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Nanostructured thermal batteries with high power density

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Abstract

Nanostructured FeS_2 has been synthesized and used as the cathode material in LiSi/FeS_2 thermal batteries. With the same weight, the nanostructured cathode pellets are 23% thinner than conventional counterparts resulting in 31% increase of pellet density. Therefore, the volume of batteries can be reduced significantly. With the nanostructure, the electrode materials of the thermal batteries react more rapidly and completely during discharge resulting with a remarkable increase of energy output. The discharge tests show that the energy density of the nanostructured thermal batteries is two times higher (109 J/g) than the conventional counterpart (58 J/g). The nanostructured pellets are more robust mechanically than the conventional counterparts that could increase productivity and lower manufacturing cost.

Keywords: Thermal battery; Nanostructured materials; Lithium; Iron disulfide; Energy density

1. Introduction

With long shelf life and high reliability, thermal batteries are widely used in projectiles, rockets, bombs, mines, missiles, decoys, torpedoes and space exploration systems, emergency escape systems and similar applications [1]. Due to limited space allowance and pay-off load, the space propulsion programs look for new types of thermal batteries with high-energy density, compact size, thermal stability and robust mechanical properties. Nanostructured materials with particle sizes below 100 nm offer unique advantages such as high surface area and compactness during consolidation over conventional counterparts that usually have particle sizes between 50 and 100 μm (micronscale). The high compactness of the nanostructured materials makes it possible to press thinner pellets that deliver greater specific power [2]. In our observation, it is found that the significant portion of electrode materials have not been reacted (or consumed) after discharge. There is the potential to increase energy density using nanostructured materials. Thinner pellets of nanomaterials reduce the diffusion distance during discharge resulting in higher discharge rates. The homogenous contact of the nanostructured electrode materials allows them to react more completely and produce more power. During manufacturing of thermal batteries, pellets are easily broken causing considerable cost. It is found that Fe_2S as the cathode materials is not stable above 400 °C [3]. Its decomposition has a negative impact on power density. It is expected that nanomaterials will mitigate this.

In this work, nanostructured FeS_2 powder (nanostructured FeS_2) was synthesized and used as the cathode material. The nanostructured LiSi/FeS_2 and conventional micronscale LiSi/FeS_2 thermal batteries were constructed for various comparative tests that include material characterization, pellet density, mechanical robustness, pellet thermal stability, and battery discharge capacity.

2. Experimentation

The experimental work consists of synthesis of the nanostructured materials, fabrication of pellets, assembly of thermal batteries, and evaluation of battery performance.

2.1. Materials preparation

The cathode materials consist of 68% nanostructured FeS_2, 30% eutectic salt mixture (LiCl 45%–KCl 55%) and 2% SiO_2 (Aldrich 99% pure) [4]. The FeS_2 nanoscale powder was synthesized from high-energy ball milling process (SPEX8000) from its micron size precursor (CERAC 99.9% pure).

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The eutectic salts enhance the diffusion of Li ions, and acts as a binder. Adding silicon oxide particles is expected to immobilize the LiCl–KCl salt while it melts. The material was dried at 90 °C and fused at 500 °C. To strengthen the pellets and prevent electrolyte flowing out of cells when melted, 35% MgO (Aldrich 99% pure) powder was added and mixed homogeneously with the powdered eutectic salt [5–7]. To compare the performance, the cathode pellets were prepared with nanostructured and micronscale FeS_2 powder separately.

Due to the difficulty of ball milling lithium alloys, the commercial Li 44%–Si 56% alloy with micronscale grain size (Syprus 99.5% pure) was used as an anode material directly.

2.2. Electrode preparation

To prevent oxidation and contamination, a VAC MO-10 glove box was used for materials processing, pellet fabrication, battery assembly and discharge testing. The glove box was filled with pure nitrogen at the slightly positive pressure (1.5 in. water). The oxygen and moisture levels were under 10 ppm, respectively.

Twenty millimeter diameter pellets of electrodes and solid electrolyte were prepared by cold press process.

Li 44%–Si 56% (0.314 g) alloy powder (with 76–422 mesh particle size) was pressed to a pellet under 6000 psi static pressure. The thickness and density of the pellets obtained were 0.84 mm and 1.25 g/cm^2, respectively.

Blended electrolyte powder (0.550 g) was pressed to a pellet under 4000 psi static pressure. The thickness and density of the pellets obtained were 0.84 mm and 2.08 g/cm^2, respectively.

Mixed micronscale FeS_2–LiCl·KCl–SiO_2 powder (0.910 g) was pressed to a pellet under 4000 psi static pressure. The thickness and density of the pellets obtained were 1.12 mm and 2.57 g/cm^2 for micronscale powder and 0.86 mm and 3.37 g/cm^2 for nanoscale powder, respectively.

2.3. Robustness testing and thermal stability measurements of cathode pellets

Free fall tests were conducted to compare the robustness of the nanostructured and the conventional cathode pellets. The cross sections of fragments of the pellets were observed under SEM after free falling tests.

To verify thermal stability of the nanostructured and the micronscale FeS_2 cathode pellets, their weight loss and decomposition temperature were measured by thermal gravity analysis (TGA). The sample weight is 45 mg with heating rate 10 °C/min. The experiments were carried in the pure nitrogen atmosphere.

2.4. Battery assembly and performance evaluation

The anode, cathode and electrolyte pellets were piled up [8]. Five pounds per square inch pressure was applied vertically to hold the pile and to secure the appropriate contact of each pellet. The single-cell thermal battery weighs 1.774 g. With the same weight, the volumes of the nanostructured and the micronscale single-cell thermal batteries are 0.854 and 0.920 cm^3, respectively. Two electrical heaters contact the connectors directly to melt electrolyte and activate the thermal battery. Each heater has 300 W of power.

To evaluate electrochemical capacity (and power density), the single-cell thermal batteries that consist of the nanostructured and micronscale cathodes (with same weight, same diameter and different thickness) were activated at 400 °C and discharged at the constant current of 1 and 0.4 A, respectively. The computerized SOLARTRON 1287 electrochemical interface and 1260 Gain/Phase Analyzer have been employed to provide the constant current and to monitor variation in potential between the anode and cathode of cells during the discharging. The cutoff potential of the discharge was set at 0.8 V.

3. Results

3.1. Nanostructured FeS_2 powder

The average grain size of FeS_2 was reduced to 25 nm from 1 μm (1000 nm) after 30 h of ball milling as the X-ray diffraction and TEM observation show in Figs. 1–4. Extending milling time brings the crystalline size down further, but the tendency slows down as Fig. 5 shows. BET analysis was used to measure the surface area of the 30 h milled nanopowder as 6.61 m^2/g, that is six times larger than its micronscale precursor (see Fig. 6). The TEM images show that the 30 h ball-milled FeS_2 powder consists of the fine particles with round shape, similar thickness and homogenous size.

3.2. The density and robustness of the pellets

Table 1 lists the preparation parameters and properties of the pellets for the cathode, anode and electrolyte. It is noted that the thickness and the density of the nanostructured cathode pellets are 23% thinner and 31% higher, respectively, than its micronscale counterparts.

Using nanostructured FeS_2 powder (average size: 25 nm), the thickness of the pellet was reduced from 1.07 to 0.86 mm under the same condition (see Table 1). To compare the mechanical strength of the nanostructured and micronscale FeS_2 pellets, the 2 ft free falling test was conducted. The nanostructured FeS_2 pellets was broken into several large pieces, but their micronscale counterparts were seriously fragmented. This indicates that the nanostructured FeS_2 pellets are more robust than the conventional micronscale counterparts during manufacturing.

