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Structural modifications related to lithium intercalation into iron thiospinels

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Abstract

$Cu_2FeSn_3S_8$ and $Cu_2FeTi_3S_8$ spinel compounds have been used as electrode materials in lithium cell. The lithium insertion mechanism was studied by characterization of chemically lithiated (via *n*-butyllithium) samples using the X-ray powder diffraction and the ^{57}Fe Mössbauer spectroscopy. The intercalation process was correlated with the electrochemical behavior. Rietveld analysis of the tin based phase shows a weak extraction of copper between 0 and 2 lithium per formula. Along this extraction, a migration of iron cations from octahedral to tetrahedral sites was observed. Regarding titanium based thiospinel, the reduction of titanium occurs in two steps. Firstly titanium (IV) is reduced to Ti (III). Secondly, following the five already intercalated lithium, the Ti reduction process is occurring towards a lower oxidation state Ti(II). © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Compounds with a spinel-related structure have been widely investigated as host materials for lithium insertion [1,2]. Using this structure as the electrodes in 'rocking-chair' or 'lithium-ion' cells would help the present limitations of rechargeable batteries to be overcome. The normal cubic spinels, commonly written $A[B_2]X_4$ (s.g. $Fd\bar{3}m$) are three-dimensional lattices owing to the presence of a rigid framework of BX_6 octahedra and AX_4 tetrahedra [3]. The structure can be described as a cubic close-packing arrangement of X anions in 32e site, B and A cations in 16d octahedral and 8a tetrahedral sites respectively. Vacancies provide a large number of theoretically available sites for lithium intercalation reactions. The effect of the insertion in spinel compounds was first described by Thackeray et al. [4]. The framework $A[B_2]X_4$ remains intact during the insertion reaction, while the A cations are displaced to the initially empty 16c sites due to the electrostatic repulsion between A cations and the inserted lithium ions in 16c sites. Recently, lithium insertion in thiospinels Cu_2-

$[MSn_3]S_8$ (M = Mn, Fe, Co, Ni) has been reported [5], but the insertion mechanism is not precisely known. In this paper, the insertion mechanism is investigated into iron thiospinel. This compound offers interesting possibilities for a better understanding of the redox insertion process, via the ^{57}Fe Mössbauer spectroscopy. A titanium-based thiospinel $Cu_2FeTi_3S_8$ has been studied because of the improved electrochemical properties [6]. Finally, during this study, the intercalation process was correlated to the electrochemical characteristics obtained from step potential electrochemical spectroscopy (SPES).

2. Experimental

Thiospinels were prepared by solid state reaction between the constituent elements. The stoichiometric mixture was placed into a silica tube and sealed under vacuum ($< 10^{-3}$ Pa). It was heated to 300°C for one day, after which the temperature was increased to achieve a final constant value at 750°C for 10 days.

Chemical lithium insertion into $Cu_2FeSn_3S_8$ was carried out via *n*-butyllithium (1.5 M) solution as already described [7]. The lithium content of the samples was obtained by atomic emission spectroscopy on a Philips spectrophotometer. For the electrochemical insertion, a

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two-electrode cell was used. The cathode was prepared by pressing a mixture containing 90% of active material and 10% of PTFE in order to improve the mechanical properties of the electrode. The anode was a metallic lithium disk, and the electrolyte solution $((1 \text{ M}) \text{ LiClO}_4$ in PC) was supported by porous glass paper disks. The SPES measurements were carried out at room temperature by using a multichannel microprocessor-controlled system (MacPile). An initial relaxation was allotted until $\Delta V / \Delta t \leq 1$ mV/h. The voltage step imposed to the cell was 10 mV/h.

X-ray powder diffraction patterns (XPDP) were recorded on a Philips θ–2θ diffractometer using CuKα radiation and a nickel filter. Rietveld refinements were carried out with the aid of a computer program DBWS-9006 developed by Wiles and Young [8]. ^{57}Fe Mössbauer spectra were recorded at 80 K in the constant-acceleration mode on an ELSCINT-AME40 spectrometer. The source was ^{57}Co(Rh). The velocity scale was calibrated with the magnetic sextuplet spectrum of a iron foil absorber. Recorded spectra were fitted to Lorentzian profiles by a least-squares method [9] and the fit quality controlled by the classical χ^2 test.

