system could sustain a current density of 32 mA cm^{−2} in single-cell tests at 300 °C. However, in follow-up battery tests, thermal runaway occurred that was traced to reaction of the bromide by the cathode material, thus making this cathode material incompatible with Br-based electrolytes. In a nitrate-based electrolyte, however, reasonable performance was observed [75]. Li–Al/Ag₂CrO₄ cells showed lower voltages during discharge relative to Li–Si/Ag₂CrO₄ cells because of the lower Li activity of the anode. These cells also showed greater polarization and reduced capacities relative to cells with Li–Si anodes. The best performance was observed at 200 °C at ~7 mA cm^{−2}, but with only about half of the capacity of the Li–Si cells under the same conditions. The cell discharge capacity dropped off rapidly above this temperature, much faster than that for cells with Li–Si anodes. The differences in performance of the two anodes may be related to differences in porosity, composition, and morphology of the passive oxide films that form in contact with the molten-nitrate electrolyte.

5.2.3. CrO₂

CrO₂ has been evaluated as a cathode in the CsBr–LiBr–KBr eutectic electrolyte as well [47]. It showed poor performance at 250 °C and 16 mA cm^{−2} relative to that for MnO₂ and LiMn₂O₄. The performance was improved at 300 °C but was still inferior to that for the manganese oxides.

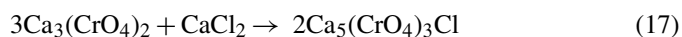
5.2.4. Chromium(V) oxides

5.2.4.1. Chemical syntheses. Since the separator material that forms upon activation of a Ca/CrO₄ thermal battery is the active cathode for the battery, it seemed logical to explore using it directly with a Li–Si anode and the LiCl–KCl eutectic electrolyte. This material can be easily chemically synthesized in a thermal process. The kinetics of the formation of a number of Cr(V) compounds were examined by thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) [76]. CaCrO₄ begins to lose oxygen and form the Cr(V) orthochromate when heated to over 850 °C in air in the presence of CaO according to Eq. (16):



Other sources of CaO such as Ca(OH)₂, or CaCO₃ can also be used. The reaction starts between 630 and 660 °C under argon.

The orthochromate reacts with CaCl₂ at temperatures above 450 °C to form the so-called “531” Cr(V) compound, Ca₅(CrO₄)₃Cl (Eq. (17)).



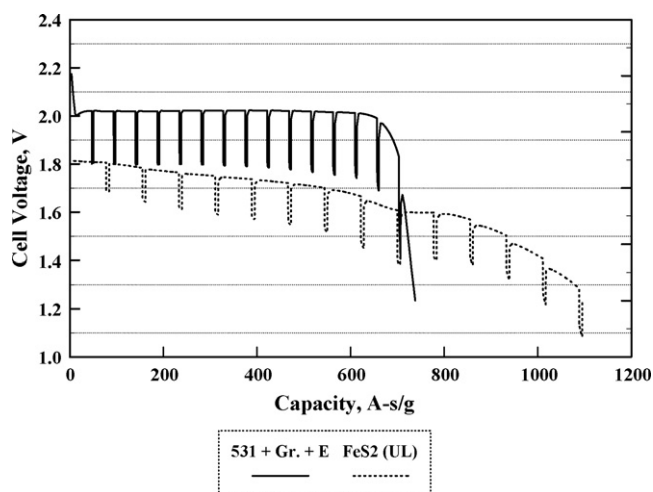
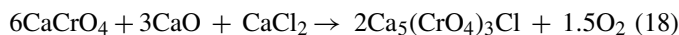
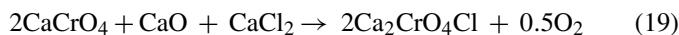


Fig. 10. Discharge of cells with $\text{Ca}_5(\text{CrO}_4)_3\text{Cl}$ and natural (lithiated) FeS_2 cathodes and flooded (25% electrolyte) Li–Si anodes at 500°C and 125 mA cm^{-2} .

The 531 phase can also be prepared by heating a mixture of CaCrO_4 , CaO , and CaCl_2 under argon temperatures of $750\text{--}800^\circ\text{C}$. The reactions proceed more quickly under dynamic vacuum, with rapid removal of byproduct oxygen (Eq. (18)).