Cross sections of both nanostructured and micronscale fragments were investigated by SEM. As low magnification

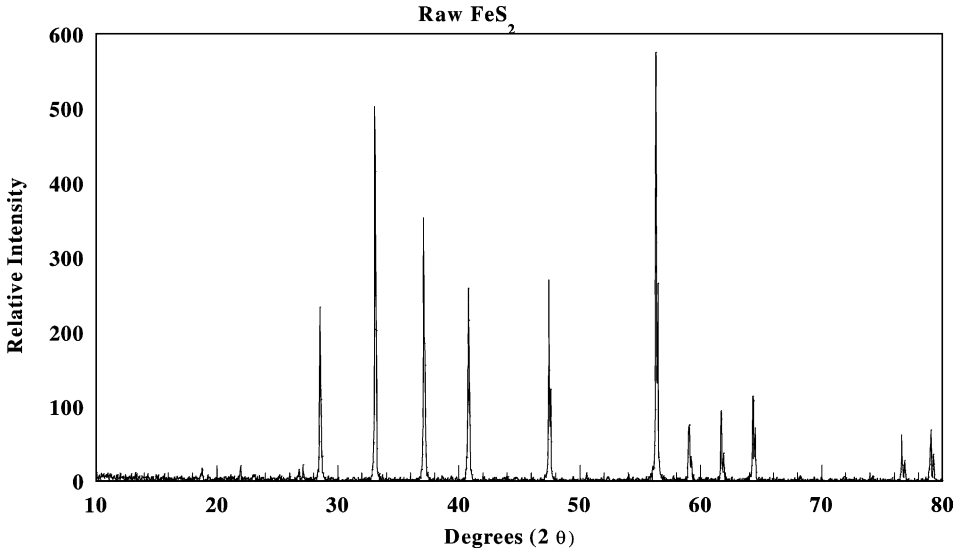

Fig. 1. X-ray diffraction spectrum of raw FeS_2 powder (micron size).

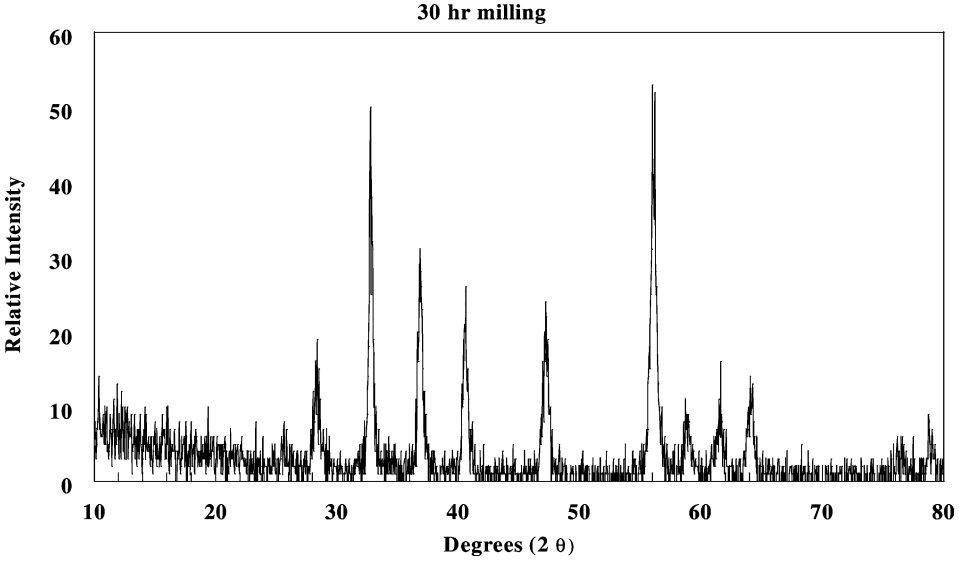

Fig. 2. X-ray diffraction spectrum of the FeS_2 powder after 30 h ball milling.

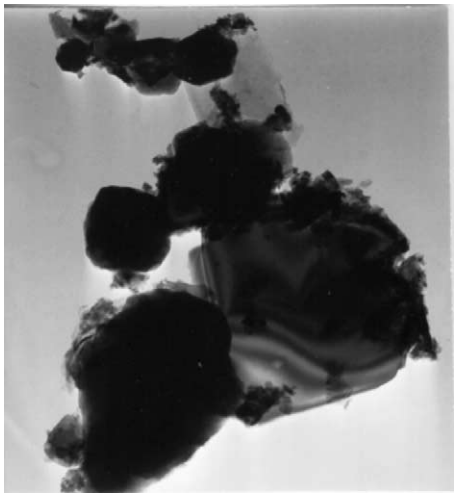

Fig. 3. TEM image of micron size FeS_2 powder (120,000×).

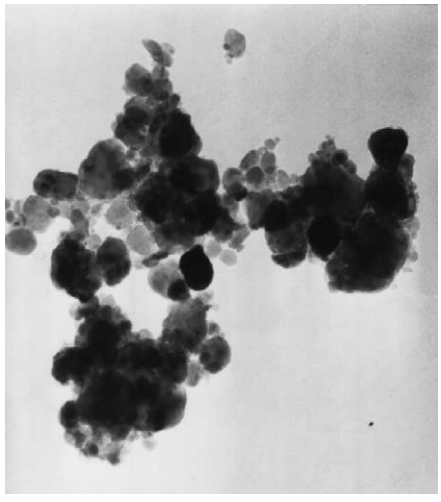

Fig. 4. TEM image of FeS_2 powder after 30 h ball milling (120,000×).

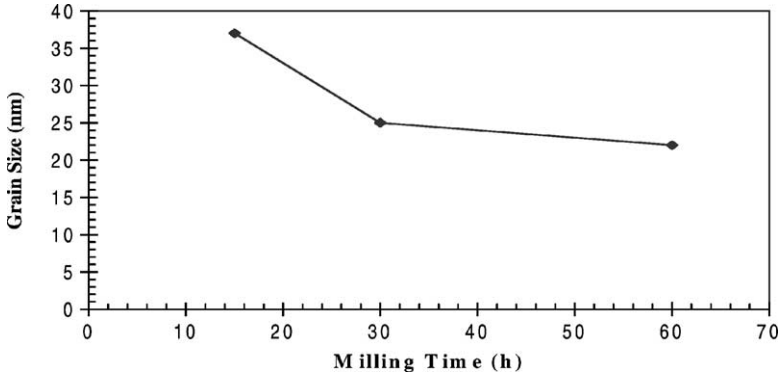

Fig. 5. The reduction of grain size with extension of milling time.

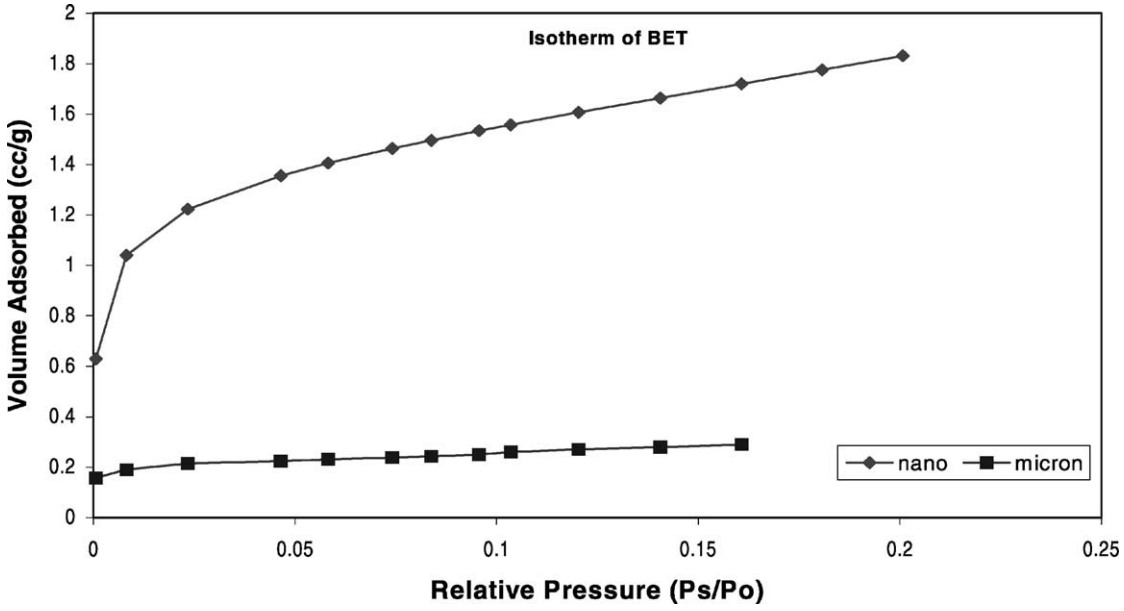

Fig. 6. BET results of the nanostructured FeS_2 and its micronscale precursor.

photos show (Figs. 7 and 8), the surface morphology of the cross section of the nanostuctured pellet appears more even and compact than the micronscale pellet. The high magnification pictures (Figs. 9 and 10) show that the particles of the nanostructured pellets are packed very closely together without large voids in comparison with the micronscale pellets.

