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Lithium insertion mechanism in CoSb₃ analysed by ¹²¹Sb Mössbauer spectrometry, X-ray absorption spectroscopy and electronic structure calculations

Isabelle Devos,^a Manfred Womes,^b Mike Heilemann,^b Josette Olivier-Fourcade,^b Jean-Claude Jumas^{*b} and José Luis Tirado^c

^aIEMN (UMR 8520 CNRS), Département ISEN, 41 boulevard Vauban, 59046 Lille Cedex, France. E-mail: jumas@univ-montp2.fr

^bLAMMI (UMR 5072 CNRS), Université Montpellier II, CC 15 Place E. Bataillon, 34095 Montpellier Cedex, France

^cLaboratorio de Química Inorgánica, Universidad de Córdoba Campus de Rabanales, C3 Planta 1, 14071 Córdoba, Spain

The lithium insertion mechanism into the skutterudite-type CoSb₃ compound has been studied using X-ray Absorption Near Edge Structure (XANES), ¹²¹Sb Mössbauer spectrometry and electronic structure calculations based on the Density Functional Theory (DFT) in the Linear Muffin Tin Orbital (LMTO) framework. ¹²¹Sb Mössbauer spectra are in agreement with a progressive restructuring which occurs during the second stage (voltage plateau at 0.6 V). The Mössbauer hyperfine parameters show the formation of Li₃Sb and of a ternary intermediate phase Li_xCoSb_y, whose variable composition depends on the insertion conditions. XANES spectra at Sb L_{I, III} and Co K edges have been compared to calculated Projected Densities of States (PDOS) of reference compounds containing Co, Sb and Li. This analysis has allowed specification of the restructuring mechanism as a distortion of the CoSb₆ octahedral units and confirms the formation of Li₃Sb. The overall characterisations have been interpreted to suggest the first discharge mechanism of restructuring in accordance with the global reaction: $\text{CoSb}_3 + (y + z) \text{Li} \rightarrow (\text{Li}_x\text{Co}_{1-m}\text{Sb}_y + m \text{Co} + \text{Li}_3\text{Sb}) \leftrightarrow \text{Li}_z\text{Co} + y \text{Li}_3\text{Sb}$

Introduction

The currently intensified search for new negative electrode materials for Li-ion rechargeable batteries is reflected by a steadily increasing number of investigations.¹ The main requirements for such active materials are that (i) they readily accept lithium under insertion and (ii) they contain elements which are easily reduced such as Sn or Sb. Among Sb based materials, CoSb₃ is a promising candidate due to its skutterudite-type crystal structure, the particularity of which is to exhibit large voids allowing the accommodation of ions.

Actually, CoSb₃ or CoFe₃Sb₁₂ have been demonstrated to be good precursors of active anode materials for lithium batteries.^{2,3} It has been shown that their cycling behaviour is similar to that observed for tin composite oxides (TCO). These TCO have been extensively studied since the work of Idota *et al.*⁴ The now generally accepted picture describes the cycling behaviour of TCO as a first discharge which involves a restructuring of the pristine material and irreversible formation of inactive lithium oxide, followed by the reversible formation of Li_xSn alloys ($0 < x < 4.4$).^{5–10} Another restructuring mechanism has been shown for 3d metal oxides (CoO, NiO)^{11,12} with formation of active Li₂O catalysed by Co⁰ nanoparticles. Recently the electrochemical reactivity mechanism of CoSb₃ *versus* lithium has been studied by *in-situ* X-ray diffraction, microscopy and magnetic measurements.¹³ In this case and as for CoO, the formation of a composite made of Co and Li₃Sb nanograins is observed.

The aim of this work is to analyse the intermediate phases formed during the first discharge in order to understand the chemical process. To this end we combined in this work the use of advanced spectroscopic techniques and theoretical calculations. Our analysis is based on the comparison between the

experimental characterisation of several samples and the calculated electronic structure of properly chosen model compounds. Samples are chosen on the first discharge profile in order to be representative of the different stages. ¹²¹Sb Mössbauer spectra have been recorded to characterise the antimony electronic structure which is indicative of its oxidation state and chemical environment. Regarding the electronic structure, XANES spectra have been recorded at Sb L_{I, III} and Co K edges. These XANES spectra have been interpreted as the ground state electronic structure of the conduction band. As they have to be compared to projected densities of states (PDOS) we have performed electronic structure calculations by using the density functional theory (DFT) in the Linear Muffin Tin Orbital (LMTO) framework. These calculations are realised for well-defined crystalline compounds containing Co, Sb and Li. As a next step we try, using the theoretical conduction bands, to reproduce trends in the evolution of the experimental XANES spectra. Considering the overall characterisations, we are able to suggest a fully coherent picture of the first discharge mechanism.

Experimental

Sample synthesis and electrochemical lithiation

The compounds were prepared by heating stoichiometric quantities of the elements, antimony powder (purity 99.5% Aldrich) and cobalt powder (purity 99.995% Aldrich) in evacuated sealed quartz tubes. The binary sample was heated at 50 °C h⁻¹ and maintained for one week at 750 °C. It was then crushed, ground and re-annealed for a further week at 700 °C and finally cooled to room temperature at 10 °C h⁻¹. The material was carefully handled in an argon-filled glove box throughout the

preparation process to prevent unexpected contamination. The purity of the sample was checked by X-ray powder analysis.

For the electrochemical studies, the CoSb₃ samples were used as positive electrode materials in Swagelok cells assembled in an argon-filled glove box with Li metal as the negative electrode and 1 M LiPF₆ in ethylene carbonate, dimethyl carbonate as the electrolyte. Electrochemical measurements were carried out using a Mac Pile system in galvanostatic mode.

¹²¹Sb Mössbauer spectroscopy

¹²¹Sb Mössbauer measurements were performed in standard transmission geometry using a ^{121m}Sn in BaSnO₃ source of nominal activity 0.5 mCi on a constant acceleration spectrometer. During the measurements, both source and absorber were held at liquid helium temperature to increase the fraction of recoil-free emission and absorption processes. Absorbers at different depth of discharge/charge were prepared in a glove box by carefully opening the cells. The electrode materials containing the active material were mixed with A-Piezon grease and placed on a specific sample holder transparent for γ rays. The velocity scale was calibrated with the standard spectrum of an iron absorber using a ⁵⁷Co(Rh) source. The zero isomer shift was defined from the spectrum of InSb at 4 K ($\delta = -8.70$ (4) mm s⁻¹ relative to the Ba^{121m}SnO₃ source). The data were processed using transmission integral analysis software GM5SIT¹⁴ with the Mössbauer source fraction f_s and source line width Γ_s held constant at 0.62 and 1.45 mm s⁻¹, respectively.

X-Ray absorption spectroscopy

XANES was performed at the LURE laboratory (Orsay, France) on the ABS2 experimental station located on the beam line D21 of the DCI storage ring. The accessible energy range of 4 keV to 30 keV allows the study of transition metal K and antimony L edges. CoSb₃ and lithiated samples were finely ground and passed through a 5 μ m sieve in order to obtain powders of the same particle size. A thin membrane was coated with this powder and protected by a capton film in order to avoid any contact with air. For the lithiated samples, the absorbers were prepared in a glove box. The data collections were carried out at room temperature in transmission mode. The intensities of the incident (I_0) and transmitted (I) beams were measured with two ion chambers. The beam line was equipped with a Si (311) double crystal monochromator for the Co K edge (7700–7800 eV) and with a Si (111) double crystal monochromator for the Sb L_{I-III} edges (4100–4750 eV) allowing a resolution of 0.2 eV and 0.4 eV respectively. Energy calibration was carried out from the standard spectra at the Ni K edge of a high purity Ni foil (8333 eV) and at the Ti K edge of TiO₂ (pre-peak at 4967.5 eV). The XANES spectra were recorded with an energy step width of 0.2 eV and treated by the following procedure, using the ORIGIN[®] software.¹⁵ First, the absorption background was subtracted supposing linear behaviour over the whole energy range. Then the spectra

were normalised to give the same absorption step amplitude in a range of pure atomic absorption.

Theoretical electronic structure calculations

To understand the trends in the evolution of the experimental XANES spectra from a structural point of view, we compared them with the electronic structures of well defined crystalline compounds containing Co, Sb and Li. From Pearson's Handbooks¹⁶ we chose CoSb (with face sharing CoSb₆ octahedra), CoSb₂ (in the layered form and in the pyrite form), the hypothetical compound Li(CoSb₃)₄ imagined with the 2a sites occupied by lithium atoms (filled skutterudite) in order to be able to reproduce the amorphisation and finally Li₂Sb and Li₃Sb since they are thought to be formed under lithiation.

