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Comparative study of $NiSb_2$ and $FeSb_2$ as negative electrodes for Li-ion batteries

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ABSTRACT

Crystalline $FeSb_2$ powder prepared by ceramic route is examined as negative electrodes for lithium-ion batteries. The complete reaction mechanism of $FeSb_2$ is investigated by ^{121}Sb and ^{57}Fe Mössbauer spectroscopy as well as magnetic measurements and the results are correlated with a previous *in situ* XRD characterization. On the first discharge the reaction with Li proceeds through a biphasic process transforming $FeSb_2$ into a new $Li_xFe_ySb_2$ phase, and this ternary phase is then converted into *fcc* Li_3Sb and metallic Fe nanoparticles. The combination of Mössbauer spectroscopy and magnetic analyses leads i) to a better understanding of the $FeSb_2 \rightarrow$ ternary phase reaction and concomitantly allowed ii) to specify the stoichiometry of the new ternary phase. On charge, the extrusion of lithium includes the back conversion of the Li_3Sb/Fe mixture into both $Li_4Fe_{0.5}Sb_2$ and metallic Sb, which are the main active species for the following cycles, responsible for the poor cycling life of the $FeSb_2$ electrode. The nature of these resulting products is quite different from that previously observed for the isotype $NiSb_2$ electrode which is characterized by a highly reversible mechanism.

1. Introduction

Many efforts have been expended in the last decade to improve Li-ion batteries. Although significant improvements in the performance were obtained (increase in energy density and rate capability), the exploration of new materials and the understanding of their electrochemical mechanisms are still primary to better control the electrode properties and the battery performances. Over the past few years, some Sb-based intermetallic compounds, such as InSb [1], $CoSb_3$ [2–4] or Cu_2Sb [5,6] have been intensively investigated as negative electrodes for lithium-ion batteries, showing higher capacities than the commercialised carbon material. Unfortunately, they suffered from an important capacity fading. A previous study of $NiSb_2$ as negative electrode [7] demonstrated the great interest to study the MSb_2 antimonides with an FeS_2 marcasite-type structure (where M is a transition metal (Fe, Co, Ni))[8,9]. In this field Xie et al. described succinctly the electrochemical behaviour of $FeSb_2$, obtained by mechanical levitation reaction and no mechanism was proposed [10]. In a more recent paper we demonstrated through a combined electrochemical and *in situ* XRD study that the electrochemical mechanism of $FeSb_2$/Li occurs in two steps on the first discharge (the galvanostatic curve of $FeSb_2$/Li cell is reminded on Fig. 1) [11]. *in situ* XRD analysis gave the following results: i) during the plateau at 0.62 V (4Li) a continuous decrease in the intensity of the main $FeSb_2$ Bragg peaks to the expense of a new set of Bragg peaks not ascribable to any known phase; ii) along the second plateau at 0.4 V (1.5Li), XRD shows a continuous shift of this new set of broad peaks to smaller angles; and iii) at the end of the discharge the formation of the high temperature cubic Li_3Sb phase ($a = 6.572$ Å, Fm3m). From these XRD *in situ* data we deduced that the intermediate unknown ternary phase was isotype to the face-centered-cubic Li_3Sb phase and has a composition close to "Li_4FeSb_2".

In order to get deeper insight in the mechanism of the $FeSb_2$/Li cell during the cycling and to better describe this new intermediate phase we decided to investigate the discharge/charge cycle by ^{121}Sb and ^{57}Fe Mössbauer spectroscopy and magnetic measurements. Both characterizations give useful information both on the nature of the electrochemically formed phases and on the changes of the electronic states during the reduction/oxidation processes. Finally the proposed electrochemical behaviour of $FeSb_2$ will be compared with the mechanism previously elucidated for its isotype $NiSb_2$ [7,12] and the differences will be discussed.

2. Experimental aspects

2.1. Synthesis procedure

$FeSb_2$ sample was prepared by direct synthesis from the pure elements: iron (Alfa Aesar, 350 mesh, 99.9%) and antimony (Alfa Aesar, 350 mesh, 99%) in silica tubes sealed under vacuum. After annealing for 7 days at 720 °C using a ramp of 1 °C/min, the tube was air-quenched.

2.2. Electrochemical tests

The setup used for the electrochemical characterization is described elsewhere [11].

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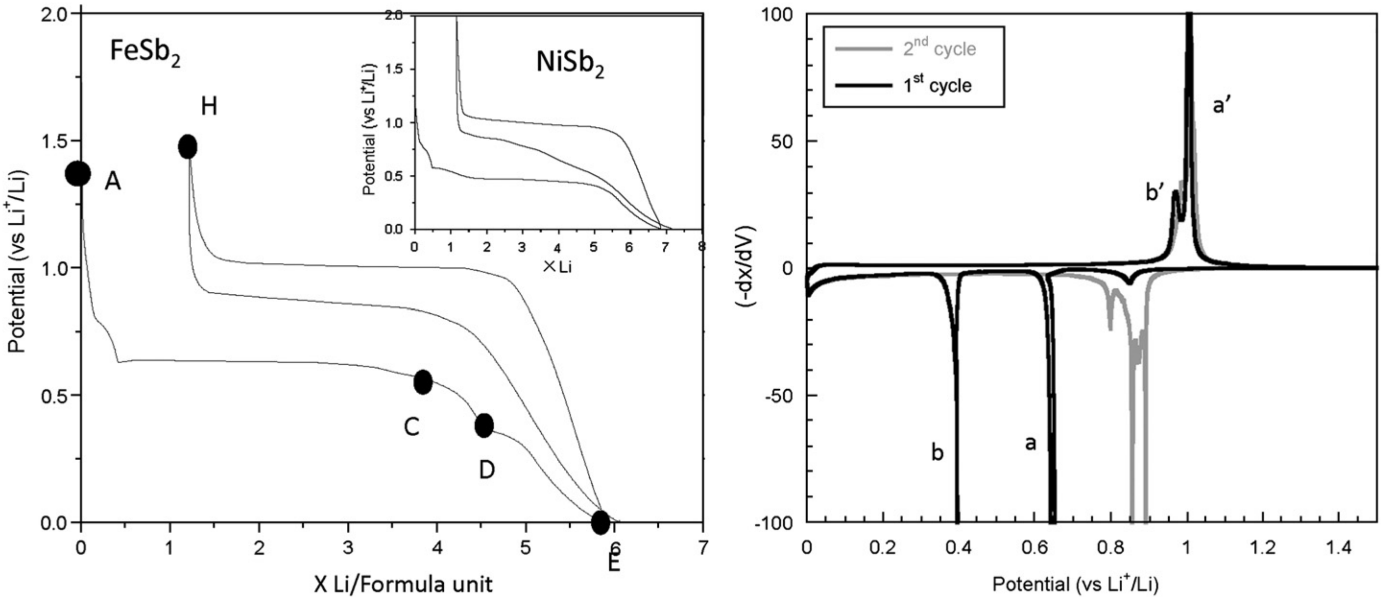

Fig. 1. Potential plotted versus composition for a $FeSb_2$/Li cell cycled between 1.5 and 0 V at C/20. The derivative $-dx/dV$ plot is shown for the first cycles. Points A to H mark the samples which were analysed by Mössbauer spectroscopy and magnetic measurements. For comparison reasons the inset presents the galvanostatic curve for a $NiSb_2$/Li cell cycled between 2 and 0 V at C/20.

2.3. Mossbauer spectroscopy

^{121}Sb Mössbauer measurements were performed using a ^{121m}Sn in $BaSnO_3$ source of nominal activity 0.5 mCi on an EG & G constant acceleration spectrometer in transmission mode. During the measurements, both source and absorbers were simultaneously cooled down to 4.2 K. The zero isomer shift was defined from the spectrum of InSb at 4.2 K ($\sigma = -8.72(4)\,\mathrm{mm\,s^{-1}}$ relative to $Ba^{121m}SnO_3$). ^{57}Fe Mössbauer measurements were carried out at room temperature, using a ^{57}Co(Rh) source with a nominal activity of 370 MBq (= 10 mCi). ^{57}Fe shifts are given with respect to the centre of the six-line-spectrum of the α-Fe foil.

