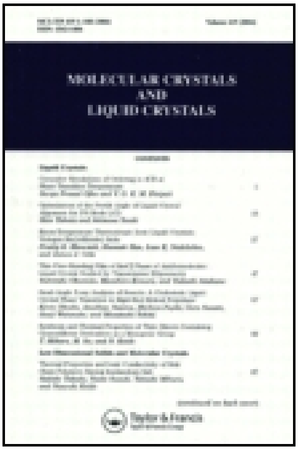

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Study of new electrode materials based on sulfides with a spinel structure

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Study of new electrode materials based on sulfides with a spinel structure.

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In this study, sulfide based spinel materials of tin and titanium were synthesised ($Cu_2FeTi_3S_8$ and $Cu_2FeSn_3S_8$). A topotactic substitution of tin by titanium atoms was performed in order to obtain electrode materials with high specific capacity associated to a good conductivity. According to the first electrochemical tests the $Cu_2FeTi_3S_8$ spinel appears as a possible anodic material for the Rocking-Chair batteries.

Keywords : Rhodostannite; Insertion ; Lithium ; Titanium ; Spinel; Electrode

I . INTRODUCTION

It is well known that the use of lithium metal as the negative electrode in rechargeable batteries introduces some problems regarding the cycleability of these cells. Using the Rocking-Chair or lithium-ion concept[1-2], with ability to store and exchange one or more lithium ions, would help the present limitations of rechargeable batteries. Since the observation by Eisenberg[3], spinels compounds have proven adequate host lattices for intercalation of lithium ions. Then, extensive studies on the insertion properties of transition metal spinel oxides[4-7], chalcogenide spinels[8-10] and selenospinels[11] have been reported. The cubic normal spinel structure $A[B_2]X_4$ [12] is illustrated in Figure 1. In this figure one can see the different coordinations of each atom. Figure 2 shows the rigid framework of alternate rows of edge-sharing BX_6 octahedra joined to AX_4 tetrahedra by corner sharing. Two types of layers are present : the first one with an occupancy of 0.75 for the octahedron and the second one with an occupancy of 0.25 for the octahedron and 0.5 for the tetrahedron.

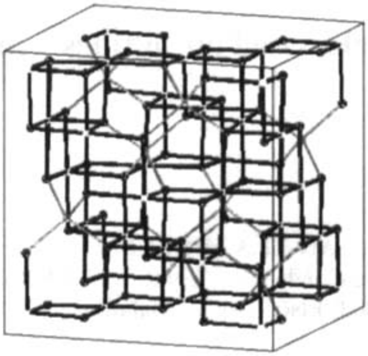

FIGURE 1 : Regular representation of a spinel

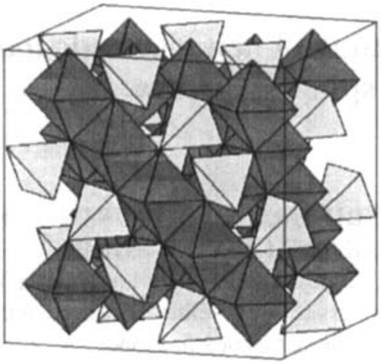

FIGURE 2 : Representation of a spinel with layers

Structure of the Rhodostannite spinel $Cu_2FeSn_3S_8$, was first described by Springer[13] and refined by single-crystal X-ray analysis. In spite of a very weak tetragonal distorsion[14] the crystal structure of $Cu_2FeSn_3S_8$ can be described in the $Fd\bar{3}m$ space group. In the sulfur framework the Cu atoms occupy the 8a tetrahedral sites and Fe, Sn atoms are randomly distributed in 16 d octahedral sites. Finally, the sulfur atoms are arranged in a cubic close packed (ccp) arrangement, giving rise to a large number of availables sites for lithium insertion. In a recent work[15], the synthesis and insertion properties of $Cu_2FeSn_3S_8$ were described. However, the small specific capacity of this compound have to be improved for use in lithium Rocking Chair cells. In this way, we substituted tin by titanium atoms.

