

# Phase separation and amorphisation in lithium inserted Cu–In–Sn sulfospinel: experimental and theoretical approach

R. Dedryvère<sup>a</sup>, S. Denis<sup>b</sup>, P.E. Lippens<sup>a</sup>, J. Olivier-Fourcade<sup>a</sup>, J.C. Jumas<sup>a,\*</sup>

<sup>a</sup>Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, CNRS UMR5072, Université Montpellier II, CC15, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

<sup>b</sup>Laboratoire de Réactivité et Chimie des Solides (UPRES-A 6007), 33 rue Saint-Leu, 80039 Amiens Cedex, France

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## Abstract

<sup>119</sup>Sn Mössbauer spectroscopy, X-ray diffraction (XRD) and electrochemical experiments were carried out to characterise the reaction mechanism of lithium with spinel phases Cu<sub>x</sub>In<sub>y</sub>Sn<sub>z</sub>S<sub>4</sub>. The electrochemical investigations have shown interesting reversible capacities for these materials, and their possible use as anode materials in lithium-ion cells. This analysis reveals a multi-phase mechanism linked to the reduction of the cations involving a spinel to rocksalt transformation followed by a structural breakdown. Density functional calculations by the linearised augmented plane wave (LAPW) method give a good interpretation of experimental results for crystalline phases. © 2001 Elsevier Science B.V. All rights reserved.

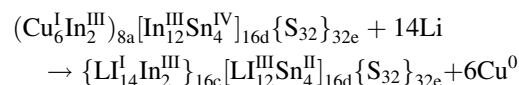
**Keywords:** Spinel sulfides; Lithium-ion; Mössbauer; Anode materials; Cycling; Calculations

## 1. Introduction

Sulfide compounds with spinel-related structure have been widely studied for their properties as host materials for lithium insertion and their potential use as electrode in lithium-ion batteries [1,2]. Particularly, indium and tin sulfospinel like FeIn<sub>2</sub>S<sub>4</sub> [3], CuM<sub>0.5</sub>Sn<sub>1.5</sub>S<sub>4</sub> (M = Mn, Fe, Co, Ni) [4] and the cation deficient In<sub>2</sub>Sn<sub>0.5</sub>S<sub>4</sub> [5] have been previously studied as host lattices for lithium insertion. The oxidation/reduction potentials observed during electrochemical tests are lower than those observed for oxide spinels, and that is why these materials are currently investigated for their possible application as negative electrodes [6]. Unfortunately, their practical use has been limited up to now by a low capacity and a high capacity fading with cycling, in contrast to carbon electrodes.

An initial work has shown the interest of copper and indium containing sulfospinel to obtain low specific potentials [7]. In a recent paper [8], we have presented a study of a family of copper, indium and tin containing sulfospinel: Cu<sub>0.5+α</sub>In<sub>2.5-3α</sub>Sn<sub>2α</sub>S<sub>4</sub> (0 ≤ α ≤ 0.5). We have discussed the structural modifications induced by lithium insertion in those materials via a chemical route (*n*-butyllithium), and evidenced a phase transformation. Indeed, the spinel

structure is described in the *Fd3m* space group, and the unit cell contains 32 anions in the 32e sites (cubic close-packing arrangement), 8 cations in 8a sites (tetrahedrally coordinated by anions) and 16 cations in 16d sites (octahedrally coordinated by anions). The cation distribution in our compounds, e.g. in the sample Cu<sub>0.75</sub>In<sub>1.75</sub>Sn<sub>0.5</sub>S<sub>4</sub> (α = 0.25), is (Cu<sub>6</sub><sup>I</sup>In<sub>2</sub><sup>III</sup>)<sub>8a</sub>[In<sub>12</sub><sup>III</sup>Sn<sub>4</sub><sup>IV</sup>]<sub>16d</sub>{S<sub>32</sub>}<sub>32e</sub>. We have shown from X-ray and neutron diffraction experiments and <sup>119</sup>Sn Mössbauer spectroscopy, that lithium insertion induces a transformation from the spinel phase to a rocksalt-related phase according to the following mechanism [8]: Cu<sup>I</sup> ions are reduced into Cu<sup>0</sup> and extruded from 8a tetrahedral sites as metallic copper, Sn<sup>IV</sup> ions are reduced into Sn<sup>II</sup>, Li<sup>I</sup> ions are inserted in the vacant octahedral 16c sites and In<sup>III</sup> ions migrate from 8a to 16c sites, which can be represented by the following equation:



In the present paper, we investigate the mechanism of electrochemical lithium insertion in those compounds by <sup>119</sup>Sn Mössbauer spectroscopy and X-ray diffraction, and their performances for possible application as negative electrode in lithium-ion batteries by cycling tests. We also present the results of density functional calculations to interpret the first part of the mechanism.

