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Experimental Investigations of Certain Side Reactions and the Initial Voltage Transient for FeS_2 Cathodes in Thermal Batteries

Jimmie Q. Searcy, Frank M. Delnick, Joseph C. D'Angelo

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The following corrections should be made in the above referenced report:

Page 7, left column, second paragraph--sentence should read "In fact, the cell is anode limited in air and cathode limited in argon".

Pages 8 and 9--The figure labeled as Figure 3 is actually Figure 4, corrected. The figure originally intended as Figure 3 is not in the report. That figure shows an elevated voltage during the first few moments of a 400°C discharge, and a flat discharge for 600°C.

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Experimental Investigations of Certain Side Reactions and the Initial Voltage Transient for FeS₂ Cathodes in Thermal Batteries

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Abstract

The direct reaction of FeS₂ with stainless steel current collectors reduces the coulombic efficiency of thermal cell cathodes. When single cells are discharged in air, the reduction of O₂ at the FeS₂ cathode represents a significant fraction of the discharge current. At least five separate phenomena contribute to the initial voltage transient observed in thermal batteries which use FeS₂ for the cathode material. These five phenomena are: (1) a thermodynamic increase in the potential caused by the initial temperature peak which results from the heat pellets when ignited, (2) electrochemical participation of surface contaminants on the FeS₂, (3) electrochemical reduction of oxygen or reaction products of oxygen with FeS₂, (4) electrochemical reduction of elemental sulfur produced by the thermal decomposition of FeS₂, and (5) the voltage decrease which accompanies the saturation of the electrolyte with the electrochemical reduction product, or products. Mitigative techniques for the observed phenomena include: (1) performing single cell tests under an inert atmosphere, (2) using a nonreactive material for current collectors, (3) using an additive with the cathode to suppress the initial voltage transient, and (4) predischarging the cathodes.

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The authors thank J. R. Armijo who purified the iron disulfide and then built and tested several batteries for us.

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Experimental Investigations of Certain Side Reactions and the Initial Voltage Transient for FeS₂ Cathodes in Thermal Batteries

Introduction

Thermally activated batteries which use iron disulfide (FeS₂) for the cathode material are being developed by Sandia National Laboratories. In order to design batteries that meet voltage regulation requirements and efficiently use the active materials, it is desirable to eliminate the initial elevated voltage and to minimize side reactions.

Several authors earlier suggested mechanisms and possible mitigative techniques for the abnormally high voltage observed with FeS₂ cathodes during the first several minutes of discharge. (This voltage transient has been commonly referred to as the "voltage spike.") Bush and Nisson suggested that the transient could be reduced by adding magnesium powder to the cathode.¹ Levy and Crafts concluded that the source of the spike was surface impurities on the FeS₂.² Dand and Pres assumed that the major mechanism leading to the observed phenomenon was the electrochemical reduction of free sulfur resulting from the thermal decomposition of FeS₂.³ Several additives were suggested by Dand and Pres as mitigative techniques. DeGruson found that the duration of the elevated voltage was dependent on the rate of heat transfer into the individual battery cells.⁴ He was able to alter the spike by changing the current collector material. Since most of the work mentioned above was performed in air, and since the different authors attribute the voltage spike to different mechanisms, it was decided to reexamine this phenomenon.

Most of the data in this report were obtained from single cell tests. The general design of the single cell testers at Sandia has been published elsewhere⁵ and will not be discussed here. The testers used here differed from the earlier design in three important

respects: (1) the voltage measurements for the reference electrode were made with a Keithley Model 610-BR electrometer, (2) the constant potential measurements were made with a Wenking ST-72 potentiostat, and (3) many of the tests were performed in an argon atmosphere.

Side Reactions With Air and Stainless Steel

In the past, it has been a standard practice in thermal battery laboratories to perform single cell tests in a dry room with the battery materials exposed to dry air. It was tacitly assumed that air did not interfere with the tests. Since it has been demonstrated⁶ that FeS₂ reacts with oxygen at temperatures substantially below 500°C (a common temperature for single cell tests on thermal battery systems), several experiments were conducted to test this assumption.