The electronic structure calculations are carried out within the Density Functional Theory (DFT) framework.^{17,18} The DFT is a first principle theory. It determines the ground state properties of an electronic system by the knowledge of its electron density $\rho(r)$. It allows mapping of the many-electron problem on a set of one-electron equations. Then, the total energy of the system is written as a functional of $\rho(r)$. The exchange and correlation energy E_{xc} , which is not known in general, appears in the equations. For purpose of practical calculations, an approximation of this term has to be introduced. The traditional one is the Local Density Approximation (LDA). It is based on the assumption that the relation between E_{xc} and $\rho(r)$ is locally the same as for a free electron gas of identical density, which is quite accurately known. Since projected densities of states (PDOS) are needed for comparison with XANES spectra, we use the ESOCS code.¹⁹ It is based on the use of the Atomic Sphere Approximation (ASA) and a Linear Muffin Tin Orbital (LMTO) expansion of the wave function. The trade off is that an excellent description of the Bloch function is obtained with a minimal basis. The LMTO-ASA expansion allows an easy computation of the projection of densities of states onto atomic sites and a good description of high energy conduction bands. Details of the compounds' electronic structures are reported in Table 1.

Results and discussion

Crystal structure

The CoSb₃ crystal structure²⁰ with the CoAs₃ (skutterudite) type crystal structure is based on a bcc lattice (cell constant $a = 9.0305$ Å) with 4 formula units per cell. The unit cell symmetry corresponds to the $Im\bar{3}$ space group. Co atoms lie in the 8e position ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and Sb atoms in the 24g position (0, 0.3351, 0.1602). The skutterudite structure (Fig. 1a) may be viewed as a simple cubic sub-lattice of Co atoms in a basic cell with dimension $a/2$. Six four-membered rings of Sb atoms are inserted in the cubes along the (100), (010) or (001) crystallographic directions, two cubes remaining vacant. The CoSb₃ crystal structure (Fig. 1b) may also be considered as corner sharing CoSb₆ octahedra which are tilted such that Sb atoms form Sb₄ rings which may be approximated as squares.

Table 1 Identification of the main structures of the valence band of CoSb₃ (Fig. 9) and of the conduction bands of CoSb₃ (Fig. 10), CoSb (Fig. 11), CoSb_{2, lay} (Fig. 12), CoSb_{2, pyr} (Fig. 13) and Li(CoSb₃)₄ (Fig. 14)

	CoSb ₃	CoSb	CoSb _{2, lay}	CoSb _{2, pyr}	Li(CoSb ₃) ₄
A (-7--12 eV)	Sb(s)				
B (-6-0 eV)	Co(d)-Sb(p)				
P1 (0-4 eV)	Sb(p)-Co(d)	Sb(p)-Co(d)	Sb ₁ (p)-Co(d)	Sb(p)-Co(d)	Sb(p)-Co(d)
			Sb ₂ (p)-Co(d)		Li _{tot}
	Sb(s)-Sb(d)	Sb(s)-Sb(d)	Sb ₂ (s)-Sb ₂ (d)	Sb(s)-Sb(d)	
P2 (4-14 eV)	Sb(d)-Co(p)	Sb(d)-Co(p)	Sb ₁ (d)-Co(p)	Sb(d)-Co(p)	Sb(d)-Co(p)
			Sb ₂ (d)-Co(p)

Fig. 1 CoSb₃ crystal structure viewed as (a) cubic cobalt (black atoms) units in which antimony (white atoms) rings are inserted or (b) CoSb₆ octahedral units.

Cycling profile

Fig. 2 shows the first discharge and charge profiles at a 1 Li (per formula unit)/78 h rate for the discharge and at a 1 Li (per formula unit)/42 h rate for the charge. The first discharge shows: i) an abrupt decrease of the voltage potential to 0.6 V for 0.2 Li/CoSb₃, ii) a large voltage plateau which characterises a two-phase process up to 8 Li/CoSb₃ close to 0.6 V in agreement with a previous study¹³ and then iii) a decrease of the potential to 0 V for approximately 9.7 Li/CoSb₃. For the first charge the voltage plateau is close to 1.0 V. Several samples have been chosen by interrupting the galvanostatic experiments at different depth of discharge and charge (Fig. 2) in order to identify the intermediate phases formed during the first cycle.

X-Ray diffraction patterns

XRD patterns have been recorded for CoSb₃ and samples A₁, A₃ and A₄. The skutterudite structure lines are clearly identified for CoSb₃. Their intensity rapidly decreases with ongoing discharge due to progressive amorphisation. They clearly disappear at the end of the first discharge indicating loss of long

Fig. 3 ¹²¹Sb Mössbauer isomer shift scale from reference compounds.

range order in agreement with previous studies.^{2,13} The refinement of the cubic unit cell parameter for CoSb₃ leads to $a = 9.011$ Å, which is in good agreement with the value reported by Kjekshus *et al.*²⁰ For the other samples, this value is refined to $a = 8.995$ Å. The difference from the initial value falls within the experimental errors. Thus, no clear expansion of the skutterudite host is detected upon lithiation in agreement with a two-phase process.

Mössbauer spectroscopy

Spectra are mainly characterised by two parameters: the isomer shift (δ) and the quadrupole splitting (Δ). The first corresponds to the peak position on the spectrum. It can be considered as proportional to the Sb (5s) electron density in the valence band.^{21,22} δ is thus correlated with the electron configuration and provides an idea of the Sb oxidation state by comparing the measured δ to a reference scale (Fig. 3). The second parameter corresponds to the splitting of the nuclear sub-levels under the influence of the electric field gradient and is thus related to the distortion of the local environment. Its analysis

Fig. 2 Cycling profiles of Li/LiClO₄ (PC + EC)/CoSb₃ cells using 30 and 50 μ A currents during charge and discharge respectively. The squares indicate the compositions for which ¹²¹Sb Mössbauer (A₁, A₃, A₄, B₁, B₂) and XANES (A₀, A₃) spectra were recorded.

Fig. 4 ^{121}Sb Mössbauer spectra of (a) CoSb_3 and CoSb_3 based electrodes during cell discharge: (b) A_1 $\text{Li}_{1.7}\text{CoSb}_3$, (c) A_3 $\text{Li}_{4.2}\text{CoSb}_3$, (d) A_4 $\text{Li}_{10.5}\text{CoSb}_3$, and charge: (e) B_1 $\text{Li}_{10.5}\text{CoSb}_3$, (f) B_2 $\text{Li}_{5.0}\text{CoSb}_3$.

allows the characterisation of the electron distribution close to the probed nucleus.

Mössbauer spectra are shown in Fig. 4 and the corresponding refined hyperfine parameters are included in Table 2. Concerning CoSb_3 , the spectral shape and the isomer shift $\delta = -1.08$ (2) mm s^{-1} relative to InSb agree with published data.^{20,23} Comparison with the reference isomer shift scale (Fig. 3) shows that this value is intermediate between those observed for elemental Sb and InSb where the Sb (5s) electrons are involved in covalent bonds. The large quadrupole splitting $\Delta = +9.3$ (2) mm s^{-1} and the asymmetry factor $\eta = 0.65$ suggest a strongly distorted environment. It corresponds to the geometrical distortion of the $\text{Sb}(\text{Co}_2\text{Sb}_2)$ tetrahedra and to the chemical difference between the antimony neighbours Co and Sb.

The hyperfine parameters of sample A_1 ($\delta = -1.17$ mm s^{-1} and $\delta = +9.5$ mm s^{-1}) are not modified in comparison to CoSb_3 and would be interpreted as a topotactic insertion of 0.2 Li/CoSb_3 (filled skutterudite). The spectrum of sample A_3 clearly shows the presence of two components. One of them ($\delta = 1.0$ mm s^{-1} and $\Delta = 0$) can be assigned to Li_3Sb by

comparison with the hyperfine parameters of the pure Li_3Sb compound ($\delta = 1.31$ mm s^{-1} and $\Delta = 0$). The other one ($\delta = -2.4$ mm s^{-1} and $\Delta = +10.9$ mm s^{-1}) is assigned to Sb in Li_xCoSb_y with an environment different from the one observed in pristine CoSb_3 . At the end of the first discharge (sample A_4) the signal of Li_xCoSb_y disappears and only the Li_3Sb signal is present. At the first charge (samples B_1 and B_2) one can observe two components assigned to Li_3Sb and Li_xCoSb_y . The relative contribution of the Li_xCoSb_y sub-spectra increases from 6% (sample B_1) to 58% (sample B_2). Thus, the reversible cycle takes place between these two phases Li_xCoSb_y and Li_3Sb .

XANES

XANES is particularly well suited to provide insight into the partial densities of unoccupied states. The XANES spectra may be split into two regions, the near edge and the post edge regions (from about 15 eV to 70 eV above the threshold). The second is generally modelled taking into account the multiple scattering of photo excited electrons. The near edge is generally

Table 2 ^{121}Sb Mössbauer data of CoSb_3 and CoSb_3 based electrodes during cell discharge: A_1 ($\text{Li}_{1.7}\text{CoSb}_3$), A_3 ($\text{Li}_{4.2}\text{CoSb}_3$), A_4 ($\text{Li}_{10.5}\text{CoSb}_3$), and charge: B_1 ($\text{Li}_{10.5}\text{CoSb}_3$), B_2 ($\text{Li}_{5.0}\text{CoSb}_3$). δ = isomer shift relative to InSb ($-8.70(4)$ mm s^{-1} relative to the source $\text{Ba}^{121\text{m}}\text{SnO}_3$); Δ = quadrupole splitting; Γ = line width; η = asymmetry parameter; χ^2 = chi-squared and Misfit = comparative goodness of fit criterion which gives the fraction of the experimental signal that remains unfitted

Sample	$\delta/\text{mm s}^{-1}$	$\Delta/\text{mm s}^{-1}$	$\Gamma/\text{mm s}^{-1}$	η	C (%)	χ^2	Misfit (%)
CoSb_3	-1.08(2)	+9.3(2)	1.61(4)	0.65	100	1.21	0.021
A_1	-1.17(2)	+9.5(3)	1.68(8)	0.91	100	1.11	0.034
A_3	-2.4(2)	+10.9(8)	1.6(3)	0.60	50.7	1.13	0.090
	+1.0(1)	0	2.8(2)		49.3		
A_4	+1.08(1)	0	1.46(4)	—	100	1.07	0.019
B_1	-2.3(1)	0	1.69(6)	—	6.2	1.06	0.022
	+1.08(2)	0	1.69(6)	—	93.8		
B_2	-2.08(2)	+9.7(2)	1.40(4)	—	58.2	1.06	0.022
	+0.96(2)	0	1.40(4)	—	41.8

Fig. 5 XANES spectra at the Co K-edge for CoSb₃ and Co.

Fig. 6 XANES spectra at the Co K-edge for CoSb₃ and samples A₀ (Li_{1.2}CoSb₃) and A₃ (Li_{4.2}CoSb₃).

analysed in terms of electronic transitions to empty states, assuming a weak perturbation due to the creation of a core-hole. It has been demonstrated that this is negligible in metals.²⁴ In CoSb₃, we assume that the number of valence electrons on each atom is sufficient to assure good screening of the core-hole allowing in this way an interpretation of the spectra in terms of the electronic ground state of the conduction band.

In all cases the different edges (Co K and L_{I-III} Sb) show two structures labelled S₁ and S₂ in Fig. 5–8 and which will be interpreted from band-structure calculations. A comparison between the Co K-edge spectra of CoSb₃ and elemental Co and the Sb L_{III}-edge spectra of CoSb₃ and elemental Sb has been made (Fig. 5). From this, we can deduce the following facts:

- the Co K-edge shows a reduced intensity of the pre-peak S₁ around 7709 eV in CoSb₃ with respect to Co metal (Fig. 5a) which is due to an Sb–Co charge transfer into unoccupied 3d–4p orbitals of Co. A shift of 5 eV of the main absorption edge S₂ towards lower energies in CoSb₃ (7716 eV) with respect to Co metal (7721 eV) is observed. This shift can be explained by the appearance of Co 4p states mixed with Sb 5d states at approximately 6 eV above the Fermi level (see band structure calculations);

- the Sb L_{III}-edge (2p_{3/2} → 5s, 5d) spectra of CoSb₃ and Sb metal (Fig. 5b) are very similar which indicates that the relative charge transfer per Sb atom is rather low while the relative charge transfer per Co atom is more important and thus easily detected.

The superpositions of the XANES spectra for CoSb₃ and samples A₀ and A₃ are reported in Fig. 6–8 and the peak positions are summarised in Table 3. The Co K-edge (Fig. 6)

Fig. 7 XANES spectra at the Sb L_I-edge for CoSb₃ and samples A₀ (Li_{1.2}CoSb₃) and A₃ (Li_{4.2}CoSb₃).

Fig. 8 XANES spectra at the Sb L_{III}-edge for CoSb₃ and samples A₀ (Li_{1.2}CoSb₃) and A₃ (Li_{4.2}CoSb₃).

Table 3 XANES data at the Co K-edge and Sb L_{I, III}-edges for CoSb₃ and CoSb₃ based electrodes during cell discharge A₀ (Li_{1.2}CoSb₃) and A₃ (Li_{4.2}CoSb₃)

		CoSb ₃	A ₀	A ₃
Co K-edge	S ₁	weak	7709.0 eV	7709.0 eV
	S ₂	7716.0	7716.6 eV	7717.0 eV
Sb L _{III} -edge	S ₁	weak	weak	4133.6 eV
	S ₂	4139.4 eV	4139.4 eV	4140.0 eV
Sb L _I -edge	S ₁	4702.1 eV	4701.7 eV	4701.7 eV
	S ₂			
FWHM		5.6 eV	5.6 eV	5.7 eV

shows a decrease of the intensity of the S₂ structure when going from CoSb₃ to Li_{1.2}CoSb₃ which results from the decrease of unoccupied p states. This observation is in agreement with the results of the band structure calculation for Li(CoSb₃)₄ which indicates a decrease of Co 4p electron density at 6 eV above the Fermi level. Beyond Li_{1.2}CoSb₃ further lithiation leads to the opposite behaviour, increasing the number of vacant Co 4p states. The S₁ pre-edge below the main absorption step is clearly more pronounced after insertion of 4.2 lithium atoms into the host structure. The Sb L_I-edge (2s → 5p) spectrum of CoSb₃ (Fig. 7) is characterised by a white line S₁ (4702 eV) which shows that the p conduction states are localised and a weak S₂ structure (4710 eV). After insertion of 1.2 Li the decrease of the intensity of the S₁ structure and the disappearance of the S₂ structure indicate a reduction of empty Sb 5p states (Fig. 7). This reduction does not continue beyond the 1.2 Li inserted. Concerning the Sb L_{III}-edge (Fig. 8) one can observe for CoSb₃ and sample A₀ a very weak shoulder S₁ on the rising edge and the S₂ structure (4139 eV) whose intensity slightly decreases for A₀ indicating that Sb (s, d) states are filled. Between $x = 1.2$ and $x = 4.2$, the Sb L_{III}-edge further

Fig. 9 Calculated CoSb₃ valence band PDOS.

loses intensity at 4143 eV (S₂ structure) while a shoulder appears at 4137 eV which seems to indicate a shift of vacant Sb 5d states by approximately 5 eV to lower energies. This fact can be explained by both the Co K-edge, which shows an increasing number of unoccupied Co 4p states, and the Sb L_I-edge which, after an initial lithiation, does not decrease any more. For Li_{4.2}CoSb₃ the increase of the intensity of the S₁ structure (Fig. 8) may be indicative of a local order modification.

Theoretical electronic structures of CoSb₃ and reference materials

For CoSb₃ the PDOS from our calculations (ESOCs) are reported in Fig. 9 and 10. Comparison of these results with a previous analysis of the CoSb₃ electronic structure²³ based on

CoSb₃ Conduction bands

Fig. 10 Calculated CoSb₃ conduction band PDOS.

the DOS and PDOS calculated in the CASTEP (DFT-LDA pseudo-potential) and tight binding framework, respectively, shows an overall agreement.

Concerning the valence band, two main structures A and B which are similar in width are found. Structure A is mainly due to Sb (s) states while structure B reflects interactions between Sb (p) and Co (d) states. A deeper analysis of structure A has been realised by comparison with various antimony chalcogenides, in which Sb is characterised by a lone-pair of 5s electrons.²⁴ In that case, due to the valence Sb (5s) lone pair (the corresponding theoretical population is greater than 1.9 electrons), there is a very weak antibonding contribution of the Sb (5s) states to the conduction band. Nevertheless, the Sb (5s) conducting population in CoSb₃ is calculated to be 0.23 electrons, which is more than the maximum 0.1 electron in Sb lone-pair chalcogenides. From these considerations and previous Mössbauer results,²⁵ we have concluded that the Sb (5s) electrons are delocalised and spread in the conduction band; they do not participate in an antibonding state. With regard to the conduction band, methods correctly describe states within the first 10 eV energy range. The PDOS features are i) in the first 4 eV range a peak labelled P1, whose major character is Sb (p) and Co (d) states [Sb (s) states participate weakly as they are spread in the conduction band, Co (p) states also weakly participate], ii) higher in energy (4–12 eV), a second peak P2, mainly due to Sb (d) and Co (p) states which we attribute to the octahedral CoSb₆ environment. Its energy position is similar to that in the CoSb₂ compound where Co is also in an octahedral environment. Its width is consistent with a strong angular distortion of the Co–Sb bonds.

