

INFLUENCE OF REDUCTIVE PREPARATION CONDITIONS ON THE MORPHOLOGY AND ELECTROCHEMICAL PERFORMANCE OF NANO-SIZED Sn/SnSb INTERMETALLICS

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In the recent years, there has been a great interest in the development of new anode materials for lithium-ion batteries. In particular, various metallic and intermetallic lithium storage hosts have been studied. So far, tin-based materials have been in the center of interest. The main motivation for the use of metallic and intermetallic materials are the great amounts of lithium which can be stored and the high lithium packing densities which can be achieved, eventually resulting in high theoretical specific charges and charge densities [1-3].

However, the main drawback of metallic and intermetallic compounds are their large volume changes upon lithium uptake, which lead to the mechanical disintegration of the electrode [1-3] and subsequently to a drastic capacity fade during cycling. Only by a proper design of the chemical composition and the morphology of the active materials is it possible to enhance the cycling stability.

It was demonstrated in recent work, that Sn/SnSb is an interesting anode material. Both, (i) the practical discharge capacities yielding 600 mAhg^{-1} , i.e., exceeding those of graphite by approx. a factor of 2, and (ii) the cycling stability, as more than 30 cycles with stable discharge capacity can be typically reached, are favorable. We have reported previously [1-4], that the good cycling performance is attributed to several effects: (i) the small particle size morphology of the active material, (ii) a sufficient porosity of the active material and the electrode, (iii) the use of multi-phase instead of single-phase materials, and (iv) the use of intermetallic components, which show reversible phase separation and restoration upon the reaction with Li. In conclusion, porous multiphase small particle size intermetallics perform much better than compact single phase large particle size pure metal hosts. Moreover, when nano-sized particles are used, good kinetic behaviour can be observed due the large surface area and the short ion diffusion length. On the other hand, a larger surface area induces also irreversible capacities due to solid electrolyte interphase (SEI) formation on the surface, which again may deteriorate the power capabilities of the material to some extent. Low surface area nano-sized materials may be a compromise in this respect.

Several methods have been developed to synthesize nano-structured and nano-sized anode materials such as high-energy ball milling [6], electroplating [1,2] and reductive precipitation in aqueous [4,5] or non-aqueous solution [7]. Here, we report on various reductive precipitation mechanisms for the preparation of nano-structured small particle size Sn/SnSb powders, their structural and morphological characterization as well as on their electrochemical performance as active material in composite electrodes. Basically, the synthesis process is a reductive co-precipitation from aqueous solutions, in which metal ions of Sn^{2+} and Sb^{3+} are dissolved. In previous works we have used alkaline aqueous solutions and NaBH_4 as reducing agent, which involved undesired impacts and consequences: (i) The alkaline solution conditions during precipitation result in the formation of a large fraction of surface oxides and hydroxides, which cause irreversible side reactions during charge (irreversible formation of Li_2O and LiOH) and thus enlarge the irreversible capacities. Furthermore, one might assume that the formed lithium oxides and hydroxides may hinder the electronic and to some part the ionic transport properties within the electrode. (ii) The high costs of the reductive agent NaBH_4 are a major obstacle for the practical realization of this synthesis process. Our recent efforts (cf. also Ref. [8]) are therefore focussed on a replacement of the NaBH_4 reduction process in alkaline solution by reduction with Zn in neutral aqueous solution, which is a much cheaper process and furthermore results in much less surface oxide and hydroxide formation.

Experimental

Active material synthesis. Sn/SnSb (= composite of Sn metal and the intermetallic SnSb) was synthesized by reductive co-precipitation of Sn^{2+} and Sb^{3+} in aqueous solution in the presence of complexants (sodium citrate), by using either NaBH_4 or Zn powder as the precipitation agent. The details are as follows: (i) NaBH_4 reduction procedure: Two aqueous solutions: (A) containing the respective metal precursors and trisodium citrate dihydrate as complexant and (B) being an alkaline solution and containing the precipitation agent NaBH_4 , were cooled to approximately 1 – 3 °C, and were mixed rapidly under strong stirring. (ii) Zn reduction procedure: The active material was obtained by adding Zn powder to neutral aqueous solution containing Sn^{2+} and Sb^{3+} as metal cations and trisodium citrate dihydrate as complexant. Then, the mixed solutions were ultra-sonicated for 1 h at $T = 0^\circ\text{C}$. For both procedures, the obtained metal powders were separated by filtration and subsequently washed with water, then with 0.25 M HCl, water and finally with acetone. The powders were dried under dynamic vacuum at $T = 120^\circ\text{C}$ and then stored under argon before use.

Electrode preparation and electrochemical characterization. Composite electrodes were prepared by painting a slurry containing 82 wt.-% active material (Sn/SnSb), 10 % Ni powder (Nilaco), and 8 % poly(vinylidene)fluoride (PVdF, Aldrich), and decane (Aldrich) as solvent onto a stainless steel mesh to give an electrode with a geometric electrode area of $2 \times 16 \text{ mm}^2$ and a mass of 2.1-2.3 mg, followed by pressing with 7 to for 1 min and drying at $\sim 120^\circ\text{C}$ under dynamic medium-high vacuum overnight.

