THE RELATIVE PERFORMANCE OF FeS$_2$ AND CoS$_2$ IN LONG-LIFE THERMAL-BATTERY APPLICATIONS

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ABSTRACT

The relative performance of FeS$_2$ and CoS$_2$ was measured in single cells based on the LiBr-KBr-LiF eutectic electrolyte over a temperature range of 400° to 550°C using both standard (dry) and flooded anodes. This electrolyte is designed to be used in long-life (>1 h) thermal-battery applications because it has a lower melting point (313°C) and a higher electrical conductivity than the standard LiCl-KCl eutectic (m.p. = 352°C). The cells were continuously pulsed for 1 ms every 10 ms from a background current density of 190 mA/sq cm to 1,130 mA/sq cm until end of life.

INTRODUCTION

The Li(Si)/FeS$_2$ electrochemical system has been used extensively by Sandia National Laboratories in the design of thermally activated ("thermal") batteries for nuclear-weapons applications. The batteries function only when the electrolyte becomes molten, which occurs at 352°C for the LiCl-KCl eutectic typically used. The first-generation thermal batteries utilized the Ca/CaCrO$_4$ couple. This system suffered from a number of shortcomings, however, such as lot-to-lot variability in Ca (1) or the cathode mixes (2,3) and liquid Ca-Li alloy formation which tended to result in shorting when not properly controlled. In contrast, the Li-alloy/FeS$_2$ couple has functioned quite well for almost all of its intended applications and, from a design perspective, is a much easier system to engineer than the Ca/CaCrO$_4$ system.

Thermal batteries utilize a molten salt immobilized in a MgO matrix as the separator between the Li-alloy anode and FeS$_2$ cathode. Normal operating temperatures for a thermal battery are generally between 550°C and the melting point of the electrolyte. By use of the LiBr-KBr-LiF eutectic, a much greater liquid range is possible. This makes this
electrolyte ideally suited for thermal-battery applications where lifetimes in excess of one hour are needed.

The main limitation of the use of FeS$_2$ as the cathode in long-life thermal batteries is its thermal stability. The FeS$_2$ thermally decomposes to FeS and elemental sulfur vapor when held at temperatures above 550°C for prolonged periods. The evolved sulfur can then migrate to the anode and chemically react with it generating considerable heat which in turn causes even more thermal decomposition of the FeS$_2$.

In contrast, CoS$_2$ is much more thermally stable than FeS$_2$ and has excellent kinetics for high-temperature secondary-battery applications, as reported by researchers at Westinghouse (4,5). These results indicate that CoS$_2$ should perform equally as well in primary (thermal) batteries. The greater thermal stability of CoS$_2$ relative to FeS$_2$ makes this material attractive for long-life (>1 h) thermal batteries, as it allows a much higher initial temperature to be sustained without degradation of the cathode.

This report describes the relative electrochemical performance of Li(Si)/FeS$_2$ and Li(Si)/CoS$_2$ thermal cells under high-rate conditions when formulated with the low-melting LiBr-KBr-LiF eutectic, which was adapted at Sandia for thermal-battery applications (6). Single cells were discharged isothermally over a temperature range of 400° to 550°C using standard (dry or unflooded) Li(Si) anodes as well as flooded anodes—anodes containing free electrolyte.

The cells were subjected to a continuous cycle of pulsing during discharge. The performance parameters for characterization included the maximum time for sustaining the pulse current, the steady-state voltage prior to pulsing, the minimum voltage during pulsing, and the polarization (voltage loss) that occurred during pulsing.

**EXPERIMENTAL PROCEDURES**

**Equipment**

Li(Si)/FeS$_2$ and Li(Si)/CoS$_2$ single cells (3.2 cm dia.) were discharged between heated platens in a glove box under high-purity argon. The moisture and oxygen contents were maintained at <10 ppm each. An HP6060B programmable electronic load was used to step the background current from 1.5 A (~190 mA/sq cm) to 9 A (~1,130 mA/sq cm) during a 1 ms pulse. A duty cycle of 10% was used for pulsing, i.e., a pulse duration of 1 ms followed by 9 ms at the steady state or background current. The cell was subjected to this cycle continuously for five minutes until the cathode capacity was exhausted. The current through the cell and the voltage across the cell during the a pulse was periodically monitored during discharge using HP3458A high-speed DVMs. The experiment was under the control of a HP9000 Series 200 computer.
Materials and Processing

The catholytes contained 73.5% FeS$_2$ or CoS$_2$, 25% electrolyte-binder (EB) mix, and 1.5% Li$_2$O as a lithiation agent (in the case of FeS$_2$) or as a wetting agent (in the case of CoS$_2$). (Unless otherwise stated, all compositions are in weight percent.) The CoS$_2$ was obtained from Cerac (Milwaukee, WI) and was used as received after vacuum drying at 80° to 100°C overnight. The -325 mesh FeS$_2$ was obtained from American Mineral and was purified by leaching with 1:1 v/v HCl and then concentrated HF. After treatment, the nominal FeS$_2$ purity was 98.6% or better.

The catholyte mixes were fused under argon at 400°C for 16 hours and were then granulated and cold pressed into pellets using a graphite paper backing. The FeS$_2$-based cathode was 0.581 g and the CoS$_2$-based cathode was 0.636 g, so as to have comparable capacities.

The low-melting (313°C) LiBr-KBr-LiF eutectic electrolyte used in the EB was prepared by fusing the appropriate amounts of reagent-grade halides (57.33% LiBr, 42% KBr, and 0.67% LiF) together in a fused-quartz crucible at 600°C for three hours in a dry room where the relative humidity was maintained at <3%. The EB used in the catholyte was also used as the separator for the cell. It was prepared by blending the electrolyte with 25% Maglite S MgO (Calgon, Pittsburgh, PA) that had been calcined at 600°C for four hours. The mixture was then fused at 400°C for 16 hours in a dry room. The calcined EB mix was then granulated and cold pressed into 0.38-mm thick separator pellets or blended into the catholyte mix.

The Li(Si) anode material was -100+325 mesh in size and contained 44% Li by weight. This material was cold pressed as is (0.3 g pellet) for unflooded anodes and 25% electrolyte was added before pressing for the flooded anodes (0.41 g pellet).

The single cells consisted of a separator pellet sandwiched between an anode and cathode pellet. The cells were assembled between 0.25 mm stainless steel current collectors and held together by stapling between two mica sheets.

RESULTS

Pulse Current

The CoS$_2$ was able to sustain the pulse current for a longer period of time relative to FeS$_2$. As shown in Figure 1 for a temperature of 400°C, a current density of 1,130 mA/sq cm was maintained for ~156 s for CoS$_2$ compared to only 78 s for FeS$_2$. (The run time has been corrected for the time required for data acquisition and data transfer.) At higher temperatures, this time increased to 234 s for both cathodes after which
the peak current density dropped. The drop was greater for the FeS$_2$ cathode in all cases.

When flooded anodes were used, the pulse current density could be sustained for 234 s at 400°C for the CoS$_2$ cells. For the corresponding FeS$_2$ cells, the pulse current density could be sustained for about the same time as for cells with unflooded anodes (about 78 s). However, the relative rate of decrease in the maximum sustained pulse current density after 78 s was reduced.

Cell Resistance

The apparent cell resistance was determined by dividing the voltage drop by the current change during pulsing. It includes both ohmic as well as concentration polarization. The cell resistances at 400°C are compared in Figure 2 for unflooded anodes. The resistance did not increase very much with depth of discharge for the CoS$_2$ cells. In contrast, the cell resistance of the FeS$_2$ cells rose dramatically near the end of life. The same trends were observed at the higher temperatures, except that the absolute magnitude of the resistance was reduced. The use of flooded anodes reduced the differences in resistance between the CoS$_2$ and FeS$_2$ cells at all temperatures as well as the absolute values of cell resistance.

Minimum Pulse Voltage

The open-circuit voltage for the Li(Si)/FeS$_2$ cell at 500°C is 1.99 V which is higher than that of 1.85 V for Li(Si)/CoS$_2$. Thus, at the beginning of discharge, the CoS$_2$ cells showed a slightly lower minimum voltage during pulsing. However, since the CoS$_2$ cells had a lower resistance, they outperformed the FeS$_2$ cells later in life. As shown in Figure 3, this crossover occurred at 25 s at 400°C, where polarization losses were greatest. As the temperature was increased, the time for crossover lengthened. Similar trends occurred when flooded anodes were used, except that the time for crossover was markedly increased. At 500°C, for example, crossover took place at 75 s for cells with unflooded anodes and 175 s for cells with flooded anodes.

DISCUSSION

The relative differences in performance of CoS$_2$ and FeS$_2$ are related to differences in discharge mechanism. In the case of FeS$_2$, the first discharge step is:

$$\text{FeS}_2 + 3/2 \text{Li}^+ + 3/2 \text{e}^- \rightarrow 1/2 \text{Li}_3\text{Fe}_2\text{S}_4$$  \[1\]
The \( \text{Li}_3\text{Fe}_2\text{S}_4 \) is further reduced to \( \text{Li}_2\text{FeS}_2 \) according to Eq. 2:

\[
\text{Li}_3\text{Fe}_2\text{S}_4 + \text{Li}^+ + e^- \rightarrow 2 \text{Li}_2\text{FeS}_2
\]  

[2]

In the case of \( \text{CoS}_2 \), the first discharge step is:

\[
\text{CoS}_2 + 4/3 e^- \rightarrow 1/3 \text{Co}_3\text{S}_4 + 2/3 \text{S}^2^-
\]  

[3]

This material can be further discharged according to Eq. 4:

\[
\text{Co}_3\text{S}_4 + 8/3 e^- \rightarrow 1/3 \text{Co}_8\text{S}_9 + 4/3 \text{S}^2^-
\]  

[4]

The reactions of Eqns. 1 and 3 were used to calculate the capacities of the cathodes in this study. (On a weight basis, this corresponds to 1,206 coulombs/g \( \text{FeS}_2 \) and 1,046 coulombs/g \( \text{CoS}_2 \); on a volume basis, this corresponds to 6,030 and 4,465 coulombs/cc, respectively.)