These conduction band features can be attributed to corresponding S₁ and S₂ structures on the XANES spectra. Due to its strong Sb (p) character, peak P1 corresponds beyond any doubt to structure S₁ in the Sb L_I spectrum. Its weak Sb (s, d) character explains the occurrence of the pre-peak S₁ on the Sb L_{III} spectrum and its Co (p, d) character contributes to structure S₁ in the Co K-edge spectrum. Peak P2 corresponds to structure S₂ in the XANES spectra. The energy spacing between P1–P2 (7 eV) is in agreement with those observed between the S₁–S₂ structures (9 eV). The relative intensity of S₂ to S₁ is in agreement with the relative contributions to the PDOS.

Our ESOCS electronic structure is in good agreement with previously published data.²³ This method can be used to go further in the analysis of the lithiation mechanism by calculating the electronic structure of several reference materials: CoSb (Fig. 11) with face sharing CoSb₆ octahedra, CoSb₂ in the layered form (CoSb_{2, lay}, Fig. 12) which is highly distorted and in the pyrite form (CoSb_{2, pyr}, Fig. 13) with perfect CoSb₆ octahedra and CoSb₄ tetrahedra, Li(CoSb₃)₄ (filled skutterudite, Fig. 14), Li₂Sb and Li₃Sb. The discussion is limited to structures in the conduction band seen in the XANES spectra. The origin of the energy scale is positioned at the bottom of the conduction band for each crystal. The different density scales for the various contributions can be noted.

It is important here to underline several points concerning the conduction bands of these compounds, points which help to better understand the XANES spectra. We first notice that the simple insertion of lithium in the CoSb₃ structure does not modify its conduction band (see Li(CoSb₃)₄, Fig. 14). The P1 intensity in the Co (p) PDOS is more or less conserved through the CoSb_x family. A possible explanation for the increase of the intensity of the structure S₁ on the Co K-edge XANES spectra would be the formation of Co clusters. For the Sb (p) character of CoSb_{2, lay} one may notice that peaks P1 and P2 are no longer distinguished; the PDOS intensity is less in the P1 energy range as it is greater in the P1–P2 energy range (Fig. 12). For the Sb (p) character of CoSb, peak P2 is more structured and exhibits a high intensity sub-structure around 10 eV. As compared to the Sb L_I-edge spectra, the decrease of the intensity of the S₁

CoSb Conduction bands

Fig. 11 Calculated CoSb conduction band PDOS.

CoSb_{2, lay} Conduction bands

Fig. 12 Calculated CoSb_{2, lay} conduction band PDOS.

structure and the disappearance of the deep set between S₁ and S₂ are consistent with a strong distortion of the CoSb_x structure (as in CoSb_{2, lay}). Concerning the Sb (d) character

CoSb_{2,pyr} Conduction bands

Fig. 13 Calculated CoSb_{2, pyr} conduction band PDOS.

Li(CoSb₃)₄ Conduction bands

Fig. 14 Calculated Li(CoSb₃)₄ conduction band PDOS.

through the CoSb_x series, the intensity of peak P2 is much less for CoSb_{2, lay} but its PDOS can not explain the observed energy shift of S₁ (Fig. 8). The simultaneous occurrence of Co–Sb

bonds (a CoSb_{2, lay} like form) and of Li₃Sb would correspond to a shifted superposition of their L_{III} spectra. This would be able to explain the S₁ shift and the S₂ sub-structures.

