Electrochimica Acta 281 (2018) 619–623

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

On the high cycling stability of NbSnSb in Li-ion batteries at high temperature

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ARTICLE INFO

Article history:
Received 19 February 2018
Received in revised form
16 May 2018
Accepted 27 May 2018
Available online 28 May 2018

Keywords:
Cycling performance
Temperature
Alloy-based anode
High rate

ABSTRACT

Inspired by the high performance obtained previously with TiSnSb, NbSnSb was investigated as negative electrode in Li-ion batterie. After its synthesis by ball milling and full characterization by XRD and Mössbauer spectroscopy, electrochemical tests at various current rates and temperatures were realized. The electrochemical performance at 25 and 60 °C turned out to be very promising, being better than those previously obtained with the parent electrode material TiSnSb with a specific capacity higher than 450 mAh/g maintained during more than 400 cycles at 60 °C. Preliminary tests in full cells confirmed that this anode material could be considered as a potential material for future Li-ion batteries.

1. Introduction

The Lithium-ion batteries (LiB) are widely dominating the segment of portable devices. They are also rapidly penetrating the market of large-scale energy storage applications such as electrical vehicles and stationary renewable energy storage. Continuous effort is devoted to the increase of their energy density, lifetime and safety and to the reduction of their cost. Moreover due to the very different aimed applications, maintaining high performance on a wide range of temperatures (25–60 °C) is highly required. The use of intermetallic materials instead of a pure metal has shown to be an effective way to control the volume changes of the alloys based electrodes that is a major drawback of these electrode materials during the cycling of the battery [1].

SnSb for instance was widely studied and its reaction with Li at different potentials allows the unreacted component to accommodate the strain yielded by the reacted phase [2,3]. Recent studies have demonstrated that adding a transition metal in the composition of the starting electrode material, as Ti in TiSnSb, can lead to high performance with the retention of 90% of the specific capacity after 90 cycles at C rate [4,5]. *Operando* XRD, Mössbauer and XAS spectroscopy measurements demonstrated that a reversible conversion-alloying mechanism leading simultaneously to the formation of Li_3Sb and Li_7Sn_2 alloys is the electrochemical mechanism which takes place [6,7]. Ti plays a key role in the good electrochemical performance of TiSnSb. In fact, the presence of Ti in TiSnSb leads to a reversible conversion-alloying reaction mechanism rather than to an alloying/dealloying mechanism as in the case of SnSb. It is noteworthy that the electrochemical performance are much better by using TiSnSb as negative electrode rather than SnSb. The substitution of Ti by another transition metal could modify the performance. Among the rare ternary phases in the system M/Sn/Sb (M = transition metal), only NbSnSb presents the same stoichiometry than TiSnSb and a close crystallographic structure [8,9]. To complete our preliminary work we decided study this material at higher temperature (60 °C). From the application point of view, it is worth noting that niobium abundance is comparable to that of lithium [10] whereas tin and antimony are less abundant on the Earth's crust. Therefore, the use of such alloys instead of graphite should be limited to high temperature applications. For standard application, many other alternatives to graphite have been proposed in several reports [11–13].

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https://doi.org/10.1016/j.electacta.2018.05.172
0013-4686/

2. Experimental section

NbSnSb was synthetized by milling commercial powders of Nb (Fluka, 40 mesh, >99.5%), Sn (Aldrich, ≥ 99%) and Sb (Alfa Aesar, −325 mesh, 99.5%) in stoichiometric proportions in a high-energy ball mill (SPEX 8000 M). NbSnSb ternary phase was obtained after 8 h of real milling time under argon atmosphere in a grinding jar containing 6 steel balls.

The X-ray diffraction (XRD) was recorded at room temperature using a Philips X'Pert 2theta/omega diffractometer equipped with an X'Celerator detector and Cu Kα radiation. The FullProf software has been used for the refinement of data, the determination of its unit cell parameters and the crystallite size. Powder morphology and particle size were investigated by scanning electron microscopy (SEM) with a Hitachi S-4500 microscope equipped with an EDX detector. ^{119}Sn Mössbauer spectroscopy has been used at room temperature to characterize the tin chemical environments. Spectra were collected with a constant acceleration spectrometer using a $Ca^{119m}SnO_3$ source.

For the electrochemical measurements, electrodes were prepared by mixing 70 wt% of active material with 9 wt% of carbon black (Y50A, BET = 70 m^2/g, SN2A), 9 wt% of vapor grown fibers (VGCF-H, BET = 15 m^2/g, Showa Denko), 12 wt% of carboxymethyl cellulose (CMC, DS = 0.7, Mw = 250 000, Aldrich) in deionized water using a silicon nitride vial and a planetary ball-milling for 1 h. The obtained slurry was tape casted on a 17.5 μm thick copper foil (99.9%, Goodfellow) with a doctor blade at 150 μm thickness. The film was dried at room temperature for 48 h and finally 1 night in a vacuum flask at 120 °C to remove residual solvent.

Electrochemical tests were carried out in half-cells with metallic lithium as the counter electrode under [0.02–1.5 V vs. Li^+/Li] and $LiPF_6$ 1 M EC:PC:3DMC +5% FEC +1% VC as electrolyte that has been optimized for this kind of materials [5,14–17]. Coin cells were assembled inside an argon-filled glove box. Galvanostatic tests were performed at room temperature and at 60 °C on a multichannel MTI system at various C rates. In this study C/n rate means that 1 mol of Li reacts with 1 mol of active material in n hours. The measured capacities will be given in mAh/g of NbSnSb. The cycling program corresponds to a first discharge at C/2, followed by 48 h of relaxation then cycling at a high current up to 4C.

Full-cell electrochemical tests were performed in a three-electrode battery-type Swagelok cell containing $LiCoO_2$ (LCO) as positive electrode, lithium as reference (for the control of the voltages of anode and cathode materials during cycling) and NbSnSb as negative electrode (prepared in the same conditions that for the tests in half-cells, see above). Quantities of active materials needed to equilibrate the exchanged Li^+ are 1 mol of NbSnSb for 13 mol of LCO. An LCO excess was added to compensate the SEI formation and the capacity loss of NbSnSb during the first cycles. $LiCoO_2$ electrode was prepared by mixing 90 wt% of active material (Sigma-Aldrich, 99.8%), 15 wt% of polyvinylidene fluoride (Solef® 5130 PVDF) and 5 wt% of carbon black (Y50A) in 1-methyl-2-pyrrolidinone (Sigma-Aldrich, anhydrous, 99.5%) employing jar and ball-milling for 1 h. The obtained slurry was tape casted on an 18 μm thick aluminum foil (99.0%, Goodfellow) with a doctor blade at 800 μm thickness. The film was dried 48 h at room temperature and in a vacuum oven at 80 °C overnight. Then for this preliminary test the weight ratio of the NbSnSb anode to the LCO cathode was fixed at 0.1, which results to a very high loading for LCO (18 mg/cm^2) and obviously limited performance. Electrochemical performances of the LIB full-cell are investigated by galvanostatic charge-discharge process. The battery was tested at 25 °C using $LiPF_6$ 1 M EC:PC:3DMC +5% FEC +1% VC as electrolyte at a constant current density of 1C for NbSnSb (81 mA/g_{NbSnSb}). The anode working potential was fixed between [0.0–1.5 V vs Li^+/Li] and the one of the cathode was left free.

3. Results and discussion

The X-ray diffraction (Fig. 1a) of the ball-milled powder reveals a series of broad Bragg peaks indicating as expected the poor crystallinity of the sample. The pattern is indexed in the *I*4/*mcm* tetragonal space group and the refined cell parameters a = b = 6.79 (3) Å, c = 5.66 (5) Å are in good agreement with the previously reported data for NbSnSb (ICSD 90801, a = b = 6.736 Å, c = 5.727 Å) [8,18].

A minor impurity of SnSb can also be detected and is estimated to around 2%. Crystallites size of the NbSnSb phase (determined by FullProf) is around 5 nm. SEM mixrographs of the powder shows aggregates with a size distribution ranging from 1 to 30 μm. To characterize the nature of tin environments the selective ^{119}Sn Mössbauer spectroscopy was used. The Mössbauer spectrum (Fig. 1b) of the ball milled sample recorded at room temperature can be fitted with single doublet (δ = 2.16 mm/s and Δ = 1.60 mm/s) in agreement with ref [18]. At 25 K the spectrum shows some asymmetry that could not be accounted for without splitting the signal into two doublets of virtually the same isomer shifts (δ = 2.30 and 2.23 mm/s) but with different quadrupole splittings (Δ = 2.12 and 1.43 mm/s) suggesting disordered environments for tin atoms likely due to the preparation method. In addition, a minor contribution of SnSb (3% of the absorption area, δ = 2.82 mm/s and fixed Δ = 0.0* mm/s) is also detected in agreement with the XRD analysis.

The EDS mapping indicated an atomic ratio of 33.8%, 33.0% and 33.2% in Nb, Sn and Sb respectively with a homogeneous distribution of elements throughout the sample (Fig. 1c,d). Due to the nature of ball milling jars used for the synthesis, traces of iron were detected by EDS.

The electrochemical performance of NbSnSb was evaluated at 25 and 60 °C, in half-cell (vs Li) and are presented in Fig. 2a,b. At 25 °C, during the first discharge at C/2 (i.e.: 40 mA/g), the electrode reacts with 7.6 mol of Li^+ offering a specific capacity of 610 mA h/g. In charge, 6.14 atoms are de-inserted corresponding to a reversible specific capacity of 493 mA h/g, a value close to the theoretical capacity 523 mA h/g if we consider the reversible formation of Li_3Sb and Li_7Sn_2. The first cycle irreversible specific capacity is 19%. During the first ten cycles at a 4C rate (i.e.: 320 mA/g), the reversible specific capacity slightly decreases before stabilizing around 400 mA h/g during more than 400 cycles.

The previous measurements [18] realized at lower rate (typically at 1C rate) showed a capacity around 500 mA h/g, with a cyclability limited to 80 cycles at 25 °C. In the first cycle, the coulombic efficiency (CE) is 80% and rapidly increases up to 99% after few cycles. The derivative of the galvanostatic curve showed two reduction peaks during the first discharge at 0.52 and 0.14 V, and two oxidation peaks at 0.45 and 0.88 V in the first charge which cannot be ascribable at this stage of knowledge of electrochemical mechanism. However similarly to TiSnSb, after the conversion-alloying reaction in first discharge, two diffuse derivative peaks appear around 0.6 and 0.2 V in discharge, and at 0.45 and 0.9 V in charge. At 60 °C, the profile of the first discharge at C/2 indicated that NbSnSb reacts with 7.98 Li^+ corresponding to a capacity of 641 mA h/g. The extraction of 6.15 Li^+ was observed during the following charge corresponding to a reversible specific capacity of 494 mA h/g with a coulombic efficiency of 77%. After 400 cycles, a specific capacity of 450 mA h/g was retained with a coulombic efficiency of 99.3%. The profile of the derivative curve resembles to that measured as at 25 °C with two reduction peaks in first discharge at 0.62 V and