Experiments were performed in dry air and in argon. In all tests, round pellets of pressed powder with a 10.3-cm² area were used for the anode, separator, and cathode. The anode pellets were 1.5 ± 0.1 g of pressed magnesium powder, the separator pellets were 2.0 ± 0.1 g, and the cathode pellets were 4.0 ± 0.1 g. The composition of the separator pellet was 90 wt% LiCl-KCl eutectic (45% LiCl, 55% KCl by weight, fused), and 10 wt% Cabosil (EII-5, Cabot Corporation). The composition of the cathode pellet was 64% FeS₂, 33% LiCl-KCl, and 3% Cabosil (SiO₂).^{7,8} The FeS₂ (purchased from MCB) was approximately 95% pure, with the 5% impurity being largely SiO₂. An analysis of this material has been published elsewhere,^{8,9} and

except for surface impurities, FeS_2 is the only electrochemically active species. The magnesium used was purchased from ROC/RIC and labeled 99% pure. Current collectors in these tests were composed of different materials as described below. The weights of the pellets were chosen so that the anodes contained an excess of electrochemically active material for the expected electrochemical reactions. Most of the experiments used two separator pellets with a single groove on the face of each pellet along a radius of the pellet. Pellets were positioned in single cells so that the groove in the separator pellets faced each other, and a reference electrode was inserted into the resulting hole. The reference electrodes used the $\text{Ag}/\text{Ag}^+\text{C.1 m}$ couple.¹⁰

Figure 1 gives the results of two cells discharged at a constant current of 50 mA/cm^2 in dry air and in argon, using No. 304 stainless steel current collectors. The data indicate that both the anode and cathode are substantially altered by the presence of air. In fact, the cell is anode-limited in argon and cathode-limited in air. Presumably, oxygen either reacts with both FeS_2 and Mg (or is itself reduced electrochemically), to produce this effect.

Figure 1. Single Cell Discharges in Dry Air and Argon (platen pressure 1.77 psi).

In other work, cells with stainless steel current collectors were heated to 500°C at open circuit, discharged through a 2-ohm load for 10 min, then switched back to open circuit. Figure 2 gives typical results for cells discharged in this manner in air and

argon. The cells discharged in air had an initial open circuit potential characteristic of the voltage spike. After the 10-min discharge, the open circuit potential drifted upwards for a period of 30 to 50 min and finally leveled off at a value approximately equal to the initial open-circuit potential. The cell discharged in argon also had a high initial open-circuit potential, but after 10 min of discharge the open circuit potential drifted up only slightly. The reference electrode indicated that the unusual behavior in air was associated predominantly with the cathode.

Figure 2. Single Cell Discharges in Air and Argon With Switching From Open Circuit to a 2.0-Ohm Load (platen pressure 1.77 psi)

In a third series of experiments, cells with graphite current collectors were discharged in air and in argon at 500°C . The cathodes were held at a constant potential with respect to the reference electrode until the current reached essentially zero. The discharge potential ($E = -0.8\text{V}$ vs $\text{Ag}/\text{Ag}^+ 0.1\text{m}$) was chosen at a level intermediate between the reduction potentials of FeS_2 and FeS so that no current flow resulted from the reduction of FeS . The current vs time curves were graphically integrated to determine the total charge. The total charge (in faradays) was then divided by the number of moles of FeS_2 in a cathode pellet to determine F/M (or, electrons per molecule of FeS_2). When

these experiments were performed in argon, a value of $F/M = 2.08$ was obtained. In air, a value of $F/M = 3.84$ was obtained. A two-electron transfer ($F/M = 2.0$) was expected in the reduction of FeS_2 to FeS . The value of 3.84 was unreasonably high and dramatically illustrated the impact of air (presumably oxygen) on the electrochemical reaction in this system.

Cells with stainless steel current collectors were similarly discharged in argon. In these experiments, the faradays of charge delivered per mole of FeS_2 was approximately one ($F/M \approx 1$). Apparently, at operating temperatures, iron disulfide reacts with the stainless steel current collectors to significantly reduce the electrochemical utilization of FeS_2 by the following reaction:

Investigation of the Initial Voltage Spike

Since the purpose for reexamining the voltage spike was to learn how to mitigate it in batteries, the materials used were the same formulations as those currently used in thermal battery designs. Anode pellets were pressed from powered lithium-silicon alloy ($44 \pm 1\%$ lithium by wt purchased from KBI, Inc.), and the current collectors were stainless steel. The separator pellets weighed 2.0 g and were composed of 70 wt% $\text{LiCl} \cdot \text{KCl}$ eutectic and 30 wt% MgO . The cathode pellets were the same as those described above. The FeS_2 powder used in most of this work had a particle size less than 50 mesh (U. S. Standard, sieve size).

