

## A STUDY OF PYRITE-BASED CATHODES FOR AMBIENT TEMPERATURE LITHIUM BATTERIES BY *IN SITU* $^{57}\text{Fe}$ MOSSBAUER SPECTROSCOPY

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### Summary

The electrochemical behaviour of  $\text{Li}/\text{FeS}_2$  and  $\text{Li}/\text{Li}_2\text{FeS}_2$  cells near room temperature has been studied by *in situ*  $^{57}\text{Fe}$  Mössbauer spectroscopy. We describe the design of the *in situ* Mössbauer electrochemical cell which was used to monitor the electronic properties of the cathode host while the cell was charged and discharged. When  $\text{Li}/\text{FeS}_2$  and  $\text{Li}/\text{Li}_2\text{FeS}_2$  cells are charged to 2.8 V, the cathode is a mixture of non-stoichiometric  $\text{FeS}$  and  $\text{S}$ . At ambient temperature, these cells show poor reversibility.

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### Introduction

The naturally occurring mineral pyrite  $\text{FeS}_2$  has been used as a cathode material in lithium secondary batteries [1]. Studies showed that at 400 °C,  $\text{Li}/\text{FeS}_2$  cells have excellent reversibility. Chemically synthesized  $\text{Li}_2\text{FeS}_2$  has been studied in lithium batteries at room temperature [2]. Early reports speculated that  $\text{Li}_2\text{FeS}_2$  is an intercalation compound which has the  $\text{CdI}_2$  structure [2, 3]. Previous studies conducted with  $^{57}\text{Fe}$  Mössbauer and infrared spectroscopy showed that, at room temperature,  $\text{Li}_2\text{FeS}_2$  exhibits reversible behaviour with respect to lithium [4]. A new iron disulfide,  $\text{FeS}_2$ , which differs from pyrite or marcasite, was reported to be the recharge product of  $\text{Li}_2\text{FeS}_2$ . As we show here, our data do not support this conclusion.

More recently, the crystal structure of  $\text{Li}_2\text{FeS}_2$  was determined by single G-crystal X-ray diffraction [5]. The structure consists of hexagonal-close-packed layers of sulfur with iron and lithium, equally and randomly, filling all of the tetrahedral interstices between pairs of sulfur layers. The remaining lithium atoms fill the octahedral interstices between the alternate sulfur layers.

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Here,  $\text{Li}/\text{FeS}_2$  and  $\text{Li}/\text{Li}_2\text{FeS}_2$  cells operated near room temperature are studied by an *in situ* Mössbauer experiment that allows one to correlate the variation of the cell voltage with the related changes of the cathode host. We describe the design of the *in situ* Mössbauer electrochemical cell that was used in the experiment. The present study shows that  $\text{Li}/\text{FeS}_2$  and  $\text{Li}/\text{Li}_2\text{FeS}_2$  exhibit similar cell reactions. Upon recharging these cells, as the lithium atoms are removed from the cathodes,  $\text{FeS}_2$  does not form. Instead, the cathodes consist of a mixture of non-stoichiometric  $\text{FeS}$  and  $\text{S}$ .

## Experimental

Natural  $\text{FeS}_2$  crystals (Teck Mining Corporation, with 0.2 at.% Cu, 0.1 at.% each of Al and Ca, and trace amounts of Pb and Zn) were ground to a powder of less than  $45\ \mu\text{m}$  in size. Chemical syntheses of  $\text{Li}_2\text{FeS}_2$  and delithiated  $\text{Li}_2\text{FeS}_2$  were performed with reagents reported by Murphy *et al.* [6].  $\text{Li}_2\text{FeS}_2$  was prepared by reacting stoichiometric amounts of lithium metal and  $\text{FeS}_2$  in a stirred solution of naphthalene in tetrahydrofuran for 16 h. The reaction products were washed, dried, and heated at  $800\ ^\circ\text{C}$  for 16 h under a continuous flow of argon.  $\text{Li}_2\text{FeS}_2$  is air-sensitive, and handling of this material was carried out in an argon-filled glove box. In the delithiation process, finely-ground  $\text{Li}_2\text{FeS}_2$  was allowed to react in a stirred solution of iodine in acetonitrile (AN) for at least 14 h. An even layer ( $20 - 30\ \text{mg cm}^{-2}$ ) of the powdered material of interest was spread, from a binder slurry, on an aluminum substrate and evaporated to dryness. With these cathodes, lithium foil, and porous poly(propylene) separators, two-electrode electrochemical cells, which have been described elsewhere [7], and *in situ* Mössbauer cells were constructed with 1 M  $\text{LiAsF}_6/\text{PC}/\text{EC}$  (50:50 by volume) as the electrolyte.

Figure 1 shows the *in situ* Mössbauer cell. The "cathode-separator-anode" sandwich is assembled between two 0.025 cm thick beryllium windows seated in the recesses of the top and bottom contact plates. The centre beams on the contact plates provide structural support and prevent the beryllium from flexing excessively. Excessive flexing causes uneven pressure on the electrodes and leads to poor electrical connection to the cell. A greased poly(propylene) gasket provides the gas-tight seal between the two Be windows. The cell sits on top of the detector mount, which is equipped with heaters and a temperature sensor so that the cell can be operated at elevated temperatures. The lithium composition of the cathode is altered by stepping the voltage of the cell with a potentiostat equipped with a digital coulometer. Mössbauer spectra were measured when the current flow through the cell was less than  $5\ \mu\text{A}$ .

The  $^{57}\text{Fe}$  Mössbauer spectra were recorded in transmission geometry. The  $^{57}\text{Co}$  source, mounted on an electromechanical transducer, was driven back and forth at constant acceleration to scan a range of velocities, typically from  $-8$  to  $8\ \text{mm s}^{-1}$ . When the cell is aligned with the radioactive source,

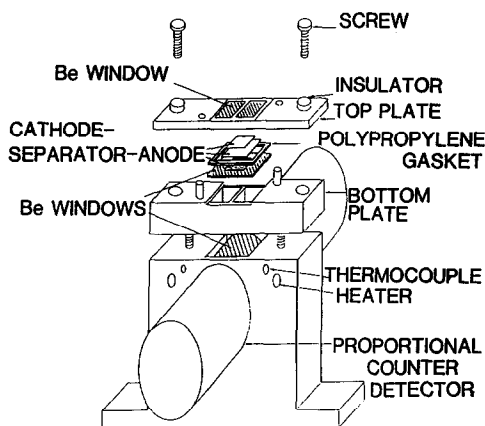


Fig. 1. An *in situ* Mössbauer cell.

the 14.4 keV gamma rays pass through the cell and enter the proportional counter detector; the signals were accumulated in a multi-channel analyzer.

## Results and discussion

Figure 2 shows the first discharge of Li/FeS<sub>2</sub> cells at 21, 30, 37, 55, and 75 °C at a rate of 20 h for the transfer of one Li per Fe. At 21 °C, the voltage curve shows a single plateau indicating a one-step reaction



The reaction becomes stepwise if the discharge current is sufficiently lowered or if the temperature is increased. At temperatures above 37 °C, the cell reaction proceeds stepwise, forming Li<sub>2</sub>FeS<sub>2</sub>, which is apparently amorphous when formed at low temperatures:

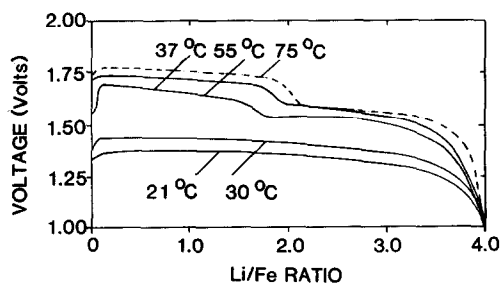


Fig. 2. The first discharge of Li/FeS<sub>2</sub> cells at temperatures ranging from 21 to 75 °C at a rate of 20 h for Li/Fe = 1.



The evidence for the presence of amorphous  $\text{Li}_2\text{FeS}_2$  at  $\text{Li}/\text{Fe} = 2$  is shown in Fig. 3. The recharge voltage profile of an  $\text{Li}/\text{FeS}_2$  cell that had been discharged to  $\text{Li}/\text{Fe} = 2$  at  $37^\circ\text{C}$  exhibits very similar behaviour to the first recharge of a cell fabricated with chemically synthesized  $\text{Li}_2\text{FeS}_2$  ( $\text{Li}/\text{Li}_2\text{FeS}_2$ ). The products of reaction (3) have been confirmed by powder X-ray diffraction and Mössbauer spectroscopy.

Figure 4(a) and (b) shows the *in situ* Mössbauer spectra of an  $\text{Li}/\text{FeS}_2$  cell that had been discharged to  $\text{Li}/\text{Fe} = 2$  and recharged to 2.45 V and 2.80 V, respectively, at  $55^\circ\text{C}$ . At these voltages, magnetic hyperfine splittings due to the formation of  $\text{FeS}$  are observed. At 2.80 V, the spectrum consists of two distinct species, a single doublet due to unreacted  $\text{FeS}_2$ , and six broad magnetic-hyperfine lines split to give a field (292 kg) approximately equal to that of  $\text{FeS}_y$  (where  $y = 1.064$ ) synthesized from its elements at  $450^\circ\text{C}$  (Fig. 4(c)). The powder X-ray diffraction profile of chemically delithiated  $\text{Li}_2\text{FeS}_2$ , shown in Fig. 5, confirms this, and shows sulfur as the other product. The observed and calculated scattering angles, and the lattice constants for  $\text{FeS}_y$  and S are given in Table 1. The lattice constants for

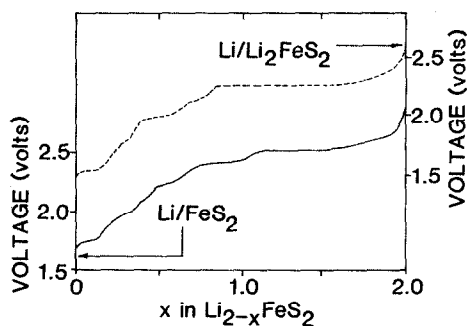


Fig. 3. A comparison of the recharge of an  $\text{Li}/\text{Li}_2\text{FeS}_2$  cell (dashed) at  $21^\circ\text{C}$  and an  $\text{Li}/\text{FeS}_2$  cell (solid) which had first been discharged to  $\text{Li}/\text{Fe} = 2$  at  $37^\circ\text{C}$ . In both cases, lithium is removed from the intermediate compound,  $\text{Li}_2\text{FeS}_2$ .

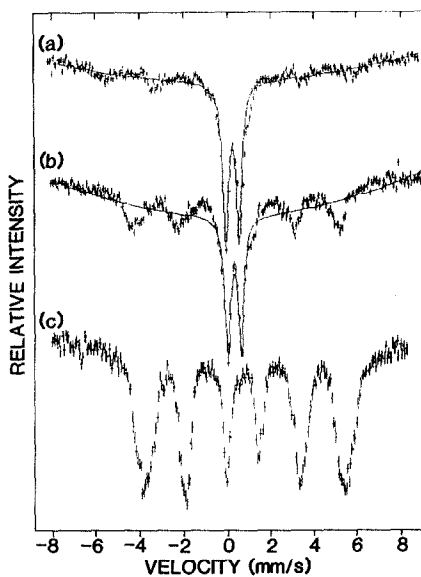


Fig. 4. An  $\text{Li}/\text{FeS}_2$  *in situ* Mössbauer cell, operated at  $55^\circ\text{C}$ , discharged to  $\text{Li}/\text{Fe} = 2$  and recharged to (a) 2.45 V, and (b) 2.80 V. The doublets (solid lines) in (a) and (b) are due to unreacted  $\text{FeS}_2$  in the cathode; (c) the Mössbauer spectrum of  $\text{FeS}_y$  synthesized from its elements at  $450^\circ\text{C}$  (where  $y = 1.064$ ).