First discharge mechanism: restructuring

The first discharge can be divided into three zones which correspond respectively to the insertion of 0.0–0.2 Li/CoSb₃, 0.2–8.0 Li/CoSb₃ and 8.0–9.7 Li/CoSb₃. At the beginning of the insertion, a weak proportion of lithium is introduced as a solid solution in CoSb₃ according to the reaction:

This new compound (Li_{0.25}CoSb₃) can be obtained by filling of the 2a vacant site in the skutterudite structure to make up a “filled skutterudite” (LiCo₄Sb₁₂) without modification of the X-ray diffraction pattern and ¹²¹Sb Mössbauer spectrum.

The second domain between 0.2 and 8.0 Li/CoSb₃ corresponds to a large voltage plateau at about 0.6 V which is characteristic of a two-phase process. X-Ray diffraction data show continuous amorphisation with progressive lithiation, while the host structure of CoSb₃ is still observed. No other structure (Li₃Sb, Li_xCoSb₂ and Li_xCoSb) can be identified. This might be due to the fact that the new phases are formed without any long range order. Mössbauer spectra at different steps of lithiation indicate the formation of the Li₃Sb compound between $x = 1.7$ and 4.2 Li and a second compound whose structure and composition is not known (Li_xCoSb_y), characterised by an isomer shift of $\delta = -2.4 \text{ mm s}^{-1}$ and a large quadrupole splitting $\Delta = +10.9 \text{ mms}^{-1}$. From stoichiometric considerations, the formation of Li₃Sb would result in Sb extrusion from CoSb₃. In other respects the XANES spectra at the Co K-edge have shown a slight shift of the S₁ structure towards lower energies in agreement with the possible formation of Co clusters. On the other hand, the Sb L_{III}-edges indicate a more important change in the electronic environment of antimony atoms between the insertion of 1.2 and 4.2 Li, in accordance with the Mössbauer spectra. The general effect of these observations allows us to propose two successive or simultaneous mechanisms for this restructuring plateau at 0.6 V with the two reactions:

Note that the intermediate phases (Li_{0.25+x}Co_{1-x}Sb₃ for reaction (1) and Li_{0.25}CoSb_{3-y} for reaction (2)) can be represented by the general formula Li_xCoSb_y. At the Sb L_{III}-edge, the disappearance of a hollow between the S₁ and S₂ structures, interpreted from the band structure calculation of CoSb_{2, lay}, may be representative of a Li_xCoSb₂ structure-type. This analysis suggests that reaction (1) occurs from the beginning of the voltage plateau when reaction (2) starts between 1.7 and 4.2 Li/CoSb₃. The kinetics of these two reactions are probably different and functions of the electrochemical insertion conditions and morphology of the materials. One cannot rule out the formation of a small solid solution domain Li₂Co whose existence has been evidenced previously.²⁶ The last stage corresponds to the formation of Li₃Sb as is shown by the ¹²¹Sb Mössbauer spectrum.

So, the first discharge mechanism can be represented from the global reaction:

During the first charge the cycle reversibility occurs between the two phases Li_xCoSb_y and Li₃Sb as is shown in the ¹²¹Sb Mössbauer spectra.

Conclusion

We have studied the first discharge mechanism of CoSb₃ lithiation. Experimental and theoretical results are combined in order to better understand the electrochemical process. The cycling profile shows three stages for the first discharge. X-Ray diffraction shows that the pristine material is quickly amorphised, although the main diffraction lines of the CoSb₃ structure are conserved. ¹²¹Sb Mössbauer spectra are in agreement with a progressive reduction of Sb atoms corresponding to the formation of an anionic Sb³⁻ species during the second stage (voltage plateau at 0.6 V). The second phase which is formed during this restructuring corresponds to a ternary compound Li_xCoSb_y, which is an intermediate phase, the composition of which depends on the insertion conditions. Regarding the electronic structure, X-ray absorption spectroscopy was carried out at Sb L_{I, III} and Co K edges. The spectra were compared to projected densities of states calculated in the DFT-LDA-LMTO framework for well defined crystalline compounds containing Co, Sb and Li. This analysis has allowed us to establish the kind of amorphisation as a distortion of the arrangement of the CoSb₆ octahedral units, as in CoSb_{2, lay}. It is also consistent with the formation of Li₃Sb clusters in a second step. Considering the overall characterisations, we are able to suggest a fully coherent picture of the first discharge mechanism of restructuring according to the global reaction:

The further cycling is realised between Li₃Sb and Li_{x+z}Co_{1-m}Sb_y.

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