3.3. Comparison of thermal stability of the nanostructured and micronscale electrodes

Iron disulfide will decompose as described in Eq. (1) when it is heated in an inert atmosphere. It results in a decrease of energy capacity of thermal batteries,

$$FeS_2 \rightarrow FeS + S \quad (1)$$

Table 1
The properties and preparation parameters of the pellets

Materials	Anode (micronscale)	Cathode (nanoscale)	Cathode (micronscale)	Electrolyte (nanoscale)
Composition	Li 44%; Si 56%	FeS_2 68%; LiCl·KCl 30%; SiO_2 2%	FeS_2 68%; LiCl·KCl 30%; SiO_2 2%	LiCl 45%; KCl 55%
Powder weight (g)	0.314	0.91	0.91	0.55
Pressure (psi)	6000	4000	4000	4000
Pellet dimension (mm)	$\phi 20 \times 0.84$	$\phi 20 \times 0.86$	$\phi 20 \times 1.12$	$\phi 20 \times 1.02$
Pellet density (g/cm^2)	1.25	3.37	2.57	1.75
Pellet number	16	8	8	16

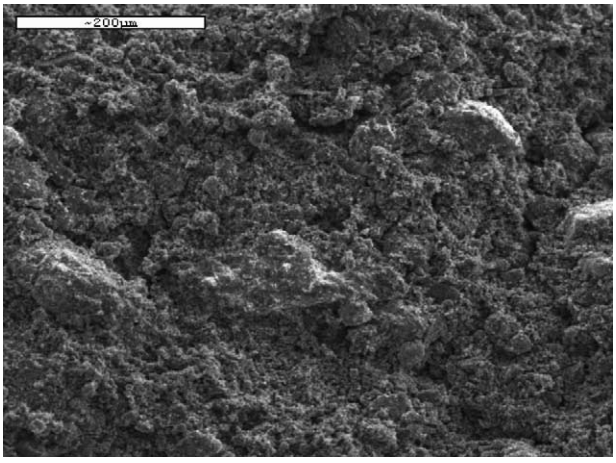

Fig. 7. The cross section of the nanostructured pellet fragment (200×).

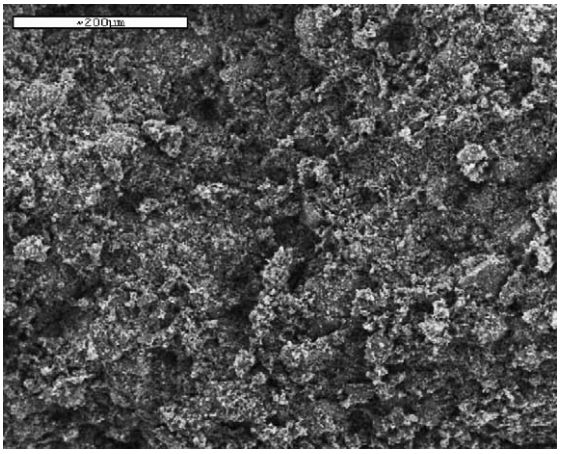

Fig. 8. The cross section of the micronscale pellet fragment (200×).