The electrochemical tests were carried out in laboratory-type glass cells in an excess (7 mL) of 1 M LiClO_4 / propylene carbonate (PC) (Mitsubishi Chem. Corp., Honeywell or Merck Selectipur) as electrolyte, and with metallic Li as counter and reference electrodes. The experiments were performed with current densities of 0.5 mA cm^{-2} ($\sim 89 \text{ mA g(AM)}^{-1}$) within a potential range of 20 - 1500 mV.

Results and discussion

Characterization of the Sn/SnSb materials by XRD, SEM, and BET. From the XRD spectra (Fig. 1) it can be seen that the main diffraction peaks of each pattern are consistent with literature data [5,9] of plain Sn and the rhombohedral phase β -SnSb. The relative content of the intermetallic SnSb is apparently much higher for the case of the material reduced with Zn.

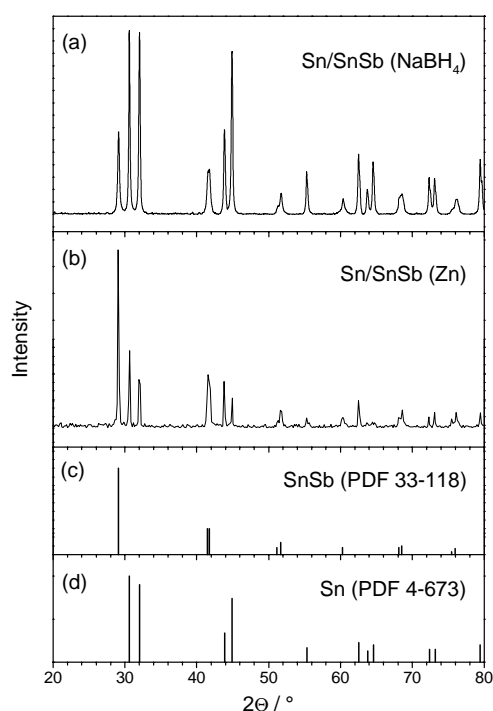


Fig. 1. XRD patterns of Sn/SnSb alloys prepared by reduction with NaBH_4 and Zn.

SEM and BET measurements (Fig. 2) reveal that the "Zn-made" material has a relatively larger particle size and lower porosity and thus correspondingly a lower BET specific surface area than the "NaBH₄-made" one. Judging from the SE micrographs, most of the nanosize particles in both samples are aggregated. However, the small particles of the NaBH₄-made powder are connected via small contact areas and thus the resulting aggregate appears highly porous, whereas for the Zn-made powder, the larger particles inevitably exhibit also larger contact areas with each other and thus the resulting aggregate is more compact.

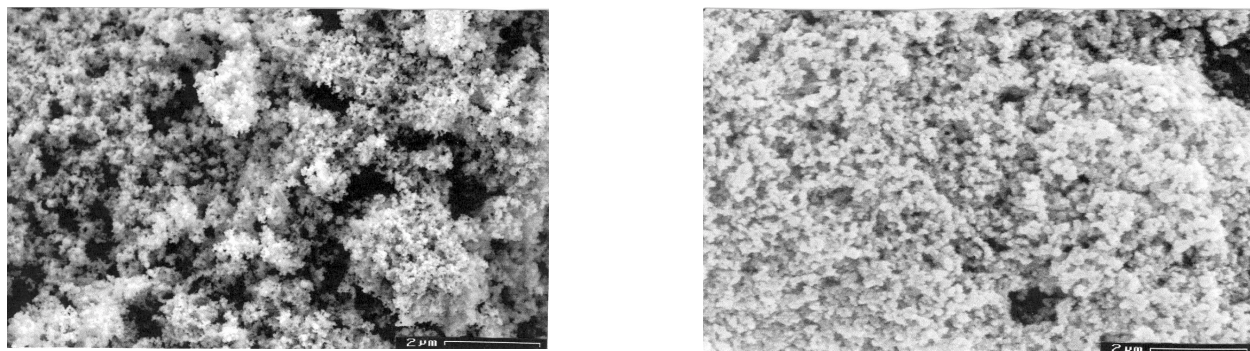


Fig. 2: SE micrographs of Sn/SnSb alloys :
(left) Sn/SnSb, prepared by reduction with NaBH₄, BET surface area = 29.0 m²/g ;
(right) Sn/SnSb, prepared by reduction with Zn, BET surface area = 15.61 m²/g

Electrochemical Characterization. The electrochemical performance of the NaBH₄-made and the Zn-made Sn/SnSb (Fig. 3, left) differ considerably with respect to the discharge/charge efficiencies (= ratio of the discharge/charge capacities). For the NaBH₄-made material, most of the irreversible capacity occurs in the first cycle and then almost diminishes in the following cycles, whereas the irreversible capacity of the Zn-made Sn/SnSb is comparatively much smaller in the 1st cycle (82% efficiency!), but then still visible in the subsequent cycles. The lower irreversible capacity in the case of the Zn-made material in the first cycle may be attributed to the smaller BET surface area and the low amount of surface oxides. The higher irreversible capacity in the following cycles can be explained by the larger particle size resulting in a relatively larger extent of particle cracking and subsequent SