



Short communication

The electrochemical insertion and safety properties of the low-cost Li-ion active material, Li_2FeS_2

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ABSTRACT

The electrochemical insertion properties and safety characteristics of the alternative Li-ion positive electrode material, lithium iron sulfide (Li_2FeS_2) are presented. The active material is synthesized by a low cost, proprietary solid-state method. In terms of specific energy, the Li_2FeS_2 material offers a significant advantage over conventional lithium-ion positive electrode materials. The fully de-lithiated (charged) $\text{Li}_{2-x}\text{FeS}_2$ phase also demonstrates outstanding thermal stability suggesting that it may represent an excellent choice for safe, large format Li-ion battery applications.

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1. Introduction

The commercial success of Li-ion batteries for the next generation of large format applications is currently limited by the choice of suitable positive electrode active materials. These materials will be required to demonstrate a combination of properties including: high specific energy, low cost and inherent thermal stability. The Li_2FeS_2 material represents a unique opportunity to penetrate the large format market—an electroactive phase with an unrivalled combination of desirable characteristics. For example, based on the reversible cycling of two Li ions per formula unit, the Li_2FeS_2 has a theoretical specific capacity of 400 mAh g^{-1} coupled with an average discharge voltage of around 2.2 V vs. Li. These characteristics correspond to a theoretical specific energy of about 880 Wh kg^{-1} —a gravimetric positive electrode performance that far exceeds all known commercial Li-ion positive electrode materials. In addition, the sulfide is expected to offer good thermal stability—a necessary pre-requisite for safe behavior under Li-ion abuse conditions.

Li_2FeS_2 possesses a layered structure, with the ideal structure having layers of octahedrally coordinated lithium between layers of edge sharing lithium and iron tetrahedral. Previous work on Li_2FeS_2 has indicated the presence of two redox centers – i.e. $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{S}^{2-}/(\text{S}_2)^{2-}$ – which represents a unique material feature and partly explains the extremely high theoretical specific capacity [1,2].

There have been limited electrochemical performance data presented on the Li_2FeS_2 material in a Li-ion configuration [1,2]. In these reports the Li_2FeS_2 active material has been synthesized from expensive precursors using high temperature calcination procedures and followed by a ion-exchange process. Overall this multi-step preparative approach is considered to be expensive as well as difficult to scale, and we believe that this will limit the commercial exploitation of the sulfide material made by this method. By contrast, in the work presented here, high purity Li_2FeS_2 has been synthesized using a low-cost, and single-step solid state approach.

2. Experimental

The Li_2FeS_2 positive electrode material was synthesized by a proprietary solid-state method using low cost precursor materials such as FeS_2 (pyrite) and lithium carbonate. The precursors were intimately mixed, pelletized and then fired at temperatures between 750 and 800 °C under and inert nitrogen atmosphere for dwell periods of between 9 and 12 h. The pellets were then removed from the furnace and ball milled to reduce the particle size and finally classified. Powder XRD analysis confirmed that a high purity product was obtained with low levels of impurities. Using the hexagonal space group $P\bar{3}m1$, the unit cell parameters were determined to be very similar to the stoichiometric composition, Li_2FeS_2 , i.e. $a = 3.9034(2) \text{ \AA}$, $c = 6.3081(4) \text{ \AA}$ [3,4]. Further information on the synthesis method may be found in the related UK patent application [5].

Due to its high intrinsic lithium activity and low operating potential the as-prepared Li_2FeS_2 material is moisture sensitive,

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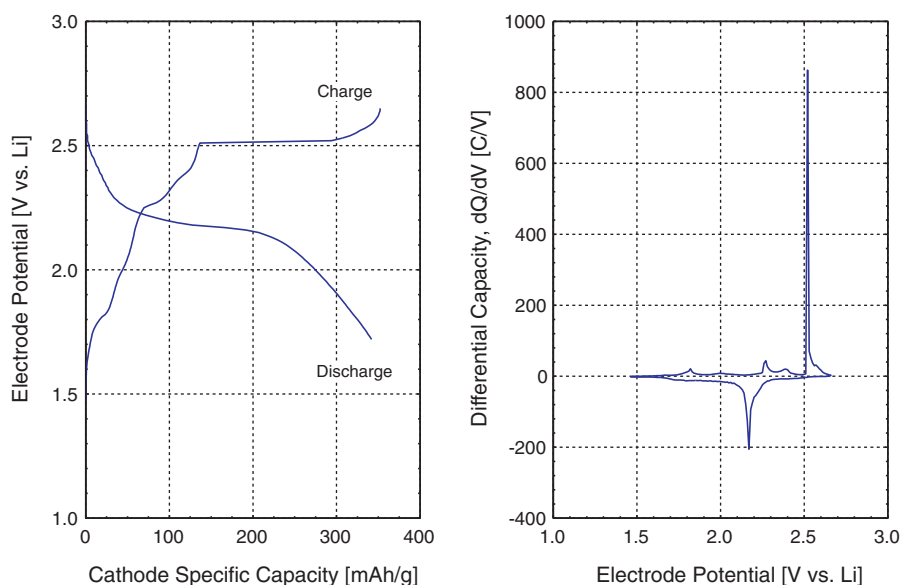