3. Results and discussion

SPES is a reliable technique which allows to obtain quasi-equilibrium cell potential curves and evaluate thermodynamic parameters for the lithiated compounds. This potentiostatic method let to perform intensity vs. potential curves in which the plateaus of reduction become sharp peaks that can be resolved more easily. The discharge
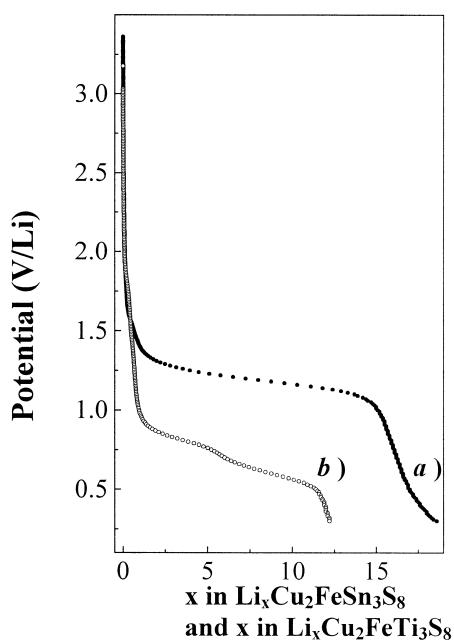

Fig. 1. Potentiostatic discharge: (a) $Cu_2FeSn_3S_8$ and (b) $Cu_2FeTi_3S_8$.
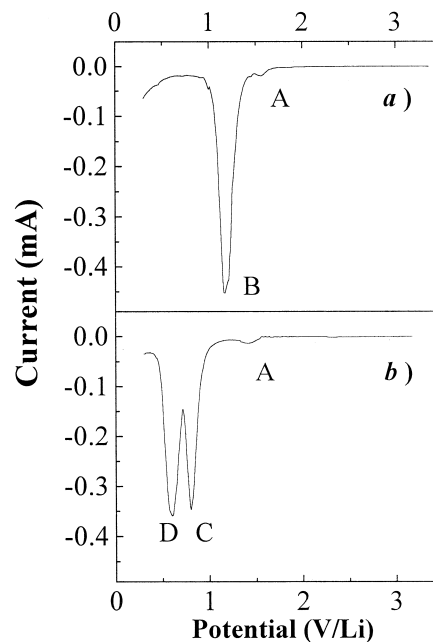
Fig. 2. Current vs. potential curves (a) $Cu_2FeSn_3S_8$ and (b) $Cu_2FeTi_3S_8$.

curves are presented in Fig. 1, and the current vs. potential curves in Fig. 2, for $Cu_2FeSn_3S_8$ and $Cu_2FeTi_3S_8$. These latter curves show the presence of two reduction peaks for the tin based compound and three ones for the titanium-based compound. The corresponding potentials are reported in Table 1.

In order to identify the different peaks some characterizations of chemical lithiated samples were investigated, on the tin-based sample.

The XPDP of pristine compounds were characteristic of a single-phase product and could be indexed in a spinel-related cubic system. A Rietveld analysis confirmed the spinel structure with the $Fd\bar{3}m$ space group. The structural fitted parameters for pristine and lithiated samples are reported in Table 2 and Fig. 3 shows the Rietveld refinement of XPDP. Some changes are observed in the intensity of the Bragg reflections during the intercalation, especially for the diffraction planes indexed (111) and (022). This evolution can be explained by a modification of the cations distribution [10]. In fact, Table 2 shows that the occupancy of copper atoms in 8a sites decreases. Lithium intercalation in the spinel structure gives rise to a weak extraction of

Table 1
Potentials corresponding to the current peaks for $Cu_2FeSn_3S_8$ and $Cu_2FeTi_3S_8$

Reduction peaks	$Cu_2FeSn_3S_8$ (V/Li)	$Cu_2FeTi_3S_8$ (V/Li)
A	1.56	1.42
B	1.17	
C		0.8
D		0.6

Table 2
Selected results of Rietveld analyses of XPDP data of $Cu_2FeSn_3S_8$ and $Li_{2.3}Cu_2FeSn_3S_8$

