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Mössbauer spectroscopy: analysis and predictions for Li-ion batteries

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Abstract Due to their high storage capacity Sn-based materials are of considerable interest as negative electrode for Li-ion batteries. However the strong volume change occurring during the alloy formation strongly limits the electrochemical performances (cycle and time life). Analysis by Mössbauer spectroscopy using model compounds (Sn, Sn-Li and transition metal-Sn alloys) shows that the volume expansion is related to the structural change from a Sn based network to a Li based network. Two types of materials are proposed here to overcome this problem: tin dispersion in an electrochemically inactive oxide matrix with buffer role to absorb volume changes or tin alloying with an inactive transition metal to minimize the volume expansion. The use of Mössbauer spectroscopy (*in situ operando* mode) allows a dynamic approach which is essential to understand the fundamental causes of ageing on cycling and to define then the key issues to be solved for material's application.

Keywords Negative electrode materials · Lithium insertion mechanism · Sn-based composites · *In situ operando* Mössbauer

1 Introduction

Sn-based materials are of considerable interest as negative electrode for Li-ion batteries because they can store more than twice as much lithium amount as that of graphite does. Metallic tin can react with lithium to form a variety of Li-rich alloys (Li_7Sn_2 or $Li_{22}Sn_5$) with high capacity storage (847 up to 994 Ah/kg). However the drastic volume change occurring during the alloy formation strongly limits their electrochemical performances. Several approaches to solve theses problems have

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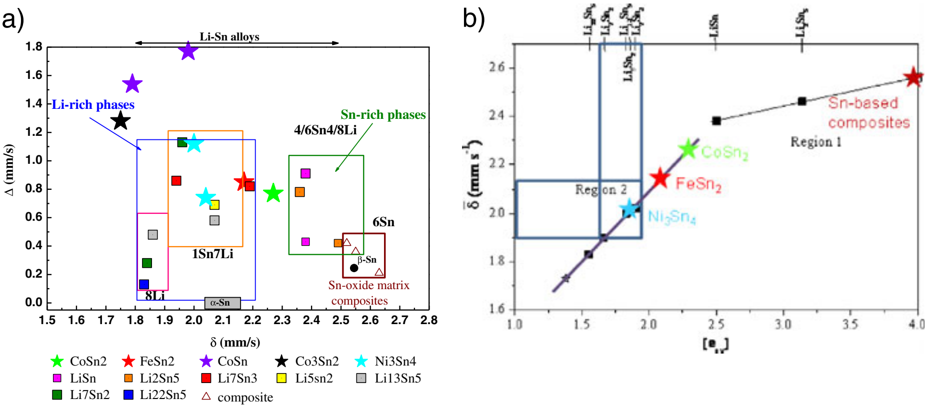

Fig. 1 **a**) .$\Delta - \delta$ correlation diagram for the different tin sites of Sn-based materials and (**b**) Isomer shift average value as a function of electronic density

been recently analyzed [1] and among the different possibilities the use of Sn-based composite materials or multi-element metallic materials seems to be the most favorable.

In this paper we present how Mössbauer Spectroscopy (MS) can be used to analyze and to predict the electrochemical behavior of such materials from correlation diagrams established for model compounds (Sn, Sn-Li and transition metal-Sn alloys). Two examples ($Sn^0/Sn^{II}B_xP_yO_z/BPO_4$ composites and M_xSn_y intermetallics) will illustrate the capabilities of MS to identify the mechanisms governing the electrochemical reactions.

2 Correlation diagrams

Figure 1 shows correlation diagrams obtained from the Mössbauer data of some reference compounds [2]. From the $\Delta - \delta$ diagram (Fig. 1a) two main domains are identified: Sn-rich phases ($\delta > 2.30\ \mathrm{mms}^{-1}$) with continuous networks based on Sn-Sn bonds of covalo-metallic character and Li-rich phases ($1.80 < \delta < 2.20\ \mathrm{mms}^{-1}$) with networks based on Li^+ close packing. The analysis of these data shows that during alloying the volume expansion is linked to the structural change corresponding to the transition from a Sn based network to a Li based network. This diagram allows identifying the nature and composition of the Li-Sn alloys formed during cycling [2].

