I O U R N A L O F

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# Enhanced salt coating on FeS<sub>2</sub> surface with the addition of Li<sub>2</sub>O

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The electrolytes in thermal batteries are nonconductive solids at ambient temperature, which prevent the self-discharge and corrosion. To meet severe environmental requirements and guarantee acceptable handling yields, all the pellets in cells should have adequate strength, especially for the cathodes due to their poor binding properties among  $FeS_2$  particles. By modifying the surface microstructure of  $FeS_2$  through molten-salt heat treatment, the inter-particle binding strength is greatly increased, resulting in the enhanced pellet strength and yield. The addition of  $Li_2O$  also promoted the soft salt coating coverage of hard  $FeS_2$  particles, which can be explained by the enhanced wettability of the molten salt.

Key words: Thermal batteries, FeS<sub>2</sub>, Li<sub>2</sub>O, Molten-salt electrolyte.

# Introduction

Thermal batteries, which can stand harsh environmental conditions, are principal reserve power sources predominantly used for guided weapons, such as missiles, torpedoes and smart munitions [1, 2]. They can be maintenance-freely stored more than 15 years without any notable loss in capacity and supply electric powers instantly [1, 3] and are typical single-shot reserve batteries which are activated with pyrotechnic heat sources [4]. They operate at a high temperature around 500 °C and the amount of heat from the heat pellets must be scaled to provide the balanced thermal energy to melt the salt electrolyte. A thermal battery consists of a cell-stack part in which several unit cells are stacked in series, pyrotechnic part of an igniter, heat pellets and heat papers, and peripheral part of thermal and electrical insulators, a header and a case. Reliability and safety of thermal batteries are principal issues for military applications along with their discharge performance [5, 6]. Many failures result from thermal runaway, which lead to the fatal breakdown of whole weapon systems. The typical causes of thermal runaway in thermal batteries can be categorized into the decomposition and/or melting of electrodes, electrolyte or other components.

This work is concentrated on the decomposition of  $FeS_2$  into thermally stable FeS and gaseous sulfur, which becomes significant above 550 °C [5]. The sulfur gas reacts with lithium in anode exothermically and further accelerates the decomposition of  $FeS_2$  and incurs the thermal runaway.

$\text{FeS}_2 \rightarrow \text{FeS} + \frac{1}{2}\text{S}_2 \uparrow$	(1)
$^{1}/_{2}S_{2} + Li \rightarrow LiS + \Delta H$	(2)

In this study, the molten-salt heat-treatment method by modifying the surface microstructure of  $FeS_2$ , which reduces not only the overheating of  $FeS_2$  cathode but also the compaction force with enhanced mechanical strength, was suggested. The effect of Li<sub>2</sub>O addition on the forming of cathode was also investigated.

# Experimental

### Design of unit cell

Among various electrochemical systems, Li/FeS<sub>2</sub>, Li(Si) for anode and FeS<sub>2</sub> for cathode, is the most widely selected as electro-active materials because it exhibits high stability and current capability at high operating temperature in the presence of corrosive molten salt [1, 3]. As for the electrolyte for a thermal unit cell, LiF-LiCl-LiBr eutectic salt is used to meet the high current requirement. A schematic of unit cell is shown in Fig. 1.

### **Cathode preparation**

 $FeS_2$  was used as the cathode material for its high voltage and low price. To make it easy to compact the hard  $FeS_2$  particles into a disk, a considerable amount of LiCl-KCl eutectic salt was added as electrolyte binder. MgO powders were also added to hold the free electrolyte. LiCl and KCl salts were mixed and melted above 400 °C, and ground and mixed with MgO, and then melt together and ground again.

When the impurities such as  $FeSO_4$  and FeO remain on the surface of  $FeS_2$ , voltage spikes present at the early stage of discharge [7]. To avoid this voltage instability and improve the electric conductivity, a small amount of Li<sub>2</sub>O was added as a lithiation agent

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Fig. 1. Schematic illustration of Li/FeS<sub>2</sub> unit cell.

[7, 8]. The mixed cathode powder with molten salt was heat-treated at around 450 °C in argon atmosphere, followed by grinding and sieving. The prepared powders were compacted into 56 mm discs in diameter with a pressing force of  $20 \times 10^3$  to  $60 \times 10^3$  kgf at room temperature.

#### Material characterizations

To examine the surface morphologies of  $FeS_2$  and semi-quantitative composition analysis, a scanning electron microscope (Phillips XL30FEG) with an energy dispersive X-ray spectrometer was adopted, respectively. The detailed microstructure of the  $FeS_2$ cathode was inspected by a transmission electron microscope (JEOL JEM-3000F).

Thermal characteristics of the prepared powders were measured using a thermogravimetric analyzer (TG SDT Q600, TA Instruments). All these powders and samples were prepared in dry air condition of relative humidity under 5%.

The mechanical strength of the cathode pellets was measured using a push-pull gauge and a compressive strength tester. Densities of all pressed pellets were geometrically calculated from the measured weight and thickness data.

# **Results and discussion**

## Salt-coated FeS<sub>2</sub>

To alleviate the  $\text{FeS}_2$  decomposition in a cathode by the direct contact of a heat pellet, heat-proof metal foils, made of stainless steel, nickel or graphite foils, can be inserted between the cathode and the heat pellet,



Fig. 2. Surface morphology of  $FeS_2$  cathode (a) without and (b) with molten-salt heat treatment.

as in the same manner for the metal foil inserted between the anode and the heat pellet in a unit cell, as shown in Fig. 1, to prevent anode overheating. However, the addition of cathode foils needs an extra heat source, which has adverse effect on the anode.

The heat generated from the decomposition of FeS<sub>2</sub> into sulfur and the consecutive reaction with Li in anode raises the inner temperature of a thermal battery, and further accelerates the decomposition of FeS<sub>2</sub>. To prevent these failures, the purity, particle size and crystallinity of FeS2 must be carefully controlled. And also by coating the electrolyte film, the surface of FeS<sub>2</sub> particles can be cooled down by the latent heat from the melting of the salt electrolyte [3]. These unique microstructures of FeS2 cathode, coated with Li2O and LiCl-KCl electrolyte, are represented in Fig. 2. The cathode without heat treatment, as depicted in Fig. 2(a), showed sharp and clear morphology with little trace of molten-salt coating on FeS2 surface. However, the cathode with heat treatment, as depicted in Fig. 2(b), showed dull and rounded FeS<sub>2</sub> morphology.

As seen in Fig. 3, the strength of cathode is greatly enhanced after the heat treatment. This is attributed to



**Fig. 3.** Compressive strength of  $FeS_2$  cathode with  $(\bullet)$  and without  $(\bullet)$  molten-salt heat treatment as a function of compaction pressure.



Fig. 4. Compressive strength of  $FeS_2$  cathode as a function of  $Li_2O$  addition amount.

the fact that molten-salt electrolyte covers the hard  $FeS_2$  particles effectively.

# Effect of Li<sub>2</sub>O addition

The addition of Li<sub>2</sub>O effectively lowers the viscosity of free electrolyte and enhances the electrolyte coverage on FeS<sub>2</sub> particles. As the addition of Li<sub>2</sub>O increases, the strength of a compacted cathode pellet increases also as shown in Fig. 4. This is attributed to the fact that the contact areas among FeS<sub>2</sub> particles are greatly enlarged, though the spring-back is remained almost the same regardless of Li<sub>2</sub>O addition. When Li<sub>2</sub>O is added more than 3.0 wt%, the specific discharge performance is deteriorated as the volume ratio of the low-density Li<sub>2</sub>O is increased in a limited cathode size.

The yellowish color of the cathode powder observed after heat treatment indicates that the lithiation reaction occurs on the surface of  $FeS_2$ , which suppresses voltage transient during the discharge. The formation of the yellowish second phase of  $Li_3Fe_2S_5$  can be more clearly observed in the SEM and TEM micrographs displayed in Fig. 5. The needle-shaped second phases





Fig. 5. Micrographs of  $FeS_2$  cathode by (a) SEM and (b) TEM.



Fig. 6. Discharge curve of a  $\text{Li}/\text{FeS}_2$  single cell with molten-salt heat treatment.

composed of Fe, S also suggest the formation of the new phase of  $Li_3Fe_2S_5$  on the surface of FeS<sub>2</sub>. The formation of  $Li_3Fe_2S_5$  is predominant where oxygen peak is prominent, indicating that  $Li_2O$  also helps to form the yellowish second phase.

## **Discharge characteristics**

Fig. 6 shows the dependence of the cell voltage of a  $\text{Li/FeS}_2$  single cell as a function of the Li equivalent



Fig. 7. Thermogravimetric analysis spectrum of FeS<sub>2</sub>.

capacity under constant current density of  $0.15 \text{ mA/cm}^2$ at 500 °C. The cell is composed of Li(Si) anode, LiF-LiCl-LiBr electrolyte and FeS<sub>2</sub> cathode. The FeS<sub>2</sub> cathode was heat-treated with LiCl-KCl eutectic salt and Li<sub>2</sub>O. Decomposition of FeS<sub>2</sub> is confirmed by thermogravimetric analysis. As shown in Fig. 7, the mass change becomes serious above 550 °C. No voltage spikes appeared during the initial stage of discharge, as predicted by the formation of the yellowish second phase of Li<sub>3</sub>Fe<sub>2</sub>S<sub>5</sub> on the surface of FeS<sub>2</sub>. No thermal runaway, caused by the decomposition of FeS<sub>2</sub> cathode, was detected during the discharge.

# Conclusions

Thermal batteries have been a primary choice among reserve batteries for their excellent reliability. However, the thermal runaway that is caused by the decomposition of  $FeS_2$  drops off in thermal stability as well as mechanical

soundness of cathode. The experimental results showed that the addition of LiCl-KCl electrolyte with 1.5 wt% Li<sub>2</sub>O to the FeS<sub>2</sub>-based cathode clearly enhanced the performance of cathode for thermal battery. By modifying the surface microstructure of FeS<sub>2</sub> through molten-salt heat treatment, the binding strength among the FeS<sub>2</sub> particles is greatly increased, resulting in enhanced pellet strength and yield. With the addition of Li<sub>2</sub>O with eutectic salt to the FeS<sub>2</sub> cathode, the strengths of the compacted pellets increased considerably due to the enhanced wettability of the salt.

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