The exact temperature at which this occurs varies considerably depending on the purity (free sulfur level) and microstructure. The thermal gravimetric analysis (TGA) spectrum shows that the micronscale and nanostructured FeS_2 pellets lost 37 and 32% weight, respectively, after heating to 900 °C

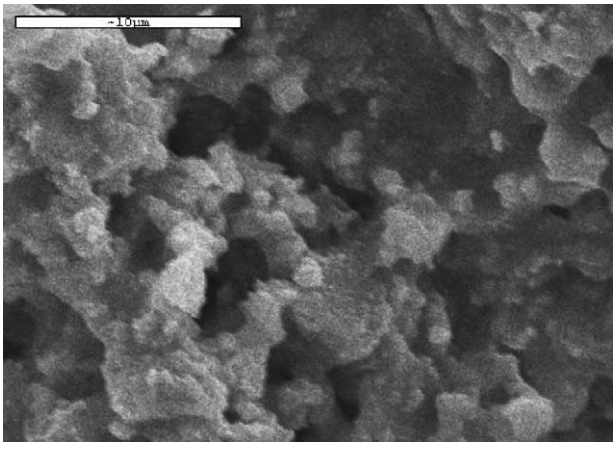

Fig. 9. The cross section of the nanostructured pellet fragment (5000×).

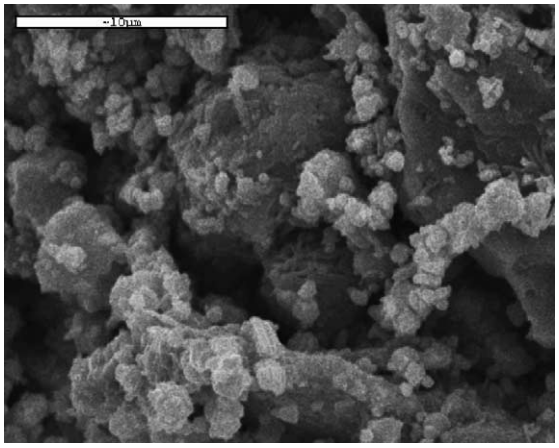

Fig. 10. The cross section of the micronscale pellet fragment (5000×).

(see Fig. 11). The micronscale FeS_2 pellet starts to decompose at 360 °C, but the nanostructured starts at 500 °C. This fact indicates that the thermal stability of the nanostructured cathode pellets is better than the micronscale counterparts.

3.4. Performance evaluation of the single-cell thermal batteries

To evaluate the performance of nanostructured and micronscale thermal batteries, electrochemical discharging was conducted. The thermal battery with the nanostructured cathode provides a 1 A constant current for 246 s until the potential falls to 0.8 V (see Fig. 12). The power density of the nanostructured single-cell thermal battery is [9,10]:

$$p_{\mathrm{W}}^{\mathrm{nano}} = \frac{(246/3600)}{1.774} = 0.0385\ \mathrm{Ah/g}$$

$$P_{\mathrm{V}}^{\mathrm{nano}} = \frac{(246/3600)}{0.854} = 0.080\ \mathrm{Ah/cm^3}$$

or

$$\varepsilon = \frac{\int_0^{246} I(t)U(t)\,\mathrm{d}t}{m} = \frac{\int_0^{246} U(t)\,\mathrm{d}t}{1.774} = 109\ (\mathrm{J/g})$$

In contrast, the thermal battery with the micronscale cathode generates 1 A of constant current for 119 s under the same discharge conditions (see Fig. 12). Its power density will be:

$$p_{\mathrm{W}}^{\mathrm{micron}} = \frac{(119/3600)}{1.774} = 0.0186\ \mathrm{Ah/g}$$

$$P_{\mathrm{V}}^{\mathrm{micron}} = \frac{(119/3600)}{0.920} = 0.0359\ \mathrm{Ah/cm^3}$$

or

$$\varepsilon = \frac{\int_0^{119} I(t)U(t)\,\mathrm{d}t}{m} = \frac{\int_0^{119} U(t)\,\mathrm{d}t}{1.774} = 58\ (\mathrm{J/g})$$

From the above calculation, it is found that the power density of nanostructured single-cell thermal battery is two times higher than the micronscale counterpart. This advantage of