II . EXPERIMENTAL

All compounds were prepared by solid state reaction. We mixed stoichiometric amounts of the constituent elements and sealed in evacuated quartz tubes, under vacuum ($P = 10^{-3}$ Pa.). Then, the mixture was heated to 300° C for one day, after which the temperature was increased to achieve a final constant value of 750° C for ten days and obtained a black powder.

The purity and structure of all compounds were examined by X-Ray Powder Diffraction (XRPD) with a Philips θ-2θ diffractometer using the $CuK\alpha$ radiation, and a nickel filter. Rietveld refinements were carried out with the aid of a computer program DBWS-9006 developed by Wiles and Young[16]. The local environment of the tin atoms was studied by means of Mössbauer spectroscopy. The spectra were measured using an ELSCINT AME 40 constant acceleration spectrometer. The γ-ray source was ^{119m}Sn in a $BaSnO_3$ matrix and used at room temperature. The spectra were fitted with lorentzian profiles by a least-squares method , with the software ISO[17]. All the isomer shifts reported here were given with respect to the centre of a $BaSnO_3$ spectrum obtained with the same source.

The conductivity measurements were performed in an evacuated pyrex chamber, connected to an impedance analyser (H.P. 4192 A) driven by a computer. All electrochemical tests were carried out in an Argon filled dry box. The charge/discharge curves were obtained automatically by means of a scanning potentiostat (EGC/PAR 362).

RESULTS AND DISCUSSION.

All the phases were identified and their XRD Patterns were refined by Rietveld analysis. Rietveld analysis are summarized in Table 1 and the diffraction patterns shown in Figure 2.

The two parameters (S and R_{Bragg}) control the refinement. R_{Bragg} gives an indication of the difference between the theoretical and experimental intensities of the Bragg reflections. S is a similar parameter but it takes into account the complete patterns. For a good refinement, the value for S has to be $1 < S < 1.5$. Data collected in Table 1 confirm the goodness of the fitting procedure.

TABLE 1 Result of the Rietveld analysis of XRPD data of $Cu_2FeSn_3S_8$ and $Cu_2FeTi_3S_8$, according to $Fd\bar{3}m$, origin 2.
(Cu(8a) : 1/8,1/8,1/8; Fe, Sn and Ti(16d) : 0,0,0 and S(32e) : x,x,x)

Compounds	a (Å)	x(S)	S	R_{Bragg}
$Cu_2FeSn_3S_8$	10.3247(1)	0.2565(2)	1.26	2.92
$Cu_2FeTi_3S_8$	9.9989(1)	0.2555(1))	1.10	3.58

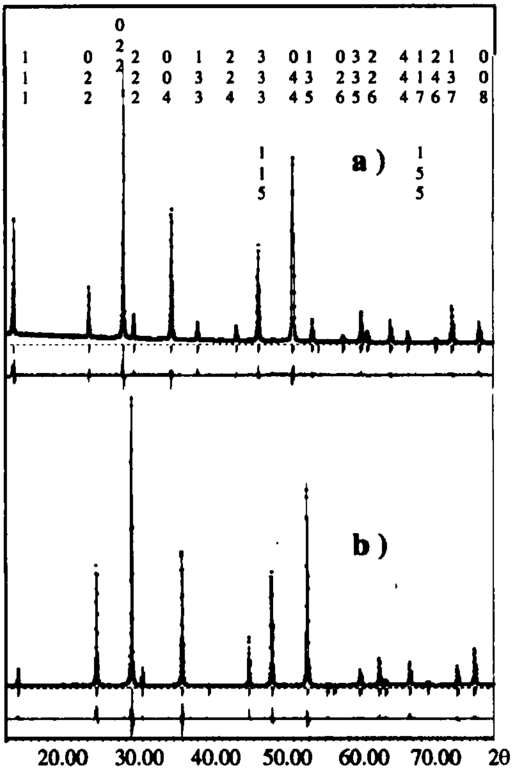

FIGURE 2 : XRD patterns of a) $Cu_2FeSn_3S_8$ and b) $Cu_2FeTi_3S_8$

In order to obtain some information about the electronic distribution around tin atoms, the ^{119}Sn Mössbauer spectroscopy was used. The parameters are given in Table 2 , and the spectra are shown in Figure 3.

