Mössbauer spectroscopy as an efficient tool to study Li insertion mechanisms in negative electrodes for Li ion batteries

Florent Robert [a],[*], Pierre Emmanuel Lippens [a], Josette Olivier-Fourcade [a], Jean-Claude Jumas [a], Mathieu Morcrette [b]

[a] *Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques (CNRS UMR 5072), Université Montpellier II,
CC 015, Place E. Bataillon, 34095 Montpellier Cedex 5, France*
[b] *Laboratoire de Réactivité et de Chimie des Solides (CNRS UMR 6007), Université d' Amiens, 33 Rue Saint Leu, 80039 Amiens, France*

Abstract

Some aspects of the influence on the electrochemical mechanisms of the anion and structure in tin based negative materials are presented. Li insertion mechanisms in SnS and tin composite oxides (TCO) are analysed by [119]Sn Mössbauer spectroscopy. For SnS, Mössbauer experiments were combined with in situ X-ray diffraction in order to determine tin oxidation states and identify the phases occurring during the discharge. The Mössbauer recoil-free fraction has been determined for TCO and the Debye temperature is found to be lower than that of crystalline SnO in good agreement with the lower network rigidity of the glass.
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1. Introduction

Introduced on the market of accumulators for portable applications 10 years ago, Li-ion batteries have created a true revolution, allowing an improvement in electric performance in terms of mass and volume capacity. The graphitic carbon anodes used in lithium cells are currently the most commonly used but have a relatively low capacity for new applications ($372 \, \mathrm{mAh \, g^{-1}}$). Alternative anode materials such as transition metal nitrides and oxides [1,2] and active/inactive composite alloy materials [3] have been investigated recently. Among them, tin based anode materials seem very promising because of the expected large specific capacity and low potential (<0.8 V/Li). Unfortunately, the Li insertion mechanism is mainly based on the formation of Li–Sn alloys that leads to volume variations of the particles on cycling and therefore strongly limits the reversibility. As proposed by Idota et al. [4], the effect of volume variations can be reduced by dispersing the electrochemically active tin based materials in an amorphous oxide matrix that compensates the strong volume variations. These materials have significantly higher reversible specific ($>600 \, \mathrm{mAh \, g^{-1}}$) and volumetric ($>2200 \, \mathrm{mAh \, cm^{-3}}$) capacities as carbon-based materials. Although many studies have been devoted to tin oxides [5,6], the optimisation of such materials seems to be rather difficult to realise [7].

In order to obtain further insights in Li-ion insertion mechanisms in tin based compounds, we used [119]Sn spectroscopy Mössbauer spectroscopy which allows to characterize the electrochemical reactions on an atomic scale. This technique is based on the recoilless resonant absorption of gamma rays and is mainly used to obtain information about the local electronic structure of the probed element ([119]Sn) from the hyperfine parameters isomer shift δ and quadrupole splitting Δ. It allows determining the oxidation state and the local structural symmetry of the probed element. Li insertion mechanisms in crystalline SnO have been widely studied. The present work is devoted to the modifications induced by changing the anion (SnS) and the structure (TCO, tin composite oxide). In the first case, Mössbauer experiments and X-ray diffraction were combined to identify the phases occurring during

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[*] Corresponding author. Tel.: +33 4 67 14 45 48; fax: +33 4 67 33 04.
E-mail address: frobert@univ-montp2.fr (F. Robert).

Li insertion into SnS. In the second case, we show that the Mössbauer effect, which also provides information on the lattice dynamics, can be used to characterize the Sn—O bonds in TCO.

2. Experimental aspects

Both α-SnO and SnS were synthesised by a sol–gel process. For SnO, a solution of 25 g $SnCl_2 \cdot 2H_2O$ in water was cleared up with hydrochloric acid and 20 g NaOH in 200 ml water. A white precipitate was formed, which turned to black powder upon heating the solution to the boiling temperature. This powder was filtered, washed and then annealed at 110 °C to achieve its crystallisation. For SnS, a flow of hydrogene sulfide was introduced into a solution of 20 g $SnCl_2 \cdot 2H_2O$ in 300 ml water during 20 min. The powder was then filtered, washed and annealed at 250 °C. The tin oxide composite glass $SnB_{0.6}P_{0.4}O_{2.9}$ was prepared by a solid-state reaction. A stoichiometric mixture of SnO, $H_2NH_4PO_4$ and B_2O_3 was heated first to 180 °C for 15 h, then to 800 °C for 15 h under argon and finally quenched to room temperature by extracting the product from the furnace. The glass was transparent and gave a white powder after grinding.

Electrochemical lithium tests were performed in Swagelok[TM]-type cells assembled in an argon-filled glove box. The cells consist in the composite positive electrode containing the active material mixed with 10% acetylene black, a Li metal disk as the negative electrode and a Whattman borosilicate glass microfiber separator with $LiPF_6$ (1 M) in PC/EC/DMC as electrolyte. The discharge/charge curves were measured by means of Mac Pile system operating in the galvanostatic or potentiostatic mode.

In situ X-ray diffraction was carried out on a SCINTAG X-ray diffractometer using monochromated Co $K\alpha_1$ radiation. Diffractograms were recorded at various stages of the discharge run of the Li/SnS system using a special electrochemical cell. The electrode material is placed on the beryllium window of the cell, which is used as current collector. The complete cell is placed in the diffractometer and connected to the Mac–Pile system. The discharge was performed in a galvanostatic intermittent mode, using current-on periods of 1 h at a rate of 1 Li/20 h. In situ X-ray diffraction technique has already proved to be a powerful tool for the study of battery electrode materials [8].

[119]Sn Mössbauer spectra were recorded by transmission in the constant acceleration mode using an EG&G spectrometer, equipped with a cryostat to work at low temperature (down to 4 K). The source was [119m]Sn in a $CaSnO_3$ matrix. The velocity scale was calibrated using the magnetic sextuplet of a high purity iron foil absorber as a standard, using [57]Co (Rh) as the source. The spectra were fitted to Lorentzien profiles by least squares method using the G.M.5.S.I.T program [9], the fit was quality controlled by the classical χ^2-test. Isomer shift values are given relative to a $BaSnO_3$ spectrum recorded at room temperature. The absorbers containing one to two milligrams of [119]Sn per cm^2 were prepared by mixing powder samples and Apiezon grease inside the glove box, and sealed with parafilm to avoid contact with air.

3. Results and discussions

The electrochemical curves obtained for SnO and SnS at C/20 (1 Li/Sn during 20 h) are shown in Fig. 1 Insertion up to about $x = 2$ Li gives a plateau for the two materials but at different potentials: 1.05 V for SnO and 1.4 V for SnS. The plateaus can be related to the two-phase electrochemical reactions:

$$SnO + 2\,Li \rightarrow Sn + Li_2O$$

$$SnS + 2\,Li \rightarrow Sn + Li_2S$$
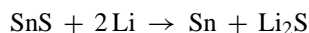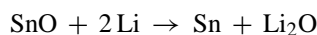
The observed potential difference between SnS and SnO is attributed to changes in the covalency of the bonds involving the tin atoms, which is more important for sulphides than for oxides. For $x > 2$ Li, the voltage profiles are similar for the two compounds but slightly shifted by about 0.2 Li. These profiles are also close to those reported in the literature for SnO [10] and mainly reflect the formation of Li–Sn alloys. In situ X-ray diffraction was performed for SnS in order to identify the phases formed during the discharge (Fig. 2). For $x = 2.4$ Li, which corresponds to the end of the first voltage plateau, the X-ray pattern mainly shows the existence of β-Sn with a small amount of SnS. For $x = 2.6$ Li some small peaks occur that are attributed to Li_2Sn_5. The accurate identification for larger values of x is rather difficult due to the broadening of the peaks that could be related to the nanosize and the poor crystallinity of the phases but the values of 2θ are in the range of the Li–Sn alloys. However, the shift of the peak around $2\theta = 28°$ to lower values is consistent with the formation of phases that are richer in Li such as LiSn [11]. Finally, it is worth noting that the amplitude of the peak at $2\theta = 38°$ for $x > 3.5$ Li increases with increasing amount of inserted Li and corresponds to the main peak of the Li-rich phases (Li_7Sn_3,
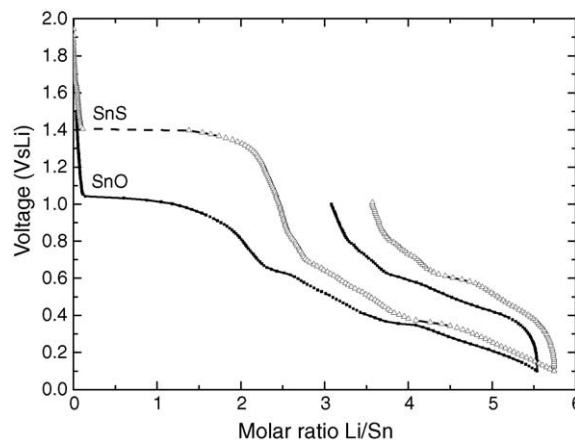

Fig. 1. First discharge/charge curves obtained for SnO and SnS under galvanostatic conditions at C/20 rate.
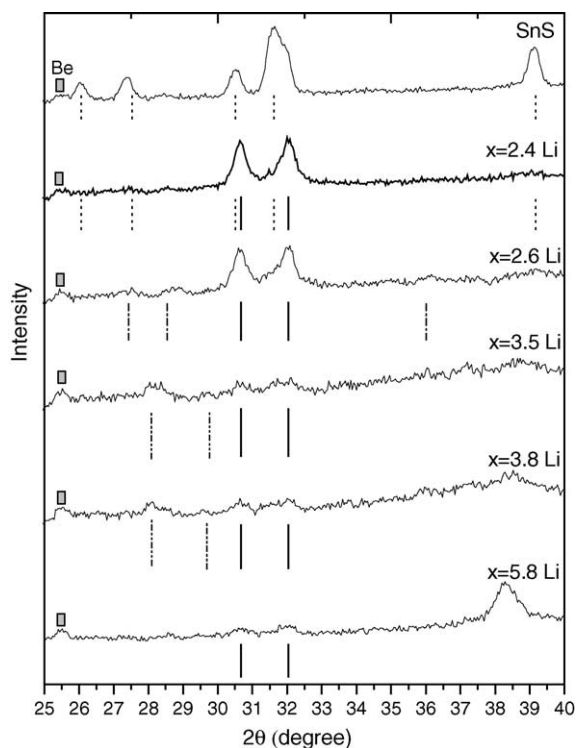
Fig. 2. In situ X-ray diffraction in for Li/SnS cell during the first discharge at C/20 rate. The X-ray pattern of the single phases SnS (dashed line), β-Sn (solid lines), Li$_2$Sn$_5$ (dotted-dashed line) and LiSn (dotted line) are shown for references.

Fig. 3. ^{119}Sn Mössbauer spectra of SnS at different depths of the first discharge.

Li$_{22}$Sn$_5$) [12]. The room temperature ^{119}Sn Mössbauer spectra recorded at different steps of the discharge are shown in Fig. 3. The spectrum of the pristine material shows a small amount of Sn(IV) due to oxidation of the sample and a doublet that can be unambiguously assigned to SnS [10]. The value of the isomer shift $\delta = 3.22$ mm s^{-1} is typical of the Sn(II) oxidation state and the rather large quadrupole splitting $\Delta = 0.88$ mm s^{-1} is due to the asymmetry of the Sn local environment in SnS. The amplitude asymmetry of the doublet is mainly due to the Goldanskii–Karyagin effect. For $x = 2.4$ Li, the Mössbauer experimental data can be fitted to two doublets with very different values of isomer shifts which can be assigned to Sn(0) in β-Sn ($\delta = 2.55$ mm s^{-1}, $\Delta = 0.30$ mm s^{-1}) and Sn(II) in SnS. The observed relative contributions of the two sub-spectra do not reflect directly the relative amounts of the two phases because of the difference in the recoil-free fractions of SnS and β-Sn. A rough estimation suggests that β-Sn represents more than 90% of the total amount of tin. This value is consistent with X-ray diffraction results which show β-Sn to be the predominant phase for $x = 2.4$ Li. For $x = 3.5$ Li, the Mössbauer spectrum is similar to that of LiSn although a small contribution of SnS should also be considered. Finally, for $x = 4.8$ and 6 Li the Mössbauer spectra do not reflect single phases but the shift of δ to lower values is typical of Sn(0) in Li-rich Li–Sn alloys and is consistent with X-ray diffraction data.
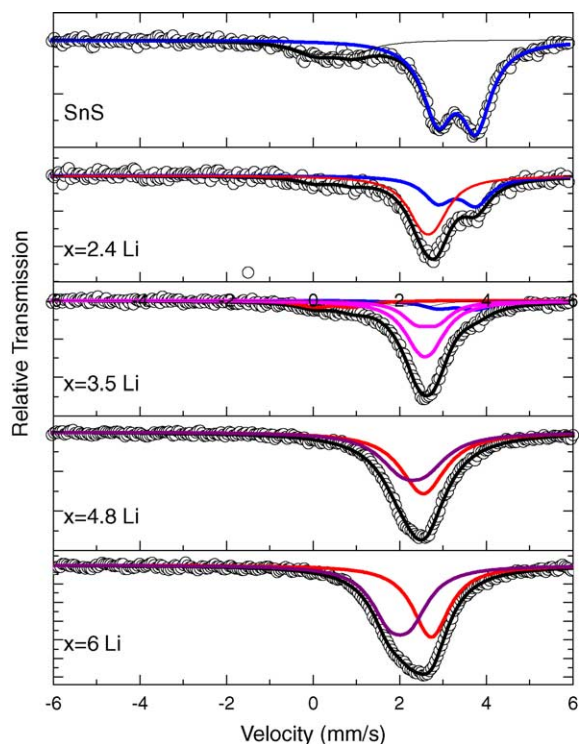
The recoil-free fraction f of TCO was evaluated from Mössbauer measurements between 4 and 300 K by considering one mean site. The values obtained at 77 K ($f = 0.8$) and 300 K ($f = 0.4$) are slightly higher that those reported for crystalline α-SnO ($f = 0.74$ and 0.35 at 77 and 300 K, respectively). The value of the Debye temperature: $\theta_D = 204$ K is lower than that of α-SnO [13]: ($\theta_D = 230$ K) confirming indicating a reduced covalency of the Sn–O bonds in TCO as compared to α-SnO. This is consistent with the lower glass network rigidity that makes the insertion of Li in TCO easier. Finally, it is important to note that value of f obtained for TCO is more than 10 times larger than that of β-Sn at room temperature ($f = 0.01$–0.04) and about twice as large at 77 K ($f = 0.4$). Thus, low temperature Mössbauer measurements are required for quantitative studies of Li insertion in TCO.

4. Conclusions

2 The Li insertion mechanism in SnS has been studied and compared to that of SnO in order to point out the influence of the anion. The overall potential profiles of the two compounds are similar except the potential of the first plateau, which is higher for SnS. This can be related to the higher covalency of the Sn–S bonds as compared to the Sn–O bonds. Both in situ X-ray diffraction and Mössbauer experiments have confirmed this result although some differences observed in Mössbauer spectra at the end of the first discharge suggest different Sn local environments in the Li-rich Li–Sn alloys obtained from SnO and SnS. The analysis of the Mössbauer

recoil-free fraction reveals a decrease in covalency of the Sn−O bonds from crystalline SnO to TCO in good agreement with the lower network rigidity of the glass, which facilitates the lithium insertion. A study of the changes in the lattice dynamics of TCO during Li insertion is currently carried out.

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