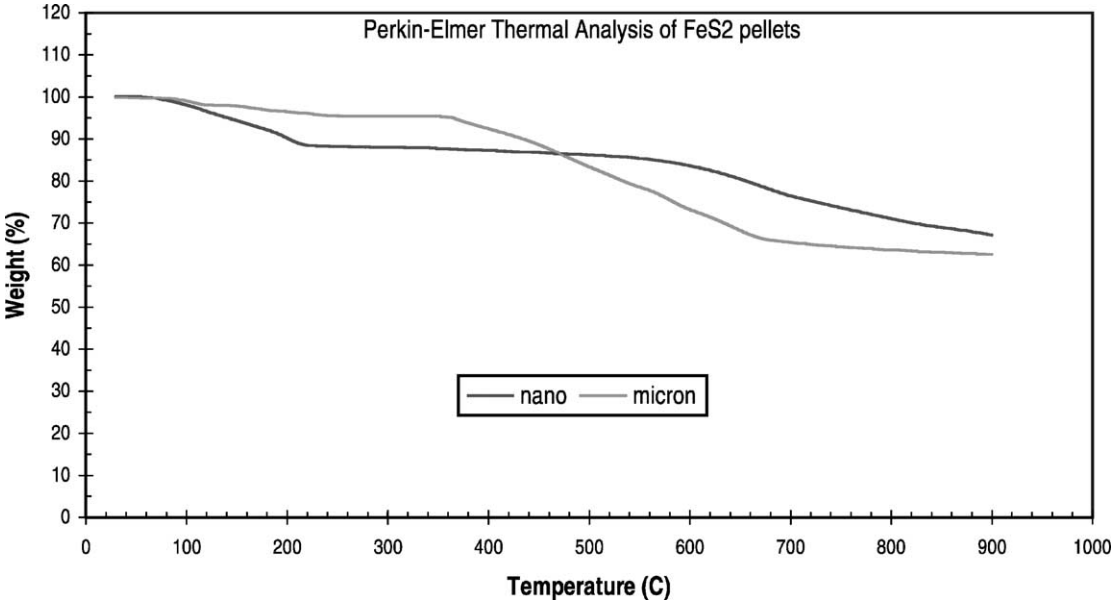

Fig. 11. Thermal gravimetric analysis of FeS_2 cathode pellets with different powder size.

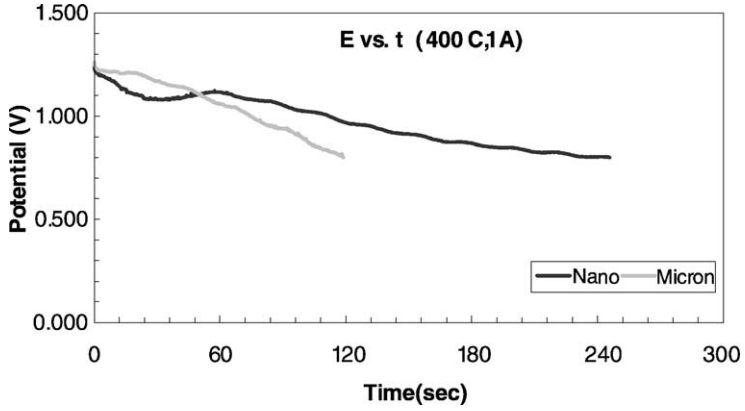

Fig. 12. A comparison in performance of the single-cell thermal batteries with the nanostructured cathode (0.86 mm thick) and the micronscale cathode (1.07 mm thick) at 1 A constant discharge current and 400 °C.

