

## REDOX PROCESSES IN THE $\text{Li}_x\text{FeS}_2/\text{Li}$ ELECTROCHEMICAL SYSTEM STUDIED THROUGH CRYSTAL, MÖSSBAUER, AND EXAFS ANALYSES

R. BREC\*, E. PROUZET and G. OUVRARD

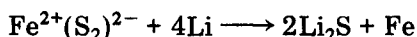
*Laboratoire de Chimie des Solides, Université de Nantes, U.A. CNRS 279, 2 rue de la Houssinière, 44072 Nantes Cédex 03 (France)*

### Summary

$\text{Li}_2\text{FeS}_2$  is a compound that can be de-intercalated, leading to a new  $\text{FeS}_2$  cathodic material. The structure of the lithiated phase is developed from hexagonal-close-packing of  $\text{S}^{2-}$  anions with tetrahedral iron ions, constituting (2D) infinite sheets. Lithium fills some of the tetrahedral and octahedral voids of the host in equivalent proportion. The first lithium removal corresponds to the oxidation of iron and to an important shift from its tetrahedral sites to others in the structure, as evidenced by Mössbauer and EXAFS measurements. De-intercalation of the second lithium results in the oxidation of sulfur, the final structure of the completely oxidized phase being  $\text{Fe}^{3+}_{(T_1)}\text{S}^{2-}(\text{S}_2)^{2-}_{1/2}$ . As shown earlier, this charged material can be re-intercalated up to its original composition.

### 1. Introduction

The capacity of lamellar transition-metal disulfides as positives for intercalation is limited to the maximum and minimum oxidation states of the cation, and corresponds generally to one Faraday per mole of  $\text{MS}_2$ . The reduction of other sulfide ionic species can be considered in cases where the sulfide anions are present in high oxidation states as, for instance, in polysulfide species.  $\text{MS}_3$  materials that, with a charge balance corresponding to  $\text{M}^{4+}\text{S}^{2-}(\text{S}_2)^{2-}$ , can be reduced at the cation and anion site may also be mentioned [1]. This is the case with pyrite,  $\text{FeS}_2$ , which, at high temperatures and with an alkali molten salt electrolyte, achieves complete reduction of the positive according to the redox process:



Such a reaction cannot be used at room temperature, however, and its reversibility, even at high temperatures, is not readily achieved.

\* Author to whom correspondence should be addressed.

Rather than using pyrite, it is possible to consider a phase such as  $\text{Li}_2\text{FeS}_2$ , in which mobile lithium can be extracted by room temperature oxidation of the phase, leading to a new  $\text{FeS}_2$  compound [2, 3]. It has been shown that such a metastable phase can be reversibly reduced by lithium up to the initial composition, enabling the system to operate on two Faradays per mole. Up to now, the open circuit potential variation *versus* lithium content features were not clearly understood. Starting with the crystal structure and following with Mössbauer and EXAFS studies, it now seems possible, as shown in this paper, to understand better the electronic and structure mechanisms taking place in the  $\text{Li}_x\text{FeS}_2/\text{Li}$  electrochemical system.

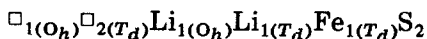
## 2. $\text{Li}_2\text{FeS}_2$ structure

Considering  $\text{Li}_2\text{FeS}_2$  as an intercalation compound of  $\text{FeS}_2$ , some sort of  $\text{TiS}_2$  structure was expected for the  $\text{FeS}_2$  host slab, especially since  $\text{Fe}^{2+}$  is commonly encountered in octahedral coordination, in which it is normally more stable. Single-crystal structure determination indicates that, if hexagonal-close-packing of the  $\text{S}^{2-}$  anions is indeed found, the iron ions are actually located in a tetrahedral environment [3] (see Fig. 1(a) and (b)). This result is in accord with the observation that the phase sublattice gives a  $c/a$  parameter ratio of 1.607, whereas two different fillings of the two tetrahedral sites explain the presence of two types of  $\text{Fe}^{2+}$ , as observed by Mössbauer spectroscopy and the superlattice network,  $2a^*2b^*c$ , of the compound.