2.4. Magnetic measurements

Magnetic properties were measured on a Superconducting Quantum Interference Design (SQUID) magnetometer MPMS XL7 between 2 and 300 K in magnetic fields between 0 and 5 T. The temperature dependent susceptibility was measured using a DC procedure. Measurements on electrode materials were carried out *ex situ* after extraction of the electrode material from the Swagelok cell.

3. Results and discussions

The phase purity of the $FeSb_2$ intermetallic was checked by X-ray diffraction. The Bragg peaks could all be indexed on the basis of an orthorhombic marcasite cell with the following refined lattice parameters: $a = 5.829(2)$ Å; $b = 6.535(1)$ Å; $c = 3.197(1)$ Å in good agreement with the values given in the literature [13].

As mentioned in the introduction the mechanism was previously proposed for the first discharge as following [11]:

$$0.62\mathrm{V} \quad FeSb_2 + 4\ Li \rightarrow \text{“}Li_4Fe_ySb_2\text{”} \tag{1}$$

$$0.4\mathrm{V} \quad \text{“}Li_4Fe_ySb_2\text{”} + 2\ Li \rightarrow 2Li_3Sb + yFe^0 \tag{2}$$

On charge, 4.5 Li are removed corresponding to a reversible capacity of 420 mAh g^{-1} (or 3500 mAh cm^{-3}) (Fig. 1). A double process appears between 1.1 and 0.9V (Fig. 1, a′ and b′ on the derivative curve). During the second discharge, we observe a single voltage plateau centered at 0.75 V.

On Fig. 2 XRD *in situ* analysis performed during the first charge shows: i) a shift of the Li_3Sb fcc Bragg peaks to the upper angles which means the restructuration of the “$Li_4Fe_ySb_2$” phase and then ii) a decrease of the peak intensity of this new phase to the benefit of another one which seems to be amorphous. During the second discharge (not shown here) XRD shows the reappearance of Li_3Sb.

Mössbauer spectroscopy and magnetic measurements were carried out in order to identify the nature of this new phase reversibly formed on discharge and charge, and to elucidate the electrochemical reaction mechanism. Fig. 3a shows the evolution of the ^{121}Sb Mössbauer spectrum recorded at different depths of the discharge (points A to E) and at the end of the charge process (point H). All the spectra have been accurately analyzed to obtain the hyperfine parameters, i.e. isomer shift (δ), quadrupole splitting (eQVzz), linewidth (Γ_a) and contribution of each component. The corresponding refined hyperfine parameters are reported in Table 1. The ^{121}Sb Mössbauer spectrum of $FeSb_2$ (Fig. 3a, point A) was fitted with two components. The isomer shift of the first of $\delta = -1.23\ \mathrm{mm\,s^{-1}}$ is characteristic of intermetallic compounds and was assigned to $FeSb_2$. [13,14] The second component $\delta = 8.83\ \mathrm{mm\,s^{-1}}$ was assigned to Sb_2O_5 formed as an impurity during the synthesis process [15]. After the first discharge plateau at 0.62 V, the Mössbauer spectrum obtained for $x \approx 4$ Li (point C) shows the appearance of a new component attributed to the formation of a new phase denoted hereafter “X phase” ($\delta \sim -2.42\ \mathrm{mm\,s^{-1}}$, eQVzz = 9.96 mm s^{-1}, 75% relative contribution), with a residual presence of the $FeSb_2$ (13%). Comparison with data from literature allowed no identification of this new “X phase”. As illustrated in Fig. 3a, point D (discharge down to 0.28 V), the contribution of the multiplet of the “X phase” decreases to 25% and that of $FeSb_2$ disappears in favour of a new component assigned to cubic Li_3Sb ($\delta \sim -1.07\ \mathrm{mm\,s^{-1}}$, eQVzz = 0 mm s^{-1}, 60% relative contribution) [8]. At the end of the first discharge the Mössbauer spectrum mainly reflects Li_3Sb and Sb_2O_5 as an impurity. On full charge at 1.5 V ($x = 1.2$ Li, point H) the Mössbauer spectrum shows a majority of metallic Sb ($\delta \sim -3.28\ \mathrm{mm\,s^{-1}}$, eQVzz = 3.13 mm s^{-1}, 56%) and also unreacted Li_3Sb (12% relative contribution) and “X phase” (22% relative contribution). The hyperfine parameters and relative contribution of the “X phase” are identical