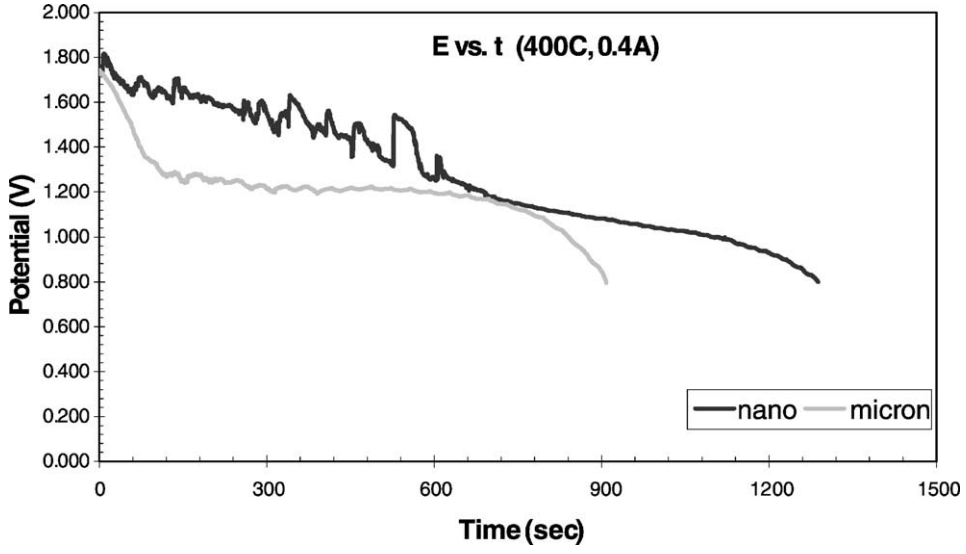

Fig. 13. A comparison in performance of the single-cell thermal batteries with the nanostructured cathode (0.86 mm thick) and the micronscale cathode (1.07 mm thick) at 0.4 A constant discharge current and 400 °C.

the nanostructured thermal battery also can be demonstrated in the small current (0.4 A) discharge test (see Fig. 13).

4. Discussion

It is understood that the power density of the thermal batteries depends on the efficiency of the electrochemical reaction which depends relies on temperature and Li ion diffusion. Because of the slow diffusion of the Li ion in the melted salt, the electrochemical reaction in thermal batteries is not always completed during the short activation period. It means that only a portion of electrode materials is consumed when electricity is generated. Obviously, it is desirable to increase the energy density of thermal batteries by consuming the active materials more completely. There are several approaches: increase the specific surface area by using nanostructured electrode materials; reduce the thickness of the electrode pellets, find a new electrolyte with a high diffusion coefficient for Li ion and so on.

The electrochemical reaction of the LiSi/FeS_2 thermal battery takes place in three steps as Eqs. (2)–(4) indicate:

$$4Li + 3FeS_2 \overset{2.1\,V}{\rightarrow} Li_4Fe_2S_5 + FeS \quad (2)$$

$$2Li + Li_4Fe_2S_5 + FeS \overset{1.9\,V}{\rightarrow} 3Li_2FeS_2 \quad (3)$$

$$6Li + 3Li_2FeS_2 \overset{1.6\,V}{\rightarrow} 6Li_2S + 3Fe \quad (4)$$

Each step has an individual contribution to the potential of the thermal battery. Because nanostructured cathode pellets are 20% thinner than their micronscale counterparts, the average diffusion distance of Li ions is shorter that allows the Li ions to penetrate the whole pellet in less time. That causes more pyrite (FeS_2) material to react with Li ion. In this case, all three electrochemical reaction steps will take place during the discharge process. However, for the micronscale thermal batteries, only one or two reactions may occur, because of the diffusion length of the Li ions. The specific surface area of the nanopowder is six times larger than the micronscale pellets which yields faster reaction rates. Both facts contribute to the higher power density of the nanostructured thermal batteries.

The mechanical robustness of the electrode pellets is increased by using nanostructured materials because of the higher compactness and the better morphology of the nanoscale powder. This advantage reduces the fragmentation of pellets, increases productivity and reduces the manufacturing cost.

In this work, nanomaterials were used for cathodes only. If a similar approach is developed to produce nanostructured anode materials, the energy density of thermal batteries will be increased further.

5. Conclusions

The nanostructured cathode materials (FeS_2) of the LiSi/FeS_2 thermal batteries can be synthesized by a high-energy ball milling process. The average grain size can be reduced from 1 μ to 25 nm after 30 h of ball milling. Nanostructured cathode pellets are 23% thinner than micronscale pellets resulting in a 31% increase of pellet density. The robustness and thermal stability of the nanostructured cathode pellets are also superior to the micronscale counterparts. The energy density of the thermal batteries with nanostructured cathodes is two times higher than their counterparts with the micronscale cathodes. It is therefore possible that using nanostructured materials will lead to a dramatic reduction of battery size and significant increase of energy density.

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