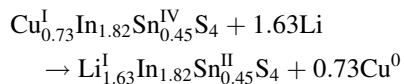
\* Corresponding author. Fax: +33-4-67-14-33-04.  
E-mail address: jumas@univ-montp2.fr (J.C. Jumas).

## 2. Experimental

All compounds were synthesised by solid state reaction between the binary sulfides  $\text{Cu}_2\text{S}$ ,  $\text{In}_2\text{S}_3$  and  $\text{SnS}_2$  in silica ampoules by heating up to  $850^\circ\text{C}$  and slow cooling to room temperature. Electrochemical lithiation was carried out with ( $\text{Li}/\text{LiPF}_6$  1 M (EC:DMC)/sulfospinel) Swagelock<sup>TM</sup> test cells as described in [9]. Galvanostatic discharge/charge curves were obtained with a cycling rate of 1Li/4 h for the first cycle, and 1Li/2 h for tests of capacity loss. Electrochemically inserted samples for Mössbauer characterisation were prepared using a slow rate of 1Li/20 h. Pristine and lithiated samples were characterised by X-ray powder diffraction (XRD) with a Philips  $\theta/2\theta$  diffractometer using  $\text{Cu K}\alpha$  radiation and a nickel filter. Rietveld refinements were carried out with the program DBWS-9411 [10]. All compounds were studied by  $^{119}\text{Sn}$  Mössbauer spectroscopy at room temperature, using  $^{119\text{m}}\text{Sn}$  in a  $\text{BaSnO}_3$  matrix as  $\gamma$ -ray source. The X-ray absorption spectroscopy (XAS) measurements were carried out at LURE (Orsay, France). The S K-edge spectra were recorded at Super ACO storage ring in the total electron yield mode, by measuring the photocurrent from the isolated metallic sample holder with a picoammeter. The powder samples were inlayed on indium foils to maximise the conduction. A monochromator with two Si(1 1 1) crystals allowing a resolution of 0.3 eV was used.

## 3. Results and discussion

Fig. 1(a) and (b) shows, respectively, the first cycle of discharge/charge, and the cycling behaviour of  $\text{CuInSnS}_4$  ( $\alpha = 0.5$ ) and  $\text{Cu}_{0.73}\text{In}_{1.82}\text{Sn}_{0.45}\text{S}_4$  ( $\alpha = 0.23$ ). Both compounds show a great capacity loss of 40% at the first cycle to give a reversible capacity of 600 mAh/g, and then this capacity decreases slowly to reach the value of 400 mAh/g after 20 cycles. Both compounds present a large plateau at 1.2–1.3 V. We can also observe a small plateau at 1.5 V, which is well-defined for  $\text{Cu}_{0.73}\text{In}_{1.82}\text{Sn}_{0.45}\text{S}_4$  and looks like a small shoulder for  $\text{CuInSnS}_4$ . For  $\text{Cu}_{0.73}\text{In}_{1.82}\text{Sn}_{0.45}\text{S}_4$ , this small plateau can be attributed to the spinel to rocksalt transformation described above, that takes place at the beginning of the insertion, associated to the reduction of  $\text{Cu}^{\text{I}}$  into  $\text{Cu}^0$  and  $\text{Sn}^{\text{IV}}$  into  $\text{Sn}^{\text{II}}$ :



which corresponds to 100 mAh/g. For  $\text{CuInSnS}_4$ , this phase transformation is more difficult and leads to an important amorphisation because not enough octahedral sites are available for lithium insertion according to the described mechanism of reduction-migration. Thus, the small plateau at 1.5 V is not so well-defined.