A recent structure determination also indicated the tetrahedral coordination of  $\text{Fe}^{2+}$  [4] with, however, no superstructure, the cell space group ( $P3m1$ ) leading to identical iron sites half-filled, equally, with  $\text{Fe}^{2+}$  and  $\text{Li}^+$ . This result may be attributed to different synthesis conditions.

The relative amounts of  $\text{Fe}^{2+}$  in the superstructure are found to be equal to 36% (Fe1) and 64% (Fe2), to be compared with the Mössbauer study made on powder samples (23% and 77%, respectively). The difference may be linked to different synthesis conditions, since producing single crystals of  $\text{Li}_2\text{FeS}_2$  requires much higher temperatures and longer reaction times (850 °C for 15 days) than does powder preparation (3 days at 750 °C). The latter procedure is, however, used for making impurity-free bulk samples. Finally, as may be seen in Fig. 1, the iron is located between two sulfur-ion sheets making a (2D)  $\text{FeS}_2$  host sandwich. Lithium cations are found:

- (i) in the octahedral sites between the ( $\text{FeS}_2$ ) sheets (one lithium);
- (ii) in various tetrahedral sites of the structure, in particular at the incompletely filled iron sites. The overall structure may be written, in agreement with past infrared study:



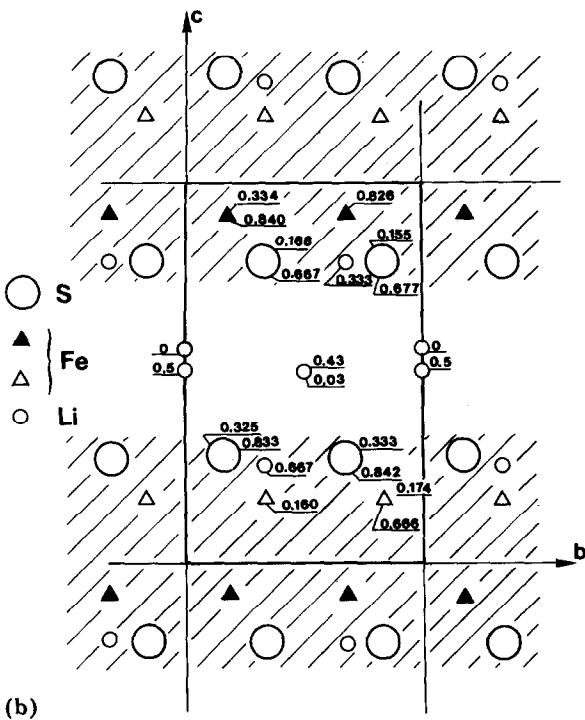
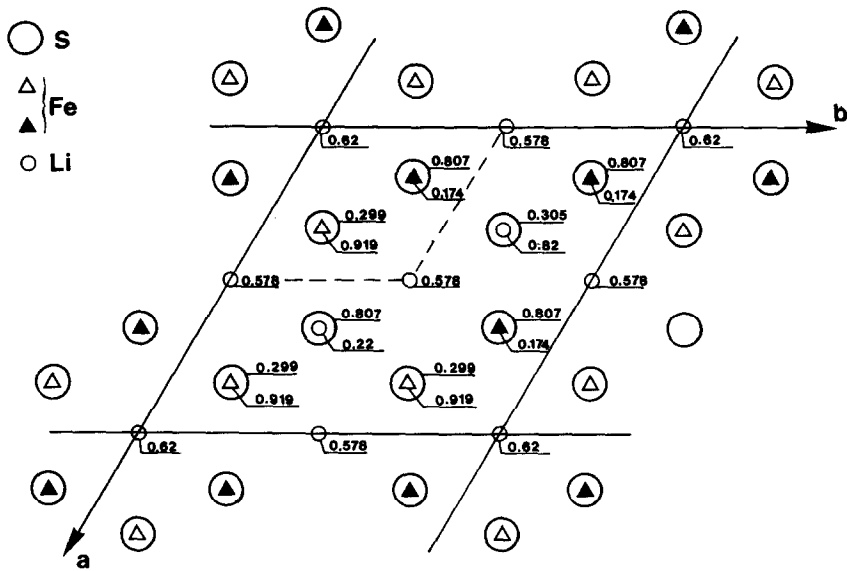


Fig. 1. (a)  $\text{Li}_2\text{FeS}_2$  structure projection in the  $(xy0)$  plane. The broken line corresponds to the subcell; (b) Projection along the  $a$  axis of the  $\text{Li}_2\text{FeS}_2$  structure. The shaded area underlines the (2D) structure of the  $\text{FeS}_2$  framework.

This leaves an empty octahedral site located (see Fig. 1) at 000 and 1/200 sites of the structure, probably too close to  $\text{Fe}^{2+}$  (Fe2) to be occupied without strong repulsion.

### 3. Oxidation of $\text{Li}_2\text{FeS}_2$ : the $\text{Li}_x\text{FeS}_2$ de-intercalates

#### (i) The $\text{Li}_2\text{FeS}_2$ - $\text{Li}_1\text{FeS}_2$ composition range

The two aspects of the oxidation of  $\text{Li}_2\text{FeS}_2$  (followed by the reduction of  $\text{FeS}_2$ ) are related to the lithium-ion and electron removal and are concerned with crystallographic and band-structure considerations, respectively.

From the crystal-structure viewpoint, one observes from  $\text{Li}_2\text{FeS}_2$  to  $\text{Li}_1\text{FeS}_2$ , the removal of tetrahedral lithium, as inferred by the strong decrease of the (Li-S4) infrared-band intensity. This is followed, on the electronic side, by oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ , as evidenced by the lowering of the isomer shifts of that cation, which go from 0.50 and 0.49  $\text{mm s}^{-1}$  to 0.35 and 0.20  $\text{mm s}^{-1}$  (see Table 1). Electrochemically, this de-intercalation corresponds to single-phase behavior of the  $\text{Li}_x\text{FeS}_2$  compound ( $1 < x < 2$ ) (see the open-circuit voltage curve in Fig. 2), in agreement with very little change in the cell parameters. However, a break in the potential curve is recorded around the composition  $\text{Li}_{1.5}\text{FeS}_2$ . This potential change has been constantly recorded in repeated experiments, on charge as well as on discharge; it was tentatively attributed to a phase transition with the presence of a narrow, two-phase domain around the composition in question. Referring to Table 1, where the Mössbauer characteristics of  $\text{Li}_x\text{FeS}_2$  phases with respect to  $x$  are recorded, it may be seen that, between

TABLE 1

Mössbauer isomer shift (IS), quadrupole splitting (QS) and relative intensities of iron sites in the  $\text{Li}_x\text{FeS}_2$  compounds ( $0.21 \leq x \leq 2$ )

$x$ in $\text{Li}_x\text{FeS}_2$	IS ( $\text{mm s}^{-1}$ ) for site			QS ( $\text{mm s}^{-1}$ ) for site			Site relative intensity		
	1	2	3	1	2	3	1	2	3
2.00	0.50	0.49		0.90	1.61		77	23	
1.78	0.45	0.38		0.84	1.39		64	36	
1.31		0.35	0.18		1.24	0.37		73	27
1.10		0.36	0.20		1.18	0.35		55	45
0.85		0.32	0.16		0.93	0.49		60	40
0.57		0.32	0.23		0.94	0.53		65	35
0.21		0.32	0.26		0.85	0.56		50	50

Between  $\text{Li}_{1.78}\text{FeS}_2$  and  $\text{Li}_{1.31}\text{FeS}_2$ , the two sites Fe1 and Fe2 become Fe1 - 2 and Fe3.

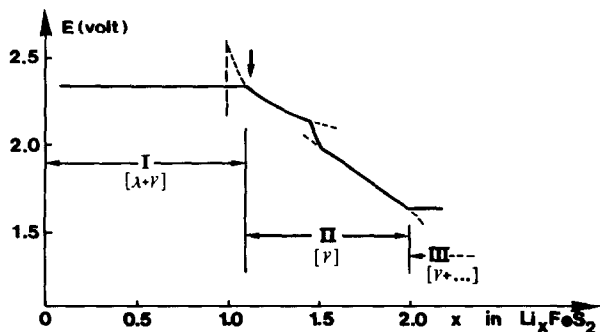


Fig. 2. OCV curve of the  $\text{Li}_x\text{FeS}_2/\text{Li}$  system with its single and two-phase domains [3].

$x = 1.78$  and  $1.31$ , the two initial iron sites (Fe1 and Fe2) give rise to two new ones, Fe1 - 2 and Fe3, the first new site being rather similar to Fe2. Since the cell parameters change very little, this transition must be related to an iron-cation site change, in conjunction with a new distribution of the positive charges. This important cation-site shift, although not very common among chalcogenides during room temperature redox processes, has also been recorded in intercalated  $\text{MPS}_3$  phases ( $M = \text{Fe}, \text{Ni}$ ) [5]. It has also been shown to be responsible, in  $\text{A}_x\text{MO}_2$  ternary phases ( $M =$  first-row transition metal [6]), for the different potential steps obtained in the OCV curves.

The nature of the new sites must now be determined. For  $\text{Li}_{1.1}\text{FeS}_2$ , the low IS of Fe3 ( $0.20 \text{ mm s}^{-1}$ ) is quite consistent with a tetrahedral sulfur coordination, and the very low value of the quadrupole splitting ( $\text{QS} = 0.35 \text{ mm s}^{-1}$ ) is in agreement with an oxidation state nearing  $3^+$ . The Fe1 - 2 IS of  $0.36 \text{ mm s}^{-1}$  is also consistent with an iron  $3^+$  surrounded by octahedral sulfur ( $0.40 \text{ mm s}^{-1}$  according to ref. 7), whereas the tetrahedral  $\text{Fe}^{3+}$ -ion IS can be found in the vicinity of  $0.20 \text{ mm s}^{-1}$ . To confirm this finding, it was thought necessary to use another local method to determine the exact nature of these iron sites, especially the second one, although an octahedral  $\text{FeS}_6$  group was finally considered for it. In Section 4, an EXAFS study provides a definite answer.

#### (ii) The $\text{Li}_1\text{FeS}_2\text{-FeS}_2$ composition range

In this domain, the OCV curve indicates the occurrence of a two-phase region corresponding to the end compounds. Iron being at its maximum oxidation state, further oxidation takes place on sulfur with the formation of  $\text{S}^{1-}$ , hence of  $(\text{S}_2)^{2-}$  groups, well evidenced by infrared spectroscopy [2]. The distortion created by this reaction is obviously responsible for the existence of two phases in the domain under study. This does not seem to change the Mössbauer characteristics of iron fundamentally; its parameters tend to converge continuously (Table 1), the relative intensities of each site becoming identical for the composition  $\text{Li}_{0.21}\text{FeS}_2$ . The final charge balance of  $\text{FeS}_2$  can be written  $\text{Fe}^{3+}\text{S}^{2-}(\text{S}_2)^{2-}_{1/2}$ . Reintercalation of  $\text{FeS}_2$  results in the reduction of the sulfur pair and then of the iron  $3^+$ .

#### 4. EXAFS study of $\text{Li}_x\text{FeS}_2$ ( $0.21 < x < 2$ )

Room-temperature EXAFS experiments were performed at the iron edge at LURE, the French synchrotron radiation laboratory. A conventional treatment of the data, which will be published with complete details elsewhere [8], shows the absence of important changes in the iron first neighbors in the de-intercalation range (see Fig. 3). This indicates that iron actually keeps the same sulfur tetrahedral coordination, contrary to what had been deduced from the Mössbauer spectroscopy. The results of the fits of EXAFS spectra corresponding to the first-coordination shell of iron are given in Table 2. These results lead to the following comments:

(i) The number of sulfur atoms around the iron is constant ( $4 \pm 0.3$ ) considering the accuracy generally accepted for this refined parameter ( $\approx 10\%$ ). This is in accord with the maintenance of iron tetrahedral coordination.

(ii) The values of  $\Delta\sigma$  that account for any possible site distortion are found to be negligible. This indicates a very small distortion of the sites and confirms their lack of change.

(iii) The refined interatomic distance in  $\text{Li}_2\text{FeS}_2$  ( $d_{\text{Fe-S}} = 2.33 \text{ \AA}$ ) is in agreement with the single crystal structure determination. A small, but significant, decrease in the distance is recorded when the lithium content decreases ( $d_{\text{Fe-S}} = 2.28 \text{ \AA}$ ), in accord with iron oxidation, as found by the Mössbauer study.

(iv) From these results, and because of the weak intensity of the second-neighbor peak (see Fig. 3), it is not possible to determine which kind of tetrahedral site is occupied by iron (intra- or inter-slab positions).

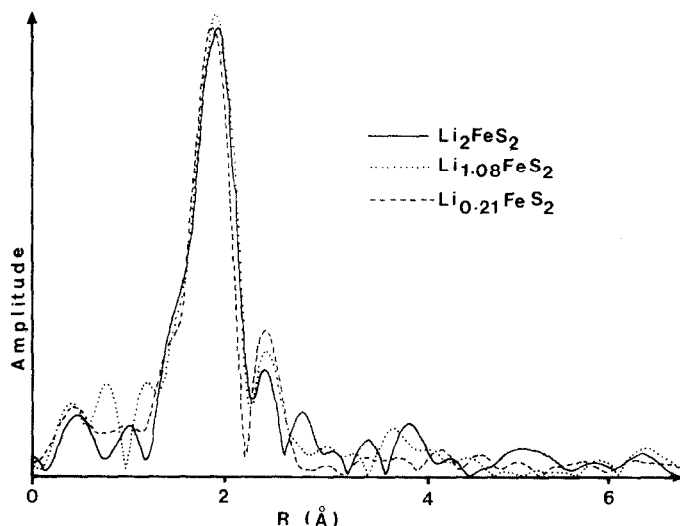


Fig. 3. Fourier transform module (Fe K edge) of EXAFS spectra obtained on some  $\text{Li}_x\text{FeS}_2$  phases.

TABLE 2

Results of EXAFS fits of the first sulfur coordination shell of iron for  $\text{Li}_x\text{FeS}_2$  de-intercalates

$x$ in $\text{Li}_x\text{FeS}_2$	2.0	1.08	0.85	0.52	0.21
Number of sulfur atoms	4.32	3.85	3.72	4.27	4.18
Distances Fe-S	2.33	2.28	2.28	2.28	2.28
$\Delta\sigma$	0	$5 \times 10^{-4}$	$8 \times 10^{-4}$	$4 \times 10^{-4}$	$4 \times 10^{-4}$

## 5. Conclusion

A combination of different techniques allowed us to understand the redox process in the  $\text{Li}_x\text{FeS}_2$  system better. The displacement of iron in the host  $\text{FeS}_2$  frame was clearly shown, with the maintenance, in  $\text{Li}_2\text{FeS}_2$ , of the original tetrahedral coordination of this cation, as found by structure determination. The structure of the new  $\text{FeS}_2$  obtained by the removal of lithium is different from that encountered in pyrite or marcasite and can be written:  $\text{Fe}^{3+}_{(Td)}\text{S}^{2-}(\text{S}_2)^{2-}_{1/2}$ . This new, electrochemically active compound is then found to be midway between the classical layered dichalcogenides ( $\text{M}^{4+}(\text{S}^{2-})_2$ ) and the pyrite-like phases  $\text{M}^{2+}(\text{S}_2)^{2-}$ . It seems to have the same structure as  $\text{IrS}_2$  [9], which is also a frontier material.

## Acknowledgement

The authors thank DRET for financial support and LURE for technical assistance.

## References

- 1 C. Sourisseau, S. P. Gwet, P. Gard and Y. Mathey, *J. Solid State Chem.*, **72** (1988) 257.
- 2 P. Gard, C. Sourisseau, G. Ouvrard and R. Brec, *Solid State Ionics*, **20** (1986) 231.
- 3 L. Blandeau, G. Ouvrard, Y. Calage, R. Brec and J. Rouxel, *J. Phys. C: Solid State Phys.*, **20** (1987) 4271.
- 4 R. J. Batchelor, F. W. B. Einstein, C. H. W. Jones, R. Fong and J. R. Dahn, *Phys. Rev. B*, **37** (1988) 3699.
- 5 G. Ouvrard, E. Prouzet, R. Brec, S. Benazeth and H. Dexpert, *Proc. Vth XAFS Conf., Seattle, 1988*.

- 6 C. Delmas, Intercalation in oxides: from 2D to 3D intercalation, *NATO ASI Series*, 1988.
- 7 J. B. Goodenough and G. A. Fatseas, *J. Solid State Chem.*, 41 (1982) 1.
- 8 G. Ouvrard, R. Brec, S. Benazeth and H. Dexpert, *Solid State Ionics*, to be published.
- 9 F. Hulliger, *Nature (London)*, 204 (1964) 644.