The hydroxy analogue of the 531 phase, $\text{Ca}_5(\text{CrO}_4)_3\text{OH}$, is obtained in the presence of water vapor. In the presence of excess CaCl_2 , the so-called “211” phase is formed under similar conditions (Eq. (19)).



It can also be made by starting with the 511 phase (Eq. (15)).

The 531 and 211 Cr(V) phases are stable to more than 1000°C in air, while the orthochromate begins to lose oxygen at temperatures $>850^\circ\text{C}$ to form a lower Cr oxide, $\text{Ca}_5\text{Cr}_3\text{O}_{12}$. Given this high thermal stability and some intrinsic electronic conductivity, this makes the 531 and 211 phases prime candidates for potential use as cathodes in thermal batteries [77].

5.2.4.2. Electrochemical characterization. Catholytes were made with the 511 and 211 compounds with 10% graphite powder and 20% LiCl–KCl eutectic electrolyte. These were tested in single cells with Li–Si anodes at 500°C and 125 mA cm^{-2} as part of screening tests. (Catholytes were not made with the orthochromate, as it is not stable in LiCl–KCl melts under these conditions.) The results of one discharge are shown in Fig. 10 along with comparable data for the Li–Si/ FeS_2 (lithiated) couple. The potential of the Li–Si/511 couple was substantially greater than that for the Li–Si/ FeS_2 one but the overall impedance was higher, due to the lower electronic conductivity relative to FeS_2 . Still, to a 1.6-V cutoff, the capacity was comparable for the two cathodes. More work is needed over a wider range of temperatures and current densities with an optimized catholyte composition based on the 531 material. Battery tests are also needed for validation purposes. Only limited cathode testing has been done with the 211 compound and initial results indicate that it does not appear to perform as well as the 511 compound.

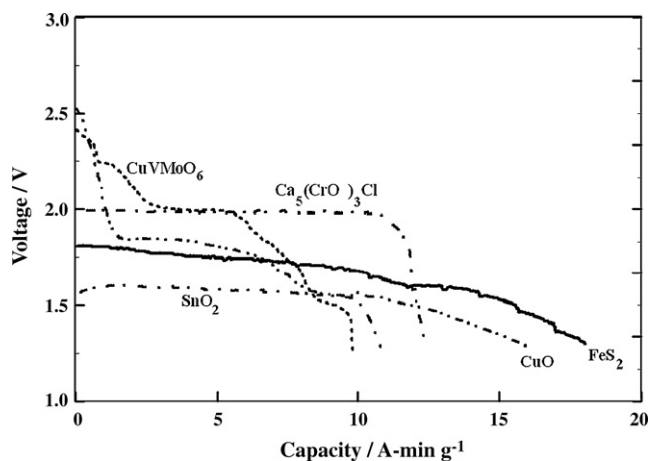


Fig. 11. Single-cell discharges of typical mixed transition-metal oxides at 500°C at 125 mA cm^{-2} in LiCl–KCl eutectic electrolyte with flooded (25% electrolyte) Li–Si anodes.

5.2.5. Mixed transition-metal oxides

A comprehensive screening study of almost 100 potential mixed transition-metal oxides that could have the necessary properties for use as cathodes in thermal batteries was conducted at SNL [78]. While some materials had higher potentials than FeS_2 , they also had reduced capacities. Representative discharge traces are shown in Fig. 11. Some materials had a higher initial voltage than FeS_2 , but then either dropped off quickly with depth of discharge – typical for intercalation reactions – or showed short voltage plateaus. While the voltage for the CuO cathode was fairly flat, it was lower than that for the FeS_2 cathode. In addition, the formation of Cu dendrites during discharge increases the possibility of cell shorting. None of the oxides performed as well as the 531 Cr(V) compound. For almost all of the oxides, the need for incorporation of a conductive additive (e.g., graphite) reduces the ultimate energy density and specific energy that can be realized.

6. Conclusions

In this paper, we have presented an overview of the various types of materials that have been used or evaluated for use as thermal-battery cathodes (except FeS_2). Typically, these are thermally stable at the battery operation temperatures (up to 600°C) and are mainly sulfides and, to lesser extent, oxides. The primary sulfides in use today in thermal batteries are FeS_2 (described in the first part) and synthetic CoS_2 (for high-rate applications). The physical and chemical properties and the discharge sequences and reaction mechanisms, including self-discharge processes, are described in detail for these materials. Similar information, where available, is presented for other transition-metal sulfides.