Experiments were conducted in a dry lab (water content < 300 ppm) and in an argon glove box. The water and oxygen content of the argon atmosphere was maintained at a level below 10 ppm.

Experiments conducted with a single cell tester have a different temperature profile than do battery tests. Single cell tests are conducted by heating platens to a desired temperature, then connecting a 3.7Ω load (nominal current density of 50 mA/cm^2) to the ambient temperature cell and placing the cell between the platens. The recorder and electrometer are then turned on to monitor the cell potential and reference potential. The cells require some time (perhaps 20 s) to reach platen temperature. In a battery the cells receive a large amount of energy in less than 1 s, and the temperature of the cell rises extremely rapidly and then continually drops. The two different temperature profiles must be considered when comparing battery data with single cell data. As previously suggested by DeGruson,⁴ the battery temperature can be partially simulated with a single cell

tester, using heat pellets.

In this work a small increase in peak voltage with increasing platen pressure was observed for cells discharged at 520°C in both argon and air. The increase of voltage probably resulted from a decreased impedance caused by better contact between the cell parts as the pressure increased. At pressure greater than 8.5 psi, the separator pellet deformed and data were not meaningful.

Experiments designed to determine the effect of platen temperature on the initial voltage spike gave different results depending on whether the cells were discharged in argon or air. Figures 3 and 4 give observed voltage traces at 400° and 600°C that illustrate this difference.

Figure 3. Single Cell Discharges in Dry Air at 400° and 600°C (platen pressure 2.96 psi)

Magnesium powder, blended with the cathode mix, has been previously suggested as one means for reducing the voltage spike.^{1,2,7} A number of single cell experiments were performed to determine if optimization of particle size and concentration would remove the voltage spike. Cells were discharged with magnesium powders of two particle size ranges, one less than 300 mesh, and the other less

than 100 mesh. Concentrations of each magnesium powder of 0.5, 1, and 2 wt% in the cathode mix were used.

Figure 4. Single Cell Discharges in Argon at 400° and 600°C (platen pressure 2.96 psi)

The six cathode mixes were pressed into 10.3-cm², 4.0-g pellets. Single cells were discharged at 520°C and 2.71 psi, through a load of 3.7 ohms. In these experiments the initial voltage spike was suppressed for all the cells in both air and argon. Figure 5 gives a typical discharge for a cell containing magnesium powder, and for one that did not. The reference electrode confirmed that the change in cell potential was associated with the cathode. The cathode potential rose at a slower rate and was rounded rather than peaked for the mixes containing magnesium powder as compared with mixes that did not contain magnesium powder. The rate at which the cathode potential reached plateau voltage was influenced both by magnesium powder concentration and particle size. A plot of time to reach cell plateau voltage vs magnesium powder concentration is given in Figure 6 for each magnesium powder. This plot illustrates data taken in air and clearly demonstrates that the time to plateau voltage in single cell tests was increased by

adding magnesium powder to the cathode. The time-to-plateau voltage was also increased with the smaller particle size magnesium.

Figure 5. Single Cell Discharge in Air for Normal Cathode and for One Containing 1.0 wt% Mg Powder (platen pressure 2.96 psi)

Figure 6. Time-to-Plateau Voltage vs wt% Magnesium in the Cathode for Single Cell Discharges in Air (Cells were Li(Si)/LiCl·KCl/FeS₂ discharged at 520°C through a 3.7-Ω load, and platen pressure was 2.96 psi.)

The single cell behaviors observed for the cathode mixes containing magnesium powder strongly suggests that the magnesium powder is reacting with the electrochemically active species in the cathode to affect the voltage. Both larger concentration and larger surface area enhance the rate and amount of reaction, and both situations increased the time-to-plateau voltage.

Battery tests conducted with cathodes containing magnesium powder did not remove the observed voltage transient. The rise times of the batteries were affected in a manner similar to that observed for single cell tests and the maximum voltage was reduced. However, a few seconds into a battery discharge, the voltage profile was not changed by the addition of magnesium to the cathode.

During the single cell discharges discussed above, it was observed that the anode potential always peaked sharply and then abruptly dropped several millivolts. In fact, the anode peaked and dropped while the cathode was still rising (see Figures 3, 4, and 5). Therefore, in the single cell tests, the anode peak did not contribute to the cell peak voltage. Presumably, the anode peaked earlier than the cathode because the anode conducted heat much more readily than the cathode, and therefore reached operating temperature quicker. In batteries, the heat input is so quick that it was presumed that the observed anode peak contributed to the cell peak voltage. This consideration, along with the fact that batteries have a large temperature gradient during the first several seconds of life, prompted the development of a method for heat-shocking single cell tests.

The basic approach used to heat-shock single cells was to place heat pellets on both sides of the cell (with current collectors between the heat pellet and the electrodes), and let the heat pellets auto-ignite as the assembly was heated by the platens. Figure 7 gives a plot of temperature vs time for the center of the separator layer in one of these cells, and a temperature-vs-time curve for a battery in which the thermocouple was placed between a cathode pellet and a separator pellet. (J. R. Armijo, Division 2523, built and tested this battery for us using a design previously reported.⁸) This technique approximates the thermal environment of a battery. All data obtained with this technique were taken in an argon glove box. When this approach was attempted in air, the lithium-silicon anode ignited. Figure 8 shows a typical discharge of a heat-shocked single cell. Note that the general shape is very similar to the earlier results (Figures 3, 4, and 5). The anode still had a sharp voltage spike that peaked and dropped off as the cathode was rising. The fact that similar behavior

was observed for two different heating rates suggests the following explanation for the observed anode spike. Heat entered the cell through the electrodes and melted the electrolyte. The anode conducted heat much better than the cathode. The electrolyte between the reference electrode and the anode melted first. At this time, little or no current was flowing through the cell; therefore, the anode was essentially at open circuit potential. As the rest of the electrolyte melted and the cathode began to react electrochemically, current flowed through the cell, and the anode was polarized. As the cathode potential increased, more current was conducted through the cell, and the anode potential dropped until the current reached a steady state. It was concluded from this rationalization that the anode did not contribute to the observed cell voltage spike.

The fraction of the voltage spike that is attributable to the temperature excursion in heat-shocked cells could be estimated by the following procedure. A plot of cell potential at 6 min into a discharge (a time well past the spike) vs temperature was made for isothermal discharges (Figure 9). Points from a temperature profile of a heat-shocked cell were then used with Figure 9 to construct a voltage trace. This constructed curve gave a voltage spike that was attributed to temperature alone, and any higher voltage spike indicated that other mechanisms were active. This approach was valid only for experiments which used similar materials and the same resistive load. Figure 10 shows a curve constructed by the above procedure (dotted line). Also plotted on Figure 10 is a discharge curve observed for a heat-shocked cell. The voltage spike for a heat shocked cell containing 1 wt% magnesium powder (not shown in Fig. 10) was ~ 0.1 V higher than that of the constructed curve. This indicated that the magnesium additive did not eliminate that fraction of the spike due to mechanisms other than temperature. In fact, the spike observed for cells with magnesium added to the cathodes was only about 0.02 V lower than that observed for normal cells.

Another experiment suggested techniques to significantly reduce the initial voltage spike. One cell was predischarged to a point well beyond the spike, then cooled, and tested with the heat-shock technique. This cell gave a peak voltage that could be completely attributed to the temperature profile.

Concurrently with this work, A. R. Baldwin, Division 2523, demonstrated that smaller particle size FeS_2 yielded pellets with better mechanical integrity.¹¹ A particle size range of -230 to +325 mesh was selected for pellet integrity. Batteries made with this material had an initial voltage spike higher than with

Figure 7. Temperature vs Time Observed in a Battery and a Heat-Shocked Single Cell

Figure 8. Single Cell Discharge for a Heat-Shocked Cell

Figure 9. Single Cell Potential vs Temperature for a 3.7-Ω Constant Load, Platen Pressure 2.96 psi, 6 min into the Discharge

Figure 10. Heat-Shocked Single Cell Discharge In Argon and a Constructed Discharge Based on the Observed Temperature Profile

the larger particle sizes used in earlier batteries. This increased voltage peak with decreased particle size had been observed previously by Levy and Crafts,² and attributed to a larger amount of surface oxides and oxysulfides on the smaller particles (larger surface area). Surface analytical data has confirmed the presence of a layer of oxidation products on the FeS_2 .⁹ Purification of the FeS_2 with a hydrofluoric acid wash (developed by J. R. Armijo, Division 2523) should remove most surface impurities as well as the silicon dioxide impurities present in mixed FeS_2 . In batteries, purifying the FeS_2 reduced the peak from 32.73 to 31.65 V. Discharge of single cells containing purified FeS_2 (-230 to +325 mesh) gave a voltage spike 0.1 V higher than that which could be attributed to temperature alone.