The large plateau observed at 1.2–1.3 V in the discharge curves is due to the destruction of the rocksalt phase to form

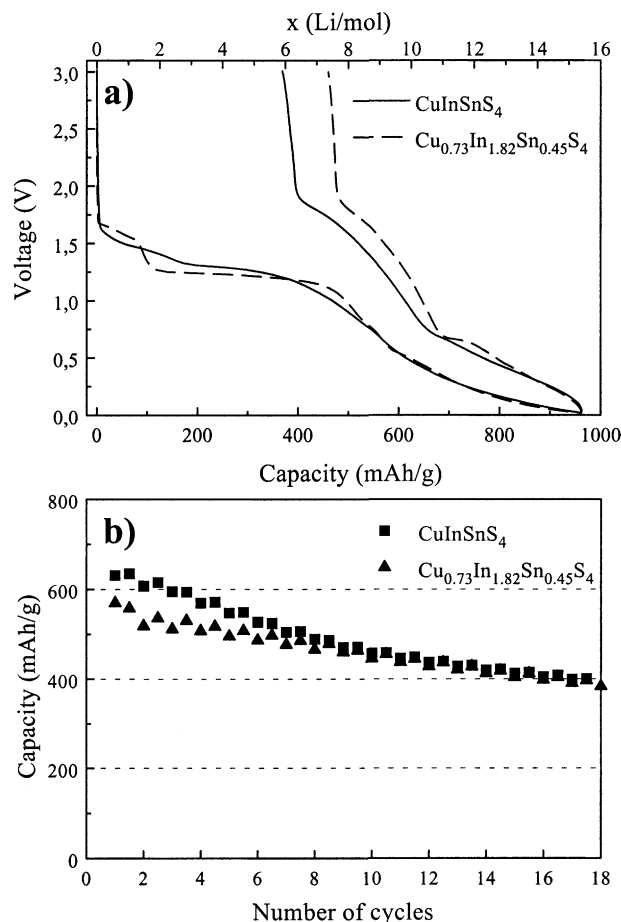


Fig. 1. (a) First cycle of discharge/charge of both compounds  $\text{CuInSnS}_4$  and  $\text{Cu}_{0.73}\text{In}_{1.82}\text{Sn}_{0.45}\text{S}_4$  (cycling rate 1Li/4 h); (b) cycling behaviour of both compounds  $\text{CuInSnS}_4$  and  $\text{Cu}_{0.73}\text{In}_{1.82}\text{Sn}_{0.45}\text{S}_4$  (cycling rate 1Li/2 h, range 0–2.5 V).

an amorphous phase. This amorphisation can be observed in the XRD patterns by the disappearance of all the reflections. The great capacity loss observed at the first cycle is due to the formation of this amorphous phase, which does not allow to get back both spinel and rocksalt phases during the charge. Further discharge leads to lithium insertion in this amorphous phase, and constitutes the reversible part of the mechanism. At this stage, the materials remains amorphous.

These mechanisms can be observed by  $^{119}\text{Sn}$  Mössbauer spectroscopy (Fig. 2). Before lithium insertion, only the  $\text{Sn}^{\text{IV}}$  peak at  $1.1 \text{ mm s}^{-1}$  can be seen. After 1Li, a  $\text{Sn}^{\text{II}}$  peak appears at  $3.8 \text{ mm s}^{-1}$ , which corresponds to the presence of the rocksalt phase. After 3Li, the  $\text{Sn}^{\text{IV}}$  peak has almost disappeared and other contributions related to  $\text{Sn}^0$  (ca.  $2.0 \text{ mm s}^{-1}$ ) and  $\text{Sn}^{\text{II}}$  (ca.  $3.2 \text{ mm s}^{-1}$ ) appear. This corresponds to the disappearance of the spinel phase, and to the formation of this amorphous phase at the beginning of the 1.2–1.3 V plateau. Further lithiation leads to a decrease of the  $\text{Sn}^{\text{II}}$  peak because the rocksalt phase is consumed, and to an increase of the  $\text{Sn}^0$  contributions. After 9Li (spectrum F), only the amorphous phase is still present. From 11 to 15Li (spectrum G to H), the isomer shift  $\delta$  decreases from 2.3 to