Fig. 1. First cycle EVS data for a representative Li//Li₂FeS₂ cell. The data were collected at 21 °C at an approximate C/15 rate for charge and discharge. Left: voltage profile; right: differential capacity.

so all material handling and electrode processing operations were carried out in controlled, low relative humidity conditions. Composite electrodes were constructed from active material, carbon black and polyethylene oxide (PEO) binder. For electrochemical testing, composite electrodes were fabricated using 90 wt% active material, 6 wt% conductive carbon and 4 wt% polyethylene oxide (PEO) binder. The coatings were dried overnight at 40 °C in a vacuum oven, and then calendared to a controlled porosity. For all electrodes an aluminum current collector was employed.

Preliminary electrochemical testing of the synthesized material was performed in metallic lithium test cells. For lithium-ion testing the Li₂FeS₂ composite electrodes were capacity balanced against a commercial crystalline graphite negative electrode. In all electrochemical tests the electrolyte comprised a 1.1 M solution of LiPF₆ in a solvent mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). Cycle life and rate tests were performed using a range of discharge current densities and fixed voltage limits. In the tests described herein the C rate for the Li//Li₂FeS₂ system is defined for a theoretical specific capacity of 400 mAh g⁻¹. These tests were undertaken using a commercial battery cycler (Maccor Inc., Tulsa, OK, USA).

High-resolution electrochemical measurements were performed using the electrochemical voltage spectroscopy (EVS) technique [6]. EVS is a voltage step method, which provides a high-resolution approximation to the open circuit voltage curve for the electrochemical system under investigation. It also allows the direct measurement of differential capacity data which is useful for the elucidation of the lithium insertion reactions.

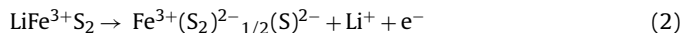
3. Results and discussion

Fig. 1 shows the first cycle EVS data for the Li//Li₂FeS₂ system and demonstrates a reversible material utilization of over 340 mAh g⁻¹. This performance compares favourably with the theoretical specific capacity of 400 mAh g⁻¹. This extremely high material utilization results from the unique combination of having two Li ions per formula unit, and the presence of two active redox centers, i.e. the Fe and S. The Li₂FeS₂ undergoes a series of complex, but reversible structural changes during the complete discharge/charge process [3]. The charge behavior may be sub-divided into two distinct voltage regions: a generally sloping area between

1.5 and 2.5 V and a voltage plateau centered at 2.5 V. In addition these regions can clearly be identified on the differential capacity plot. During the sloping voltage region the Fe²⁺ is oxidized to Fe³⁺ with the con-current extraction of one Li ion:



The voltage plateau at around 2.5 V vs. Li, corresponds to partial sulfur oxidation, again with con-current extraction of one Li ion:



Raman and infra-red studies reported by Blandeau et al. [4] indicate that this new FeS₂ phase (Fe³⁺(S₂)²⁻_{1/2}(S)²⁻) contains two distinct Fe³⁺ sites, split between octahedral and tetrahedral positions.

The discharge process is less distinct, characterized by a single differential capacity peak centered at around 2.2 V vs. Li. Both Fe³⁺ and sulfur reduction takes place during this discharge process. From inspection, we can detect that the average discharge voltage is about 2.2 V vs. Li, indicating a specific energy for the Li//Li₂FeS₂ system of more than 740 Wh kg⁻¹—a significant improvement in energy performance over commercially available Li-ion positive electrodes. The generally symmetrical nature of the differential capacity profile confirms the coulombic and energetic reversibility for the lithium insertion/extraction reactions.

In Fig. 2 we present the first and second cycle discharge voltage profiles for a typical graphite//Li₂FeS₂ lithium-ion cell. These data were collected at an approximate C/10 rate for charge and discharge. Due to the near equivalent in specific capacities (>300 mAh g⁻¹) of the two active materials in this Li-ion configuration, the electrode mass balance ratio was close to 1:1. The first cycle discharge capacity is equivalent to a positive electrode material utilization of 325 mAh g⁻¹. Combined with the average discharge voltage of around 2.0 V, this corresponds to a specific energy for the Li₂FeS₂ of about 650 Wh kg⁻¹. This active material performance compares favourably with commercial Li-ion positive electrode materials. For example, in a graphite-based Li-ion cell, the LiCoO₂ positive electrode typically operates at an average discharge voltage of about 3.7 V and with a specific capacity of around 135 mAh g⁻¹. This performance corresponds to a positive electrode specific energy of less than 500 Wh kg⁻¹. Clearly, for high energy applications the lower operating voltage of the Li₂FeS₂-based Li-ion

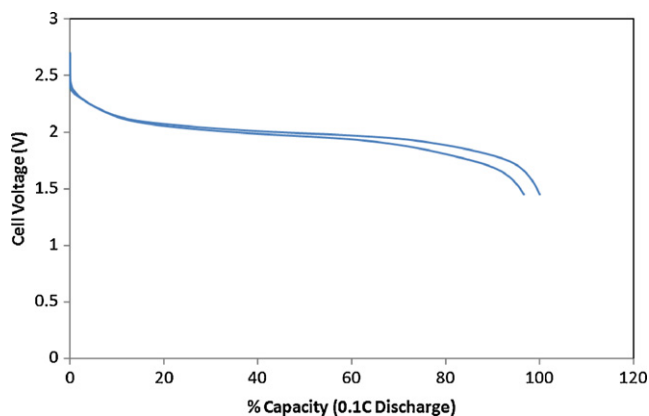


Fig. 2. First and second discharge voltage profiles for a representative graphite//Li₂FeS₂ Li-ion cell. The data were collected at 21 °C at an approximate C/10 rate for charge and discharge.

cell is easily off-set by its far superior specific capacity. In addition, in some applications the lower operating cell voltage may prove to be an advantage especially where alternative electrolytes may be employed.

Fig. 3 depicts the cycle life performance of a typical graphite//Li₂FeS₂ Li-ion cell. The data were collected at 23 °C using a C/10 rate for charge and discharge. Following 70 full charge/discharge cycles the cell discharge capacity has faded to about 70% of the original. Separate low rate tests (not shown here) indicate that the large majority of this capacity fade may be attributed to a steady increase in the cell impedance and not to

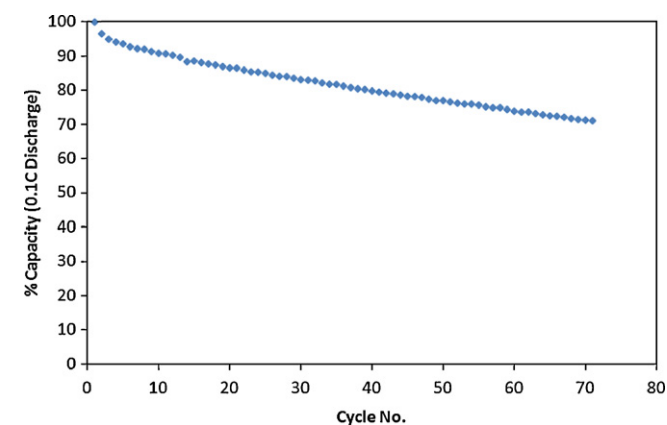


Fig. 3. Preliminary cycling behavior for a representative graphite//Li₂FeS₂ Li-ion cell. The data were collected at 21 °C at an approximate C/10 rate for charge and discharge.

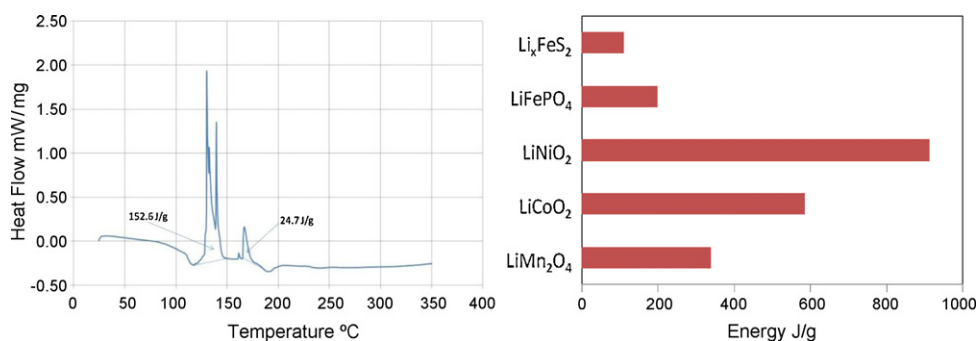


Fig. 5. The thermal stability of Li₂FeS₂. Left: the typical thermal response for a fully de-lithiated Li₂FeS₂ sample obtained using differential scanning calorimetry; right: comparison of the thermal behavior of Li₂FeS₂ and other commercial Li-ion positive electrode materials.

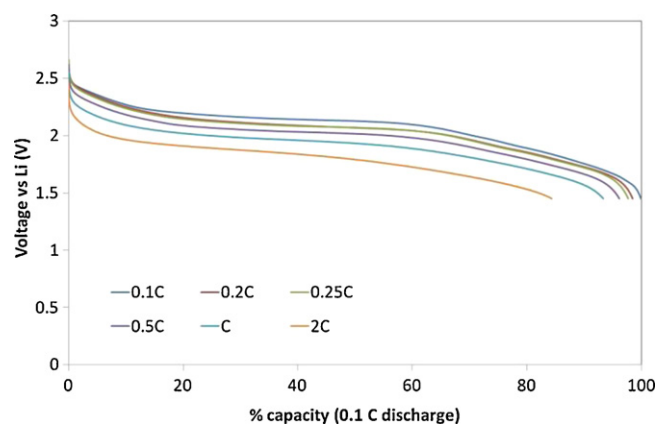


Fig. 4. The rate performance of a representative Li//Li₂FeS₂ cell. The data were collected at 21 °C using a range of discharge current densities varying between 0.1C and 2.0C.

significant irreversible active lithium loss. There is not substantial irreversible capacity loss during the cycling regimen. Additional low rate testing indicates that most of the capacity fade determined at the C/10 rate is recoverable. Recent improvements to the electrode processing method (for example, binder and electrode formulation optimization) have greatly reduced the level of capacity fade. Further improvements are anticipated.

The rate performance of the Li₂FeS₂ material, determined at 21 °C in a metallic lithium test cell, is depicted in **Fig. 4**. The positive electrode in this test has been optimized for an energy application rather than for power. It can be concluded that the active material demonstrates relatively good power capability with >80% of the rate capacity retained at the 2C rate. Within the range of measurements, the level of voltage polarization is quite low. Only a small increase in the iR drop can be noted at the higher C rate discharge regimens.

Based on chemical and structural considerations, it was anticipated that the de-lithiated Li_{2-x}FeS₂ materials should exhibit good thermal stability. For these tests, metallic lithium half-cells were fully charged and then opened inside an argon-filled glove box. The de-lithiated positive electrodes were rinsed with DMC. About 20 mg of the positive electrode and 10 mg of 1 M LiPF₆ EC/EMC electrolyte were then transferred to an Al DSC sample holder for testing. The DSC results from these tests are shown in **Fig. 5**.

From inspection one can determine that the temperature range for the exotherm (heat release) extends from about 130 to 180 °C and that the overall heat flow amounts to about 177 J g⁻¹. In summary, the exothermic response is lower even than that found in polyanion active materials such as LiFePO₄. Due to its relatively good thermal stability, the lithium iron phosphate material is increasingly regarded as the safest, commercially positive elec-

trode choice for Li-ion applications. Clearly there is no possibility for any oxygen release from the sulfide-based active material and we believe this will represent a distinct and important advantage over conventional layered oxide positive electrodes. Supplementary safety tests indicate that during an overcharge event the Li_2FeS_2 positive electrode simply decomposes with the release of no gaseous products.

Fig. 5 also shows the comparative thermal behavior for other known Li-ion positive electrode materials tested under similar conditions [7]. In summary the Li_2FeS_2 phase shown favourable thermal stability and further suggests that this material should be suitable for incorporation in large format Li-ion cells and batteries where safety behavior will be at a premium.

4. Conclusions

In this study the alternative Li_2FeS_2 positive electrode material has been synthesized using an inexpensive, proprietary method. In a first generation prototype graphite-based Li-ion cell the Li_2FeS_2 demonstrates a specific energy of over 650 Wh kg^{-1} —an active material performance that easily exceeds that of LiCoO_2 , LiMn_2O_4 or LiFePO_4 . When this electrochemical performance is considered

in combination with its excellent thermal stability we believe that Li_2FeS_2 may well represent a near ideal positive electrode choice for the next generation of large format Li-ion applications. Further material and electrode optimization will be necessary to improve other cell characteristics such as the cycle life and calendar life.

Acknowledgement

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