In order to relate the change in the activity of the reduction products to the initial voltage drop, Li_2S was added during the initial fusing of the KCl and LiCl . One gram of Li_2S was added to 1000 g of the eutectic electrolyte to form a saturated solution of Li_2S .¹² Cathodes were made using this electrolyte, and single cells were discharged. A slight reduction of the peak voltage for the cells containing sulfide in the electrolyte (about 0.02 V) was observed.

Discussion and Mitigative Techniques

The data in the preceding section indicate that the observed voltage spike is influenced by a number of factors and several mechanisms appear to be acting simultaneously. The spike is more pronounced at lower temperatures and disappears entirely at 600°C for standard single cell discharges in air (see Figures 4 and 6). In argon, an opposite trend was observed. These observations along with the data shown in Figure 2 clearly demonstrate that air influences the observed voltage spike. The trends illustrated by Figure 4 can be rationalized by the assumption that electrochemically active species are produced by the reaction of air (presumably oxygen) with iron disulfide or that oxygen is reduced at the cathode. Both the reaction rate and the diffusion rate of oxygen into the cell are increased with increasing temperature. In these experiments, the electrochemical reaction rate was maintained at a nearly constant value by the constant load, so that at lower temperatures the oxygen (or oxygen reaction products) were quickly depleted electrochemically, and the potential dropped rapidly to that of FeS_2 . At 600°C, in air, the oxygen supplied to the cathode was not depleted by the electrochemical reaction and the voltage remained high.

In this work and in previous work,² the voltage spike (measured at 520°C and higher) was reduced by treating the FeS_2 (perhaps removing surface contaminants). Since surface contaminants were present to affect the data in Figure 5, the absence of a voltage spike at 400°C in argon is somewhat puzzling. One of the several possible explanations for this is that the contaminants may form a resistive layer that must be dissolved before giving a potential greater than the FeS_2 . If this were true, the dissolution rate would increase with temperature, and the voltage spike would increase with temperature as observed.

The data taken with the normal single cell technique confirmed earlier results that magnesium powder reduced the voltage spike but the same technique was not satisfactory in batteries. Predischarging of cells and purifying the FeS_2 with hydrofluoric acid also appeared to diminish the effect of the contaminants. Adding lithium sulfide to the electrolyte slightly reduced the observed spike, confirming that the finite solubility of lithium sulfide affects the potential somewhat.

The observation that purified small particle size FeS_2 gave a peak voltage higher than that predicted by temperature considerations alone suggested that thermal decomposition of the FeS_2 contributed to the spike. Since the purified FeS_2 crystals were presumably free from the surface contaminants, which add to the spike, the higher surface area of the smaller particles should have no effect on the observed spike unless some other mechanism (such as FeS_2 decomposition) were involved. Figure 9 (which was used to predict the curves expected from temperature considerations alone) was generated using data from large particle size FeS_2 . Any effect caused by the thermal decomposition of the cathode material was automatically included for iron disulfide of a particular particle size. However, decomposition of iron disulfide is that of an ionic solid reacting to give a second ionic solid and a gas. The rate of this type of reaction is controlled by the topology of crystals of the reacting solid.¹³ A greater surface area leads to more decomposition. Since the measured thermal decomposition rate of iron disulfide indicates substantial reaction at temperatures as low as 500°C,^{14, 15} and since surface analytical data indicate migration of sulfur to the surface of heated FeS_2 ,⁹ it would appear that elemental sulfur (which would have a higher potential than FeS_2) must participate in the electrochemistry of this system. The extent of its participation necessarily depends on the current drain and the rate at which sulfur is produced by thermal decomposition. If the rate of sulfur production at the higher temperatures during the heat shock exceeded the current drain,

then the potential would begin to approach that of elemental sulfur, rather than FeS_2 , and a voltage peak would result. For smaller particle size FeS_2 , the decomposition rate is increased, and the cell is driven more towards the elemental sulfur potential; therefore, smaller particle size FeS_2 would give a larger initial voltage spike if a heat shock was involved.