The $\bar{\delta} - [e_{av}]$ diagram (Fig. 1b), drawn from the data of the Li-Sn system, allows the determination of the averaged Hume-Rothery electronic density $[e_{av}]$ for any Sn-based material by considering its $\bar{\delta}$ and the analysis of reaction mechanisms as described by Naille et al. [2].

3 $Sn^0/Sn^{II}B_xP_yO_z/BPO_4$ composite

Recently a new approach to avoid the large volume expansion during the lithiation process has been proposed with Sn particles embedded in an oxide matrix. The

$Sn/0.2BPO_4$ composite obtained by carbothermal synthesis [3] exhibits a complex structure that can be described by $Sn^0/Sn^{II}B_xP_yO_z/BPO_4$ involving metallic Sn^0 ($\delta = 2.53$ mms^{-1}, $\Delta = 0.36$ mms^{-1}) and an oxidized species $Sn^{II}B_xP_yO_z$ ($\delta = 3.31$ mms^{-1}, $\Delta = 1.63$ mms^{-1}) acting as a link between the Sn^0 and BPO_4 particles. This composite material exhibits a reversible capacity of 600 Ah/kg and the lithium insertion/extraction mechanism was characterized by *in situ operando* MS. At the beginning of the first discharge we observe the $Sn^{II} \rightarrow Sn^0$ reduction and then a progressive Li-Sn alloying reaction. At the end of the first discharge a mixture of Li-rich alloys (Li_7Sn_3, Li_5Sn_2 and $Li_{13}Sn_5$) can be evidenced with a $\bar{\delta} \sim 1.97$ mms^{-1}. During the first charge only a part of lithium can be removed leading to LiSn as final composition characterized by a $\bar{\delta} \sim 2.35$ mms^{-1}. The proposed mechanism for Sn/BPO_4 composite materials consists in two steps: i) reduction of Sn^{II} forming the interface with active species leading to a restructuration of the composite and ii) formation of Li_xSn alloys (up to Li_7Sn_3). During the discharge the conversion of the Sn-Sn network ($\bar{\delta} = 2.53$ mms^{-1}) to a Li-Li network ($\bar{\delta} \sim 1.97$ mms^{-1}) induces an important structural change responsible for the volume expansion.

4 M_xSn_y intermetallics (M = Fe, Ni)

$FeSn_2$ ($\delta = 2.18$ mms^{-1}, $\Delta = 0.83$ mms^{-1}) [4] and Ni_3Sn_4 ($\delta = 1.95$ mms^{-1}, $\Delta = 0.63$ mms^{-1}and $\delta = 1.98$ mms^{-1}, $\Delta = 1.37$ mms^{-1}) [5] are located in the same domain as that of the Li-rich phases (Fig. 1a) and present comparable $[e_{av}]$ (Fig. 1b). In both cases the first electrochemical cycle leads to the formation of a Li_7Sn_2/M^0 nanostructured composite. Ageing is then linked to the reversibility of the reaction which initially depends on the nature of M. For Ni_3Sn_4 we observe a good reversibility because there is no coalescence of Ni^0 particles during cycling [5]. For $FeSn_2$ as shown by ^{57}Fe MS we observe an agglomeration of the Fe^0 particles during cycling and the reversibility doesn't exceed 50 cycles [4]. We can notice that Ni_3Sn_4 is located (Fig. 1b) with the first Li_xSn alloys rich in lithium ($2.33 < \times < 2.60$). This domain where Sn-based intermetallic compounds and Li_xSn alloys present comparable values of $[e_{av}]$ seems to be very favourable to good electrochemical performances. In this way it is possible to predict the electrochemical behavior of Sn-based materials from their Mössbauer data by using the diagram shown on Fig. 1b.

5 Conclusions

In the field of new Sn-based materials as negative electrode for Li-ion batteries, MS has allowed us to establish correlation diagrams ($\delta - \Delta$ or $\bar{\delta} - [e_{av}]$) that make easier the analysis of the reaction mechanisms and in some cases that predict their electrochemical behavior. Thanks to MS a better understanding of Sn-based composites and intermetallics has been obtained and the combination of these two approaches, currently underway, is a promising way of creating new high-performance materials. In this context MS has a bright future [6].

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