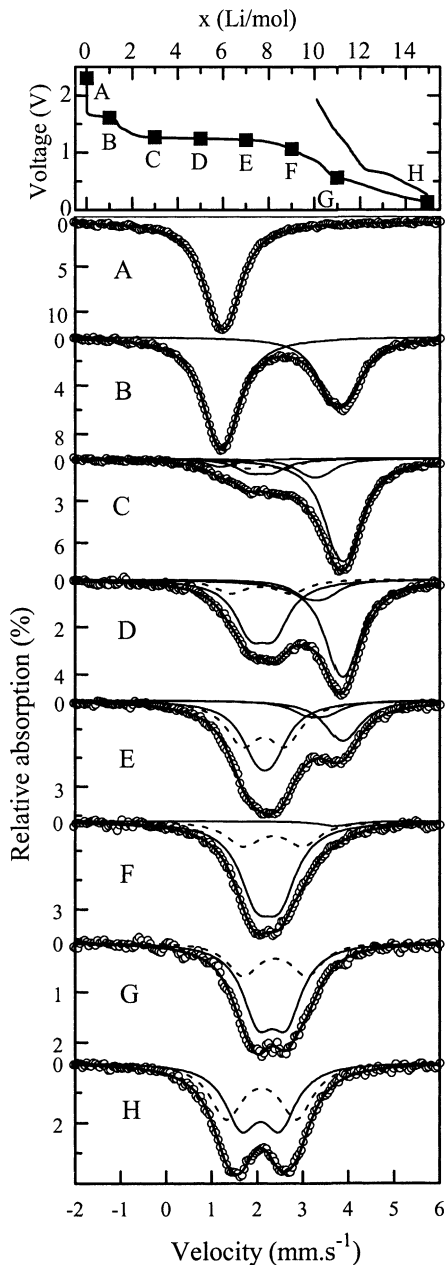


Fig. 2. Room temperature  $^{119}\text{Sn}$  Mössbauer spectra of  $\text{Cu}_{0.73}\text{In}_{1.82}\text{Sn}_{0.45}\text{S}_4$  at different lithium contents, shown on the voltage vs. composition curve.

$2.0 \text{ mm s}^{-1}$ , indicating the increase of the number of Li–Sn interactions, like in the  $\text{Li}_x\text{Sn}$  alloys [11,12]. The same mechanism can be observed in  $\text{CuInSnS}_4$ , but the formation of the amorphous phase occurs at a lower amount of inserted lithium, before complete reduction of  $\text{Sn}^{\text{IV}}$  into  $\text{Sn}^{\text{II}}$ , due to the bad phase transformation of spinel into rocksalt.

The exact composition of this amorphous phase is not completely resolved. The occurrence of  $\text{Sn}^0$  peaks with different quadrupole splittings indicates the presence of metallic bonds and different sites, where tin can be bound to other tin atoms, to indium or to lithium. The great values of the quadrupole splittings show a highly distorted tin environment that can be due to the presence of strong

interactions between tin and sulphur present in the matrix. We think that formation of nanoparticles occurs, which would be the electrochemically active form of the material.

The full potential linearised augmented plane wave (LAPW) method [13] was used to study the crystalline phases (spinel and rocksalt) by evaluating the densities of states, the  $^{119}\text{Sn}$  Mössbauer parameters and the XAS spectra including the transition probabilities. For simplicity, the spinel compound  $\text{CuInSnS}_4$  and the lithiated compound  $\text{Li}_{1.75}\text{In}_{1.75}\text{Sn}_{0.5}\text{S}_4$  (rocksalt-related phase  $\text{Li}_{14}\text{In}_{14}\text{Sn}_4\text{S}_{32}$ ) are considered for the pristine and the lithiated phases, respectively. The calculated values of the electron density and the electric field gradient at the Sn nucleus are found to increase from  $\text{CuInSnS}_4$  to  $\text{Li}_{1.75}\text{In}_{1.75}\text{Sn}_{0.5}\text{S}_4$  in quantitative agreement with the observed increases of the Mössbauer isomer shift and the quadrupole splitting, respectively. This can be correlated to the change in the Sn oxidation state from  $\text{Sn}^{\text{IV}}$  to  $\text{Sn}^{\text{II}}$  and to a weak increase in the asymmetry of the Sn electron distribution from  $\text{CuInSnS}_4$  to  $\text{Li}_{1.75}\text{In}_{1.75}\text{Sn}_{0.5}\text{S}_4$ . The comparison between the calculated and the experimental XAS spectra shows an overall good agreement which allows to determine the atomic origins of the main peaks. For example, the observed two main peaks of the S K-edge XAS spectrum of  $\text{CuInSnS}_4$  (Fig. 3) can be assigned to transitions from the  $1s(\text{S})$  core level to the  $p(\text{S})$ -type empty states. These states arise from the  $3p(\text{S})$ – $5s(\text{Sn})$  and  $3p(\text{S})$ – $5s(\text{In})$  interactions (peak A) and from the  $3p(\text{S})$ – $5p(\text{Sn})$  and  $3p(\text{S})$ – $5p(\text{In})$  interactions (peak B). The analysis of the experimental XAS spectra of the lithiated compounds are somewhat more difficult since these phases are never