Many candidate transition-metal oxides, while thermally stable, suffer from low electronic conductivity, necessitating the use of conductive additives, such as graphite, for them to function adequately as thermal-battery cathodes. Ones that form low-melting metals as discharge products are not suitable as that can

cause cell shorting. Similarly, Cu-based materials tend to form Cu⁰ dendrites that can also cause cell shorting.

A detailed discussion of the older Ca/CaCrO₄ technology is presented describing the complex interaction between electrochemical and competing chemical processes that occur during discharge. The Cr(V) intermediates that form are found to be suitable for cathodes by themselves. The cell voltages are higher than that for FeS₂ but the overall cell impedances are somewhat higher due to lower electronic conductivities. Ca₅(CrO₄)₃Cl (the “531” compound) has a slightly lower gravimetric capacity (A-s g⁻¹) and a similar energy density to FeS₂. The volumetric capacities (A-s cm⁻³) for the two catholytes are very similar, which makes this material promising for select applications. More single-cell tests over a wide range of temperatures and current densities are merited along with battery validation tests.

References

- [1] R.A. Guidotti, P. Masset, J. Power Sources 161 (2) (2006) 1443.
- [2] P. Masset, R.A. Guidotti, J. Power Sources 164 (1) (2006) 397.
- [3] P.J. Masset, R.A. Guidotti, J. Power Sources (2007), doi:10.1016/j.jpowsour.2007.11.017, in press.
- [4] R.B. Goodrich, R.C. Evans, J. Electrochem. Soc. 99 (8) (1952) 207C.
- [5] H. Goldsmith, J.T. Smith, J. Electrochem. Soc. 6 (1/2) (1968) 16.
- [6] S.M. Selis, L.P. McGinnis, J. Electrochem. Soc. 106 (1959) 900.
- [7] S.M. Selis, L.P. McGinnis, J. Electrochem. Soc. 108 (1961) 191.
- [8] S.M. Selis, L.P. McGinnis, E.S. McKee, J.T. Smith, J. Power Sources 110 (6) (1963) 489, 108.
- [9] N. Papadakis, Proceedings of the 35th International Symposium on Power Sources, 1992, p. 285.
- [10] H.N. Sieger, Proceedings of the 34th International Symposium on Power Sources, 1990, p. 334.
- [11] N. Papadakis, Proceedings of the 34th International Symposium on Power Sources, 1990, p. 339.
- [12] S.K. Preto, Z. Tomczuk, S. von Winbush, M.F. Roche, J. Electrochem. Soc. 180 (2) (1983) 264.
- [13] R.A. Guidotti, P.J. Nigrey, F.W. Reinhardt, J.G. Odinek, Proceedings of the 41st Power Sources Conference, 2004, p. 149.
- [14] R.A. Guidotti, F.W. Reinhardt, J. Dai, D.E. Reisner, Materials for energy storage, generation, and transportation, in: R. Schwarz (Ed.), Proceeding of the Materials Research Society, vol. 730, 2002, p. 207.
- [15] H. Rau, J. Phys. Chem. Solids 37 (1976) 931.
- [16] O. Kubaschewski, C.B. Alcock, P.J. Spencer, Materials Thermochemistry, 6th ed., Pergamon Press, 1997.
- [17] P.G. Neiswander, A.R. Baldwin, Sandia report SAND87-0143, October 1988.
- [18] A.R. Baldwin, Proceedings of the 27th International Symposium on Power Sources, 1976, p. 152.
- [19] Z. Tomczuk, D.R. Vissers, J.L. S Saboungi, Proceedings of the 4th International Symposium on Molten Salts, The Electrochemical Society, Pennington NJ, PV 84-2, 1984, p. 352.
- [20] C.H. Liu, A.J. Zielen, D.M. Gruen, J. Electrochem. Soc. 120 (1) (1973) 14.
- [21] J. Phillips, H.F. Gibbard, Proceedings of the Second Intern. Symposium on Molten Salts, The Electrochemical Society, Pennington NJ, PV, 81-10, p. 45.
- [22] D. Warin, Z. Tomczuk, D.R. Vissers, J. Electrochem. Soc. 130 (1) (1983) 64.
- [23] S. Sharma, J. Electrochem. Soc. 133 (5) (1986) 859.
- [24] M.L. Saboungi, J.J. Marr, M. Blander, J. Electrochem. Soc. 125 (10) (1978) 1567.
- [25] M.L. Saboungi, J.J. Marr, M. Blander, Met. Trans. 10B (1979) 477.
- [26] R.A. Sharma, R.N. Seefurth, J. Electrochem. Soc. 131 (5) (1984) 1084.
- [27] R.A. Guidotti, F.W. Reinhardt, Proceedings of the 9th International Symposium on Molten Salts, 1994, p. 820.
- [28] L. Redey, Proceedings of the 35th Meeting of the International Society of Electrochemistry, Berkeley, CA, August 5–10, 1984, Extended Abstract B7-7.
- [29] Z. Tomczuk, R.F. Roche, D.R. Vissers, J. Electrochem. Soc. 128 (10) (1981) 2255.
- [30] Z. Tomczuk, S.K. Preto, M.F. Roche, J. Electrochem. Soc. 128 (4) (1981) 760.
- [31] T.D. Kaun, W.E. Miller, L. Redey, J.D. Arntzen, in: H.V. Venkatesetty (Ed.), Proceedings of the Symposium on Lithium Batteries, The Electrochemical Society, Pennington NJ, PV, 81-4, 1981, p. 421.
- [32] D.R. Vissers, Z. Tomczuk, R.K. Steunenbergh, J. Electrochem. Soc. 121 (5) (1974) 665.
- [33] L. Redey, D.R. Vissers, J. Newman, S. Higuchi, in: H.C. Maru (Ed.), Proceedings of the Symposium on Porous Electrodes: Theory and Practice, The Electrochemical Society, PV 84-8, 1984, p. 322.
- [34] M. Hiroi, H. Shimotake, J. Electrochem. Soc. 130 (1) (1983) 12.
- [35] R.A. Guidotti, P.J. Nigrey, F.W. Reinhardt, J.G. Odinek, Proceedings of the 40th Power Sources Conference, 2002, p. 250.
- [36] Proceedings of the 40th Power Sources Conference, p. 339.
- [37] L. Redey, D.R. Vissers, Proceedings of the 35th Meeting of the International Society of Electrochemistry, Berkeley CA, August 5–10, 1984, Extended Abstract A2-14.
- [38] L. Redey, D.R. Vissers, in: J. McBreen, R.S. Yeo, D.-T. Chin, A.C.C. Tseung (Eds.), Proceedings of the Symposium on Advances in Battery Materials and Processes, The Electrochemical Society, Pennington NJ, PV 84-4, 1984, p. 53.
- [39] S. Dallek, T.C. Murphy, T. Nguyen, Proceedings of the 36th Power Sources Conference, 1994, p. 329.
- [40] R.A. Guidotti, Metal sulfides for battery applications, in: Proceedings of the 92nd National Western Mining Conference and Exhibition, Denver, CO, February 8, 1989.
- [41] N. Margalit, in: J.-P. Gabano (Ed.), Lithium Batteries, Academic Press, New York, 1983, p. 137.
- [42] Moli Energy Ltd., Burnaby, B.C., Canada, private communication, 1988.
- [43] J.J. Murray, J.E. Alderson, J. Power Sources 26 (1989) 293.
- [44] W.L. Bowden, L.H. Barnette, D.L. DeMuth, J. Electrochem. Soc. 135 (1) (1988) 1.
- [45] W.L. Bowden, L.H. Barnette, D.L. DeMuth, J. Electrochem. Soc. 136 (6) (1989) 1614.
- [46] E.J. Plichta, W.K. Behl, J. Power Sources 37 (1992) 325.
- [47] R.A. Guidotti, unpublished data.
- [48] G. Eichinger, J. Power Sources 1 (1976/77) 237.
- [49] P.J. Nigrey, R.A. Guidotti, F.W. Reinhardt, Hydrothermal synthesis of manganese disulfide and its electrochemical behavior, in: Proceedings of the 200th Meeting of The Electrochemical Society, San Francisco, CA, September 2–7, 2001.
- [50] J. Prakash, L. Redey, D.R. Vissers, J. De Gruson, J. Appl. Electrochem. 30 (11) (2000) 1229.
- [51] J. Prakash, L. Redey, D.R. Vissers, J. Electrochem. Soc. 147 (2) (2000) 502.
- [52] R.C. Galloway, J. Electrochem. Soc. 134 (1) (1987) 256.
- [53] C.-L. Yu, J. Winnick, P.A. Kohl, J. Electrochem. Soc. 138 (1) (1991) 339.
- [54] J. Coetzer, J. Power Sources 18 (1986) 377.
- [55] R.J. Bones, D.A. Teagle, S.D. Brooker, F.L. Cullen, J. Lumsdon, Proceedings of the Extended Abstracts of the Spring Meeting of The Electrochemical Society, vol. 87, 1987, p. 786, 1.
- [56] K.T. Adendorff, M.M. Thackeray, J. Electrochem. Soc. 135 (9) (1988) 2121.
- [57] J.L. Sudworth, in: M. Barak (Ed.), “High temperature batteries”, in Electrochemical Power Sources, Primary and Secondary Batteries, Peter Peregrinus, Ltd., NY, IEE Energy Series 1, 1980, p. 403.
- [58] R.J. Vaughn, R.A. Carpio, L.A. King, US Patent 4,764,438, August 16, 1988.
- [59] D.M. Ryan, R.A. Marsh, R.K. Bunting, Proceedings of the 28th Power Sources Symposium, 1978, p. 90.
- [60] J.K. Erbacher, C.L. Hussen, L.A. King, Proceedings of the 28th Power Sources Symposium, 84.