Compared to \( \text{FeS}_2 \), the \( \text{Li}_3\text{Fe}_2\text{S}_4 \) phase is more resistive by several orders of magnitude at 400°C, while \( \text{Li}_2\text{FeS}_2 \) is only four times more resistive (7). This accounts for the shape of the resistance-discharge time curves for the \( \text{FeS}_2 \) cells. While comparable data do not exist for the discharge phases for the \( \text{Li}(\text{alloy})/\text{CoS}_2 \) system, the resistance data for the \( \text{CoS}_2 \) cells (Fig. 3) suggest that they are as good or better conductors than the parent \( \text{CoS}_2 \).

Note that the discharge phases of \( \text{CoS}_2 \) do not depend upon the presence of \( \text{Li}^+ \) as do those of \( \text{FeS}_2 \). Thus, \( \text{Li}^+ \) concentration gradients at the cathode in the case of \( \text{FeS}_2 \) can severely limit the discharge rate. \( \text{CoS}_2 \) also has negligible solubility in the molten electrolyte when compared to \( \text{FeS}_2 \).

The presence of electrolyte in the anode improves the performance by providing a larger reservoir (relative to dry anodes) for assimilation of \( \text{Li}^+ \) generated during discharge. It also prevents wicking of electrolyte from the separator which results in a higher separator resistance. The use of flooded anodes results in a lower cell resistance because it reduces the anodic contribution to the overall cell polarization. As a consequence, the time that the maximum pulse current density can be sustained is increased.

For a long-life thermal battery, the performance at the end of life becomes critical, relative to short-duration (e.g., 5 min) applications. Since the temperature will be at its lowest at this time, the relative performance of \( \text{FeS}_2 \) and \( \text{CoS}_2 \) at the lower temperatures becomes increasingly important. The relative performance data at 400°C indicates that \( \text{CoS}_2 \) should outperform \( \text{FeS}_2 \) for such applications. To test this theory, single
cells were subjected to a ramped-temperature profile comparable to that of a long-life battery during discharge. The cells were discharged under a resistive background load of 15.7 ohms and a pulse load of 1 ohm for 5 s at 500 s and 3,580 s into discharge. The test results are shown in Figure 4.

The FeS₂ cell performed better initially but was surpassed by the CoS₂ cell after ~30 min. The discharge curve for the CoS₂ cell was also much flatter. The minimum pulse voltage at the first pulse was slightly higher for the FeS₂ cell but was much lower than the CoS₂ cell at the second pulse near the end of life. The substantial drop in voltage after 55 min for the FeS₂ cell is a consequence of thermal decomposition of the FeS₂ to sulfur vapor and FeS which has a much lower open-circuit potential. Clearly, CoS₂ is the preferred cathode choice for long-life thermal batteries. These data have since been corroborated in tests with full-sized thermal batteries (8).

CONCLUSIONS

CoS₂ shows superior performance to FeS₂ in single-cell tests with Li(Si) anodes at temperatures of 400° to 550°C with the low-melting LiBr-KBr-LiF eutectic electrolyte. The CoS₂ cells show a higher rate capability and a lower voltage loss during heavy-current pulses as a result of their lower internal resistance, even though the FeS₂ cells have a higher open-circuit voltage. The use of flooded anodes improves the performance of both types of cells relative to the use of dry (unflooded) anodes. Because of its superior discharge characteristics and higher thermal stability, CoS₂ is preferred to FeS₂ for use in thermal batteries with lifetimes of 60 min or more.

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Figure 1. Maximum Pulse Current Density as a Function of Time of Li(Si)/FeS₂ and Li(Si)/CoS₂ Thermal Cells During Continuous Pulsing at 400°C.

Figure 2. Apparent Cell Resistance as a Function of Time of Li(Si)/FeS₂ and Li(Si)/CoS₂ Thermal Cells During Continuous Pulsing at 400°C.
Figure 3. Minimum Pulse Voltage as a Function of Time of 
Li(Si)/FeS$_2$ and Li(Si)/CoS$_2$ Thermal Cells During 
Continuous Pulsing at 400° C.

Figure 4. Voltage as a Function of Time of Li(Si)/FeS$_2$ 
and Li(Si)/CoS$_2$ Thermal Cells Under a 15.7 Ohms Steady-
State/1 Ohm Pulse Load While Subjected to a Temperature 
Profile of a Long-Life Thermal Battery.