TABLE 2 Mössbauer parameters of $Cu_2FeSn_3S_8$ and $Li_6Cu_2FeSn_3S_8$.

Compounds	Site	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	C	X^2
$Cu_2FeSn_3S_8$	1	1.246(3)	0.295(7)	1.001(9)	100	0.488
$Li_6Cu_2FeSn_3S_8$	1	1.252(5)	0.287(8)	0.941(7)	72	0.478
	2	2.62(3)	1.24(3)	1.0(1)	12	
	3	3.11(2)	0.91(2)	0.95(3)	16	

In Table 2, δ is the isomer shift relative to $BaSnO_3$, Δ the quadrupole splitting, Γ the full-width at the half-maximum, C the contribution and Chi-squared tests (X^2) allowed calculation controls. Isomer shift of the pristine spinel (1.246(3) mm/s) is characteristic of tin (IV) in octahedral site in good agreement with the crystal structure. The weak quadrupole splitting shows that tin is in a slightly distorted octahedral environment.

Indeed, the ^{119}Sn Mössbauer of the lithiated spinel show a partial reduction of Sn(IV) toward Sn(II) (δ = 3.11(1)mm/s) and probably Sn(0) (δ = 2.62(3)mm/s).

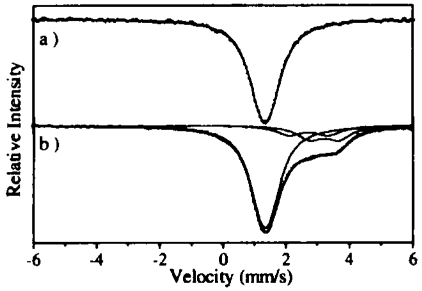

FIGURE 3 : ^{119}Sn Mössbauer spectra for a) $Cu_2FeSn_3S_8$ and b)$Li_6Cu_2FeSn_3S_8$.

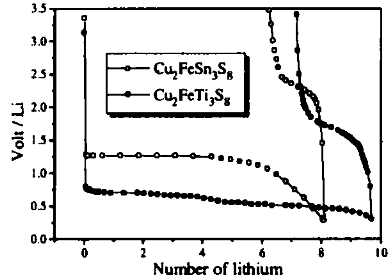

FIGURE 4 : Charge/discharge curves of both spinels .

From an electrochemical point of view, the conductivity of the starting materials is close to 10^{-5} S/cm for the $Cu_2FeSn_3S_8$ spinel and much higher (approximately 10^{-1} S/cm) for the titanium based spinel. Lithiation increases slightly the conductivity (10^{-4} S/cm) of the tin spinel while the conduction of the titanium spinel remains in the same range order.

Regarding the charge/discharge curves, they were carried out galvanostatically at current density of 500 μA/cm^2 between 3.3 and 0.3 V/Li. In the Figure 4, two characteristics of these materials can be pointed out. The first one concerns the specific capacity of the samples. The substitution by titanium atoms improves the amount of intercalated lithium. The second one concerns the value of the reduction potential. The potential corresponding to the tin reduction (confirmed by ^{119}Sn Mössbauer) is close to 1.26 V/Li while the titanium reduction process occurs at 0.7 V/Li. Although the reversibility of this material is limited since only 2 Li are deintercalated, this process is occurring at an interesting potential value. Nevertheless, a similar reversibility is obtained when only 4 Li are intercalated during the reduction process. In both cases, at the beginning (0 to 1 Li) a copper reduction may be envisaged[15].

CONCLUSION

In this study the characterization of $Cu_2FeTi_3S_8$ spinel was performed and a topotactic substitution of tin by titanium atoms was demonstrated. This material was tested in galvanostatic cells. The high specific capacity associated to low reduction/oxidation potentials makes these materials a possible candidate as negative electrode for Rocking-Chair batteries. Experiments are currently in progress in order to optimize the cycling conditions as well as the elaboration of this material with different ratios of substitution.

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