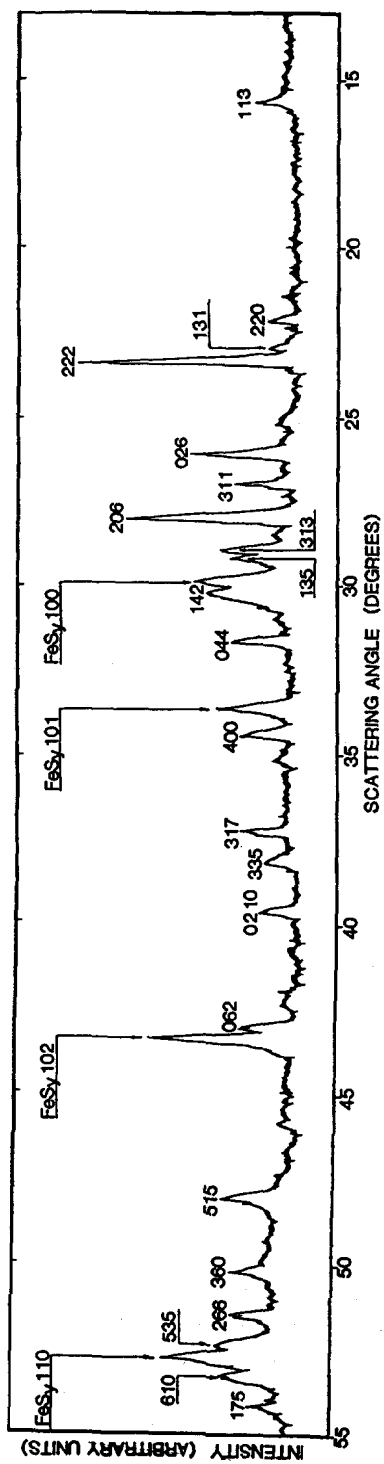


Fig. 5. Powder X-ray diffraction of chemically delithiated Li<sub>2</sub>FeS<sub>2</sub>. All the peaks can be indexed with FeS<sub>y</sub> ( $y = 1.025$ ), and S. The peaks arising from sulfur are labelled by Miller indices only, while the FeS<sub>y</sub> peaks are denoted by FeS<sub>y</sub> and the Miller indices.

TABLE 1

The observed and calculated scattering angles for FeS<sub>y</sub> and S. Lattice constants are results of least squares fitting 4 peaks for FeS<sub>y</sub> and 22 peaks for S

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{calc}}$ (degrees)	$2\theta_{\text{obs}}$ (degrees)	$d_{\text{calc}}$ (Å)
(a) FeS <sub>y</sub> * ( $y = 1.025$ ); $a = 3.485(2)$ Å, $c = 5.818(8)$ Å					
1	0	0	29.640	29.600	3.018
1	0	1	33.432	33.448	2.679
1	0	2	43.198	43.193	2.094
1	1	0	52.505	52.521	1.742
(b) Sulfur**; $a = 10.4562$ Å, $b = 12.8648$ Å, $c = 24.4809$ Å					
1	1	3	15.433	15.399	5.754
2	2	0	21.885	21.907	4.057
1	3	1	22.735	22.704	3.917
2	2	2	23.105	23.095	3.851
0	2	6	25.847	25.858	3.446
3	1	1	26.737	26.748	3.333
2	0	6	27.737	27.733	3.217
3	1	3	28.708	28.702	3.110
1	3	5	28.938	28.965	3.083
1	4	2	29.988	29.969	2.982
1	4	4	31.439	31.420	2.847
4	0	0	34.241	34.303	2.614
3	1	7	37.092	37.079	2.425
3	3	5	37.973	38.006	2.368
0	2	10	39.374	39.380	2.288
0	6	2	42.796	42.816	2.112
5	1	5	47.800	47.820	1.902
3	6	0	49.952	49.937	1.826
2	6	6	52.253	51.201	1.784
5	3	5	52.153	52.120	1.755
6	1	0	53.054	53.025	1.727
1	7	5	53.955	54.009	1.698

\*FeS<sub>y</sub> [8];  $y = 1.00$ ,  $a = 3.45$  Å,  $c = 5.88$  Å.

$y = 1.04$ ,  $a = 3.45$  Å,  $c = 5.79$  Å.

$y = 1.15$ ,  $a = 3.43$  Å,  $c = 5.69$  Å.

\*\*Sulfur [9];  $a = 10.467$  Å,  $b = 12.870$  Å,  $c = 24.493$  Å.

FeS<sub>y</sub> and S, calculated by the least-squares method, are in good agreement with those previously reported [8, 9] (see Table 1). Structural similarities between Li<sub>2</sub>FeS<sub>2</sub> and FeS apparently favor the formation of non-stoichiometric FeS instead of the formation of pyrite. As a result, as shown in Fig. 6, the second discharge and the first discharge of the Li/FeS<sub>2</sub> cell bear no resemblance.

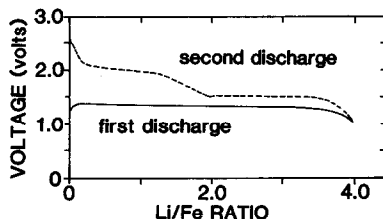


Fig. 6. The first (solid) and second (dashed) discharges of an  $\text{Li}/\text{FeS}_2$  cell at 21 °C.

## Conclusions

Using *in situ*  $^{57}\text{Fe}$  Mössbauer spectroscopy, we have shown that at 2.80 V, when all the lithium is removed, the recharge products of  $\text{Li}/\text{FeS}_2$  and  $\text{Li}/\text{Li}_2\text{FeS}_2$  cells are non-stoichiometric  $\text{FeS}$  and  $\text{S}$ . This indicates that the cell mechanisms cannot simply be described as intercalation for all values of the  $\text{Li}/\text{Fe}$  ratio. Since the formation of  $\text{FeS}_2$  does not occur, these cells have poor reversibility when they are operated at room temperature.

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