Site	$Cu_2FeSn_3S_8$; $a = 10.323(1)$ Å, $x = 0.256(2)$					
	Occupancy				Correlation factors
	Cu	Fe	Sn	S	
16c					
16d		4	12		$R_{Bragg} = 2.7$
8a	8				
32e				32	$S = 1.29$

Site	$Li_{2.3}Cu_2FeSn_3S_8$; $a = 10.346(1)$ Å, $x = 0.245(1)$					
	Occupancy					Correlation factors
	Li	Cu	Fe	Sn	S	
16c	9.2					
16d			3.6	12		$R_{Bragg} = 7.58$
8a		7.6	0.4			
32e					32	$S = 3.38$

Space Group $Fd\bar{3}m$.
Origin 2: 8a(1/8,1/8,1/8), 16c (0,0,0), 16d(1/2,1/2,1/2) and 32e(x,x,x).

copper atoms according to: $Cu^{(1)} \rightarrow Cu^{(0)}$. The reduction corresponding to the peak labeled A in Fig. 2, occurs between 0 and 2 lithium. In any case, no more than two

electrons are consumed by the cathode in this reaction. As this value is corresponding to a partial reduction of the copper (I) atoms, the peak A can be ascribed to a partial reduction towards metallic copper. This mechanism has already been observed in a copper-based thiospinel [11]. In order to justify the other electrons inserted in the framework, since only 0.4 Cu per formula (with 32 S) were extracted, a reduction without extraction can be envisaged. Concerning iron atoms, a migration from 16d sites toward the 8a sites can be observed during lithium intercalation. Regarding this migration, [57]Fe Mössbauer measurements have been done on the tin based compound in order to confirm the Rietveld refinement. The pristine spectrum presented in Fig. 4 and previously described [12] shows the presence of two paramagnetic quadrupole-split doublets with marked difference in the hyperfine parameters (Table 3).

Both the subspectra can be ascribed to the Fe^{2+} ions in octahedral 16d sites with a high-spin (HS) electronic configuration for the doublet with the large quadrupole splitting and a low-spin (LS) for the other. In the lithiated spectra presented in Fig. 4, a third subspectrum is observed with an isomer shift nearer to that of a tetrahedral site [10], and consequently can be ascribed to 8a site. Its area
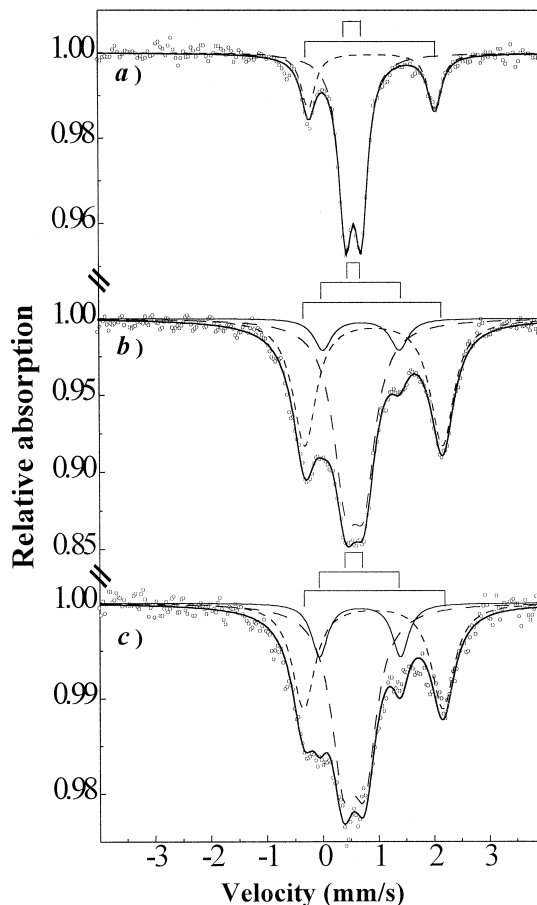

Fig. 3. XPDP and proposed Rietveld refinement of (a) $Cu_2FeSn_3S_8$ and (b) $Li_{2.3}Cu_2FeSn_3S_8$.

Fig. 4. [57]Fe Mössbauer spectra of (a) $Cu_2FeSn_3S_8$, (b) $Li_{0.8}Cu_2FeSn_3S_8$ and (c): $Li_2Cu_2FeSn_3S_8$.

Table 3
Hyperfine parameters of ^{57}Fe Mössbauer spectra of $Li_xCu_2FeSn_3S_8$

Site	x	IS (mm/s)	QS (mm/s)	LW (mm/s)	RA (%)
16d (HS)	0	0.935(9)	2.42(2)	0.38(2)	34
	2	0.925(5)	2.48(1)	0.492(1)	41
	4	0.91(1)	2.50(2)	0.514(2)	34
16d (LS)	0	0.556(5)	0.310(7)	0.39(1)	66
	2	0.580(5)	0.332(7)	0.492(1)	48
	4	0.552(8)	0.37(1)	0.514(2)	49
8a	2	0.70(2)	1.36(3)	0.492(1)	11
	4	0.67(2)	1.46(4)	0.514(2)	17

IS: Isomer shift.
QS: Quadruple splitting.
LW: full-width at half-maximum.
RA: Relative area.

increases with the amount of intercalated lithium, confirming the iron migration ($Fe^{2+}(16d) \rightarrow Fe^{2+}(8a)$). Regarding the two other doublets, no important variation in the hyperfine parameters is shown after intercalation. Nevertheless, the relative area of the LS signal decreases significantly and indicate a variation of the crystal field. For the tin-based thiospinel $Cu_2FeSn_3S_8$, the environment of tin atoms during the intercalation of lithium was previously studied [6] by ^{119}Sn Mössbauer spectroscopy. It was shown that a complex and simultaneous $Sn^{(IV)} \rightarrow Sn^{(II)}$ and $Sn^{(0)}$ reduction over 2 already intercalated lithium occurred. As the total number of electrons transferred in this reaction corresponds to 12 electrons, the peak labeled B in Fig. 2 can be ascribed to this reduction step. Concerning the titanium-based compound $Cu_2FeTi_3S_8$, the first peak corresponds to approximately the same potential value as the one observed for the tin-based compound. Peak A can also be attributed to a copper reduction. In order to elucidate both the last reduction peaks C and D, some measurements by EPR (electronic paramagnetic resonance) have been performed. This technique allows to make in evidence the presence of paramagnetic ions. The pristine compound contains only diamagnetic ions and there is no signal in EPR. On the contrary, the spectra of lithiated compounds present a high paramagnetic signal which can be attributed to titanium (III). The reduction of titanium atoms ($Ti^{(IV)} \rightarrow Ti^{(III)}$) theoretically corresponds to 3 electrons, and can be ascribed to the reduction peak C. Finally, following five lithium already intercalated (two for the copper reduction and three for the first step of titanium reduction), the other electrons inserted in the framework can probably reduce the titanium (III) to a lower oxidation state (II).

4. Conclusion

Results of SPES showed that during the lithium intercalation into $Cu_2FeSn_3S_8$ and $Cu_2FeTi_3S_8$ two and three steps were observed, respectively. For the tin-based thiospinel, during the first step, the refinement of the XPDP by Rietveld method evidences a reduction and extraction of copper between 0 and 2 lithium per formula. Along with this reduction, a migration of iron atoms from octahedral site 16d to tetrahedral site 8a was observed. This migration of cations was correlated by ^{57}Fe Mössbauer spectroscopy. In fact, a new quadrupole splitting appears during insertion, which can be attributed to the Fe (II) in tetrahedral site 8a, with no reduction of iron cations occurring. The second step, has been attributed to a complex and simultaneous reduction of tin atoms $Sn^{(IV)} \rightarrow Sn^{(II)}$ and $Sn^{(0)}$ according to the result of ^{119}Sn Mössbauer spectroscopy [6]. Regarding the titanium based compound, the first reduction step corresponds to the similar copper reduction process between 0 and 2 lithium per formula. The two last peaks (C and D) were attributed to a reduction of titanium $Ti^{(IV)} \rightarrow Ti^{(III)}$ and $Ti^{(III)} \rightarrow Ti^{(II)}$ according to the result of EPR. From an electrochemical point of view, the titanium thiospinel reduction occurs at a lower voltage and may appears as a suitable candidate for anodic materials in 'Li-ion' batteries. Work is presently in progress in order to evaluate the cycleability of this new material.

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