- [61] J.D. Briscoe, Fluoride based cathodes and electrolytes for high energy thermal batteries, in: Proceedings of the 33rd Intersociety Engineering Conference on Energy Conversion, Colorado Springs, CO, August 2–6, 1998.
- [62] D.D. Briscoe, G.L. Castro, Transition metal fluoride cathodes for lithium thermal batteries,” SAE Technical Paper 1999-01-1401, 1999.
- [63] W. Rogers Jr., S.J. Ward, R.A. Guidotti, Sandia Report SAND84-0236, April 1984.
- [64] F.M. Delnick, D.K. McCarthy, J. Electrochem. Soc. 130 (9) (1983) 1875.
- [65] R.A. Guidotti, F.W. Reinhardt, G.C. Nelson, Sandia Report SAND83-2269, April 1985.
- [66] R.A. Guidotti, F.W. Reinhardt, Sandia Report SAND83-2270, July 1985.
- [67] R.A. Guidotti, F.W. Reinhardt, D.R. Tallant, K.L. Higgins, Sandia Report SAND83-2272, June 1984.
- [68] R.P. Clark, J. Chem. Eng. Data 14 (4) (1969) 465.
- [69] R.P. Clark, J. Chem. Eng. Data 15 (2) (1970) 277.
- [70] R.A. Guidotti, F.W. Reinhardt, ITE Letters on Batteries, vol. 2, New Technologies & Medicine, 2001, p. 26, 1.
- [71] R.A. Guidotti, F.W. Reinhardt, Proceedings of the 39th Power Sources Conference, 2000, p. 470.
- [72] R.A. Guidotti, F.W. Reinhardt, Proceedings of the 41st Power Sources Conference, 2005, p. 141.
- [73] Z. Johnson, R. Guidotti, D. Pickett, J. Wilkes, B. Burns, S. Preston, Proceedings of the 42nd Power Sources Conference, 2006, p. 103.
- [74] R.A. Guidotti, F.W. Reinhardt, Proceedings of the International Symposium on Molten Salts, XII, The Electrochemical Society, Pennington, NJ PV 99-41, 2000, p. 451.
- [75] R.A. Guidotti, F.W. Reinhardt, Proceeding of 201st ECS Meeting, Molten Salts, XIII, The Electrochemical Society, Pennington, NJ PV 2002-19, 2002, p. 31.
- [76] W.F. Hammett, R.A. Guidotti, J.T. Kish, F.W. Reinhardt, Kinetics of formation of $\text{Cr}\{\text{V}\}$ compounds in Ca/CaCrO_4 thermal batteries, in: Proceedings of the 1982 Fall Meeting of The Electrochemical Society, Detroit, MI, October 17–22, 1982.
- [77] F.M. Delnick, R.A. Guidotti, D.K. McCarthy, US Patent 4,508,796, April 2, 1985.
- [78] R.A. Guidotti, F.W. Reinhardt, Proceedings of the 37th Power Sources Conference, 1996, p. 251.