At least five different mechanisms appear to be involved in the production of the abnormally high voltage spike observed with thermal batteries which use FeS_2 for the cathode material. The phenomena involved can be listed as follows: (1) An initial temperature spike caused by the very rapid input of energy leads to a thermodynamic variation of the potential, (2) oxygen is reduced on the FeS_2 surface, (3) surface contaminants on unpurified FeS_2 contribute to the spike, (4) thermal decomposition of the FeS_2 produces elemental sulfur that contributes to the potential, and (5) the finite solubility of reduction products in the electrolyte causes the potential to decrease slightly as the cell discharges and saturates the electrolyte.

The above discussion suggests several techniques that would minimize the observed voltage spike without adding a reducing agent to the cathode. Three guidelines appear to be most important. First, the iron disulfide crystals should be as large as can be conveniently pelletized to insure a minimum surface area. Minimizing the surface area of the FeS_2 would minimize the contribution to the spike from three of the five phenomena listed above (the mechanisms numbered 2, 3, and 4 in the preceding paragraph). The second guideline for minimizing the initial voltage spike is to use FeS_2 that has been purified with an acid wash to remove the surface contaminants.

A third technique that is important in reducing the voltage spike involves thermal energy management in the battery. A battery designer can reduce the voltage spike by reducing the temperature spike in the battery cells. This can be accomplished by several means and the optimum design would depend on the battery requirements. Some suggestions to reduce the temperature spike are as follows: (1) reduce the heat pellet weight, (2) use a heat pellet with more iron powder and less potassium perchlorate, (3) use a thicker current collector or one made from a material with a lower thermal conductivity and diffusivity. These suggestions would obviously increase the rise time of a battery, but to some extent this effect can be reversed by making the anode, separator, and cathode pellets thinner.

Adding lithium sulfide to the electrolyte will also reduce the observed spike slightly, but this does not

appear to be a significant enough effect to recommend its adoption. One method for essentially eliminating the voltage spike is predischarging of the individual cells. This method has been previously reported³ and was rediscovered during this work. Batteries built with cells predischarged to a level beyond the usually observed spike did not have the initial voltage transient.

Addition to the cathode of a material that is electrochemically oxidized is another mitigation technique that may be used. Such materials are normally anode materials and probably function to eliminate the spike by creating an internal electrochemical short circuit in each cathode when the electrolyte is melted. Since certain mechanisms contributing to the spike in batteries (sulfur evolution and the thermodynamic temperature effect) are active for several minutes, a material that reacts very rapidly (such as magnesium) would not eliminate the voltage transient in batteries. An anode material that is normally very polarizable and slow to reduce would be a desirable additive (to the cathode) to remove the spike. Such a material has been tested and batteries built with a 1.5 wt% added to the cathode exhibited essentially no voltage spike. (The specific material cannot be named in this report because of possible patent interest by the DOE.) Such batteries have a slightly increased rise time and a somewhat lower weight heat pellet.

Conclusions

Air (presumably oxygen) interacts with the cathode to produce an electrochemically active species or oxygen itself is directly reduced. The presented data are not complete enough to define the reacting species, but are complete enough to mandate that future testing be done in an inert atmosphere. Stainless steel interacts with FeS_2 chemically to substantially decrease its electrochemical utilization. Any battery requiring high energy density should use current collectors that do not react with FeS_2 . Materials which appear to meet this requirement are graphite and molybdenum.

The initial voltage transient observed with thermal batteries which use FeS_2 is a very complicated phenomenon that results from a number of different mechanisms. The five following mechanisms are suggested as contributors: (1) a thermodynamic increase in the potential is caused by the initial temperature peak which results when the heat pellets are ignited, (2) surface contaminants on FeS_2 function as cathode materials with a potential higher than that of FeS_2 , (3)

oxygen, or reaction products of oxygen with FeS_2 , participate in the cathode reaction with a potential higher than FeS_2 , (4) free sulfur produced by the thermal decomposition of the FeS_2 participates in the cathode reaction with a potential higher than FeS_2 , and (5) a voltage decrease occurs as electrochemical reduction products are dissolved by the electrolyte until the electrolyte becomes saturated with the solute.

The voltage spike can be minimized by (1) using FeS_2 with a surface area as low as possible, (2) using FeS_2 that has been purified of surface contaminants, and (3) minimizing the heat input into the individual cells.

The voltage spike can be eliminated by precharging the individual cells of a battery and by adding a small percentage of a very polarizable anode material to the cathode. One additive has been shown to remove the voltage spike, but it cannot be named in this report because of patent interest by DOE.

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