

# Lithium-ion/iron sulphide rechargeable batteries

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## Abstract

Lithium-ion batteries are now well known and widely available commercially. The vast majority use lithium cobalt oxide or variants as the cathode material. This has the advantage of good performance but the cost of the cobalt is high and it is slightly toxic. Iron would be preferable on grounds of cost and safety but unfortunately lithium iron oxides cannot be cycled. Iron compounds are cheap and iron sulphides can readily be obtained as minerals, without the need for chemical synthesis. However, to make a lithium-ion battery, the cathode material must contain lithium so the iron sulphide must be lithiated to use this as a cathode material. This can be synthesised by literature methods involving solid state syntheses at high temperature for long times. New syntheses have been developed which are much quicker and easier. Results on cycling of lithium-ion cells using lithiated iron sulphide prepared by the new method will be described using laboratory and envelope (pouch) cells. Because of the use of cheaper materials, these should be preferable to existing technology, particularly for larger size applications, such as electric vehicles.

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## 1. Introduction

Lithium-ion batteries are now well known and many developments are possible and significant improvements are likely in the next few years [1,2]. At present, lithium-ion batteries use lithium cobalt oxide,  $\text{LiCoO}_2$ , (or variants) as the cathode material. This has the advantage of a long cycle life but the cost of the cobalt is high. This is acceptable for small items, such as mobile phones, but not for larger items, such as electric vehicles. Ideally, the cobalt should be replaced by a cheaper metal, such as iron. Unfortunately, lithium iron oxides do not cycle and cannot be used as cathode materials in lithium-ion batteries. However, it was established in the early days of lithium rechargeable batteries that transition metal sulphides, such as titanium or molybdenum sulphides, did cycle well and these were used in lithium metal rechargeable batteries [3–5] but, since the introduction of the lithium cobalt oxide cathode material, sulphides have not been investigated much recently. On grounds of cost, an iron sulphide would be preferred, and for a lithium-ion battery, the cathode material must be a lithiated iron sulphide,  $\text{Li}_2\text{FeS}_2$ . Although the voltages for sulphides are lower than for oxides, their capacities are higher, so high energy den-

sities are achievable. Properties of  $\text{LiCoO}_2$  and  $\text{Li}_2\text{FeS}_2$  are compared in Table 1 (below). The capacities are calculated and the voltages are typical observed ones. The calculated energy densities suggest that  $\text{Li}_2\text{FeS}_2$  has considerable advantages as a cathode material for lithium-ion batteries.

Lithium/iron disulphide primary batteries are now well known and are commercially available [5]. High temperature lithium/iron disulphide rechargeable batteries using molten salt electrolytes have been investigated extensively [3] but have not reached production. Ambient temperature lithium/iron disulphide rechargeable batteries have been investigated [6]. However, on grounds of long cycle life and safety, a lithium-ion rechargeable battery would be preferable. One difficulty in making a lithium-ion/iron disulphide battery is the need to synthesise the discharge product: lithiated iron sulphide,  $\text{Li}_2\text{FeS}_2$ . The literature process [7] involves heating lithium sulphide and iron sulphide at  $870^\circ\text{C}$  for 35 days. This is clearly inconvenient and very wasteful of energy and is obviously impossible for industrial production. A more recent process involved heating lithium sulphide and iron sulphide for 5 h at  $950^\circ\text{C}$  in a vitreous carbon crucible inside an evacuated silica tube [8]. New syntheses have been developed in which a solvent, such as a molten sulphur [9] or a molten salt [10], is used to reduce the temperature of the reaction and to speed the process. These materials have been tested in laboratory cells, similar to those described previously [11] and also in envelope (pouch) cells.

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Table 1  
Theoretical comparisons of LiCoO<sub>2</sub> and Li<sub>2</sub>FeS<sub>2</sub>

Cathode	Reaction	Molecular weight	No electrons	Capacity (C/g)	Capacity (mAh/g)	Voltage	Energy density (Wh/kg) cathode
Li <sub>2</sub> FeS <sub>2</sub>	Li <sub>2</sub> FeS <sub>2</sub> → 2Li + FeS <sub>2</sub>	133.85	2	1442	400	2.3	921
LiCoO <sub>2</sub>	LiCoO <sub>2</sub> → 0.5Li + Li <sub>0.5</sub> CoO <sub>2</sub>	97.87	1/2	493	137	3.6	493

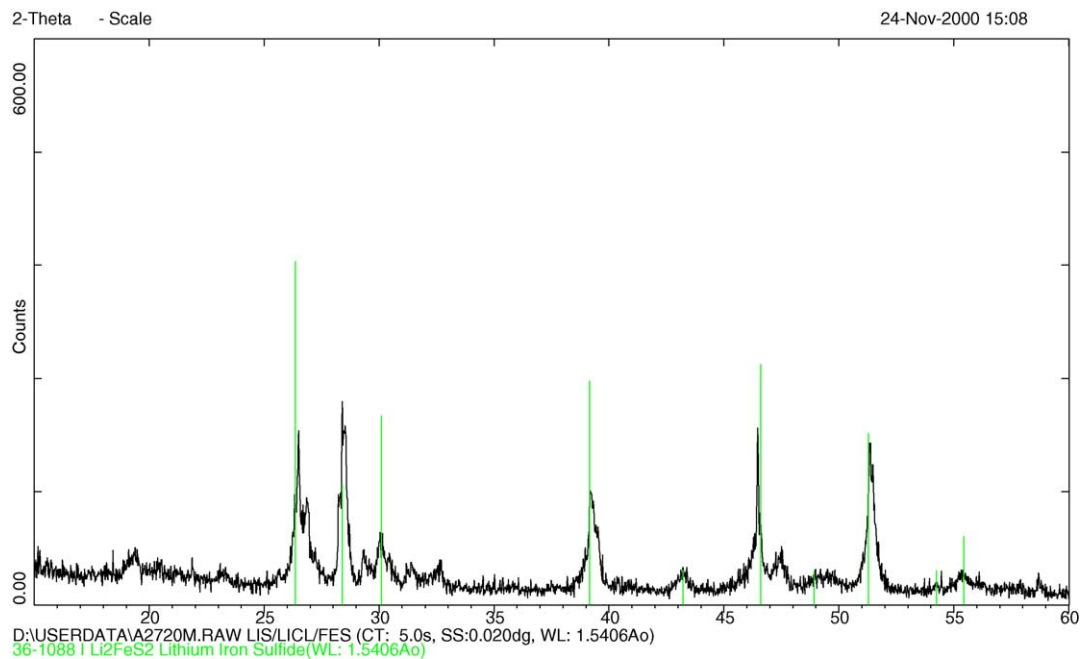


Fig. 1. Li<sub>2</sub>FeS<sub>2</sub> made from LiCl.

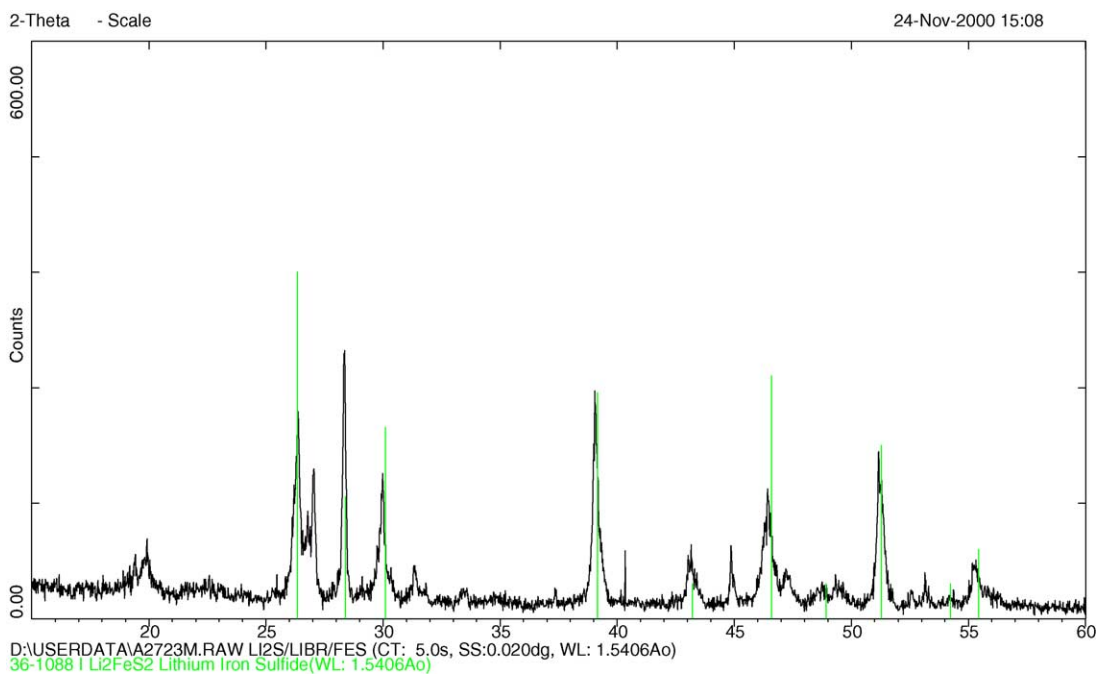


Fig. 2. Li<sub>2</sub>FeS<sub>2</sub> made from LiBr.

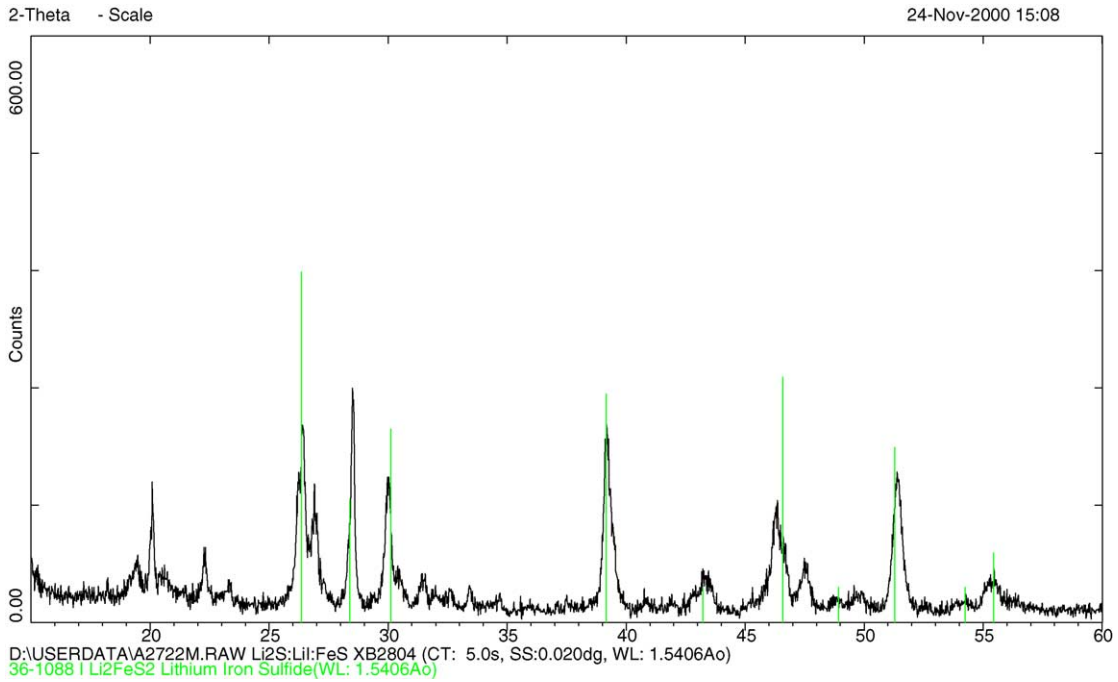
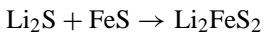


Fig. 3.  $\text{Li}_2\text{FeS}_2$  made from  $\text{LiI}$ .

## 2. Experimental

Lithium iron sulphide was synthesised by the reaction of lithium sulphide and iron sulphide in a solvent of molten lithium chloride according to the reaction:



Stoichiometric amounts of reagents were mixed together and a salt, either lithium chloride, bromide or iodide, was added. The furnace was heated to temperatures above the melting points of the added salts (lithium chloride  $610^\circ\text{C}$ , lithium bromide  $552^\circ\text{C}$  or lithium iodide  $446^\circ\text{C}$ ) and held at that temperature for about an hour. After cooling, the