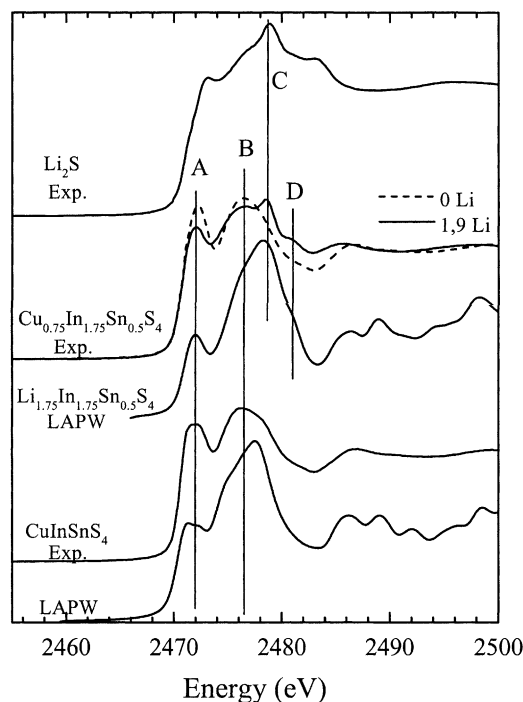


Fig. 3. Experimental and calculated sulphur K-edge absorption spectra (XAS) of  $\text{CuInSnS}_4$ , pristine and lithiated  $\text{Cu}_{0.75}\text{In}_{1.75}\text{Sn}_{0.5}\text{S}_4$ , and  $\text{Li}_2\text{S}$ .

isolated. The observed four main peaks in the S K-edge experimental spectrum can be compared in positions with those of the calculated spectrum of  $\text{Li}_{1.75}\text{In}_{1.75}\text{Sn}_{0.5}\text{S}_4$  but not in amplitude. This is mainly due to the contribution of the different phases to the experimental spectrum. The comparison of the latter spectrum with that of the spinel compound shows the existence of two additional peaks at about 2478 and 2481 eV labelled C and D, respectively. The peak C is found in both the experimental spectrum of  $\text{Li}_2\text{S}$  and the calculated spectrum of  $\text{Li}_{1.75}\text{In}_{1.75}\text{Sn}_{0.5}\text{S}_4$  and reflects interactions between the 3p(S) orbitals and both the 2s(Li) and 2p(Li) orbitals. The peak D which does not occur in  $\text{Li}_2\text{S}$  is due to the 2p(Li)–3p(S) interactions within the rocksalt-related lithiated compound and can be considered as an additional evidence of the existence of this phase.

#### 4. Conclusion

The compounds  $\text{CuInSnS}_4$  and  $\text{Cu}_{0.73}\text{In}_{1.82}\text{Sn}_{0.45}\text{S}_4$  were investigated as host materials for lithium insertion, and tested in galvanostatic cells. The good capacity and the low reduction/oxidation potentials of these materials make them possible candidates as negative electrodes for lithium-ion batteries. Two mechanisms were evidenced. At the beginning of the insertion, a spinel to rocksalt transformation occurs. Then, an amorphous phase is formed, where tin is bound to other metallic atoms and is still in strong interaction with the sulphur present in the material. Density functional calculations on crystalline phases have shown a

good agreement between experimental results and theoretical interpretations. The next step of this study will be to model the mechanisms that occur at lower potentials.

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