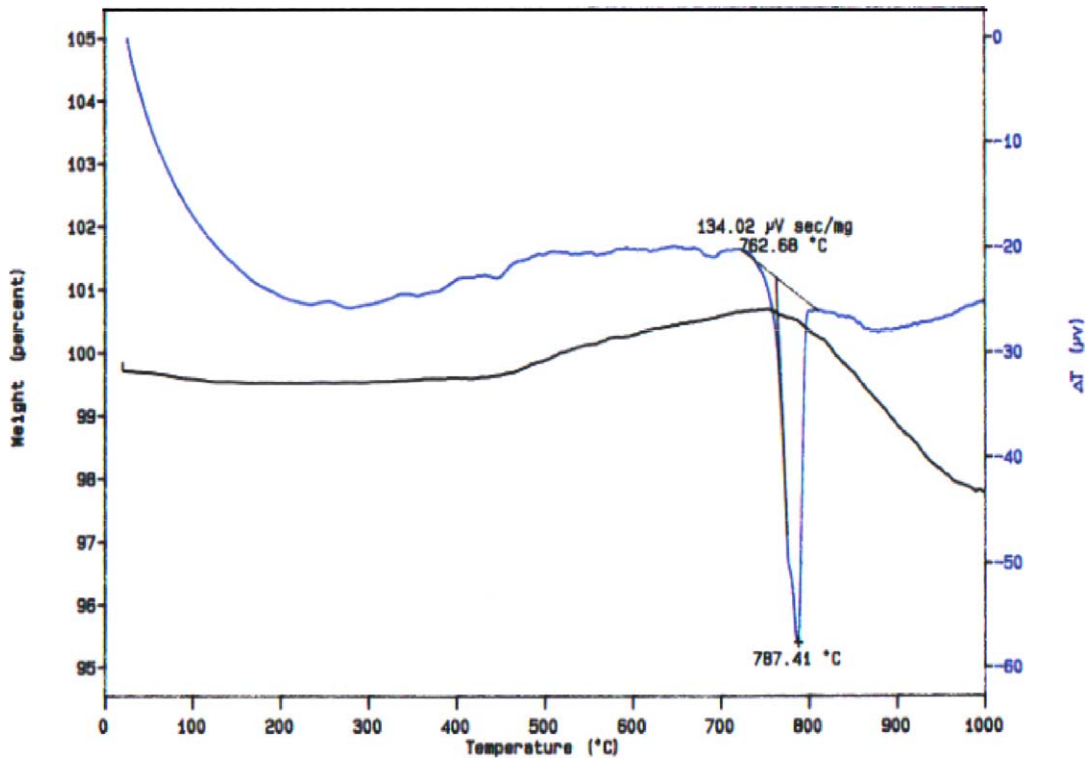


Fig. 4. Thermal analysis of  $\text{Li}_2\text{FeS}_2$ .

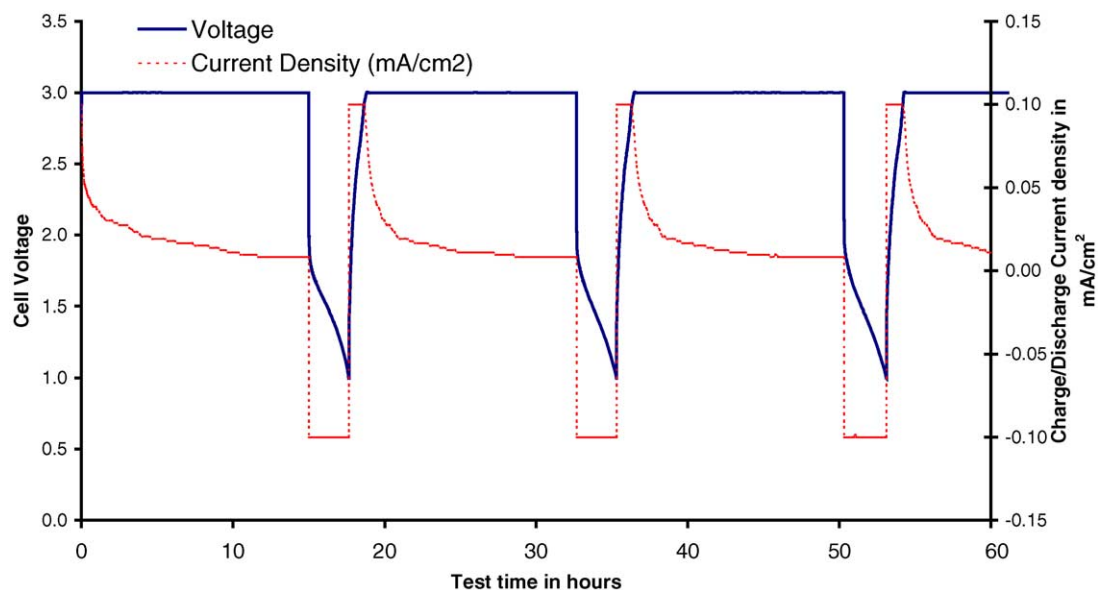


Fig. 5. Cycling of a Li-ion  $\text{Li}_2\text{FeS}_2$  laboratory cell made in LiCl cycled at  $0.1 \text{ mA/cm}^2$ .

salt was removed from the lithium iron sulphide product by Soxhlet extraction by refluxing with a suitable organic solvent (pyridine for LiCl, ether for LiBr, acetonitrile for LiI) to dissolve the salt. The lithium iron sulphide product was characterised by X-ray (Figs. 1–3) and by thermal analysis (Fig. 4). This showed that the material made by this method was identical to the product described in the literature, made by high temperature synthesis.

The anode and cathode coatings were made by normal doctor blade procedures. As  $\text{Li}_2\text{FeS}_2$  is very moisture sensitive, cathode coatings were done in an argon-filled glove box. Because of the sensitivity of  $\text{Li}_2\text{FeS}_2$  to moisture, coatings used a hydrophobic solvent, hexane, to dissolve a hydro-

carbon binder, ethylene propylene diene monomer, EPDM. Coatings made by this technique showed good adherence to the backing foil, aluminium, which is used as the positive electrode current collector.

### 3. Results

Materials made as described above, have been cycled in lithium-ion laboratory cells. Results are shown in Figs. 5 and 6. It can be seen that the cells cycled. The voltage range used was 3.0–1.5 V. The discharge plateau was about 2.0 V. These results are in agreement with the results of Hansen and West

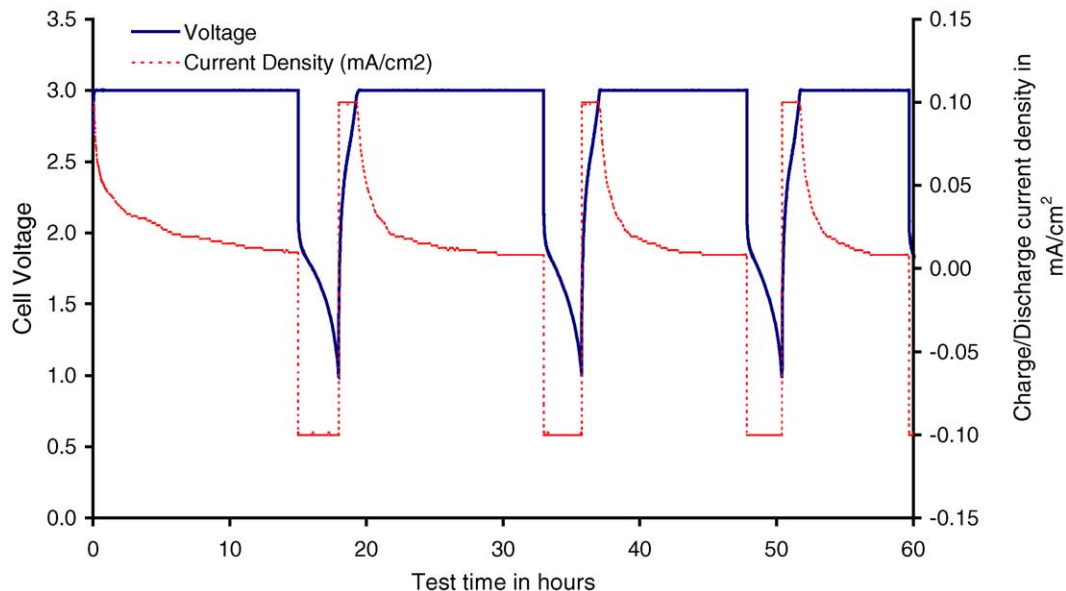


Fig. 6. Cycling of a Li-ion  $\text{Li}_2\text{FeS}_2$  laboratory cell made in LiI cycled at  $0.1 \text{ mA/cm}^2$ .

[6] who cycled lithium metal/iron disulphide cells. While iron disulphide discharges in lithium primary cells at 1.5 V, Hansen and West have shown that this chemistry recharges at about 2.5 V and then discharges at around 2.0 V, indicating that chemical changes have taken place and that different phases have formed during the cycling. Direct cycling of lithium-ion/iron sulphide cells shows the same behaviour.

#### 4. Conclusions

It has been shown that a lithium-ion/iron disulphide battery can be made by chemically synthesising lithium iron sulphide and using this as the cathode for a lithium-ion battery. This system has the potential for cheaper lithium-ion batteries as it uses iron instead of cobalt in the standard cathode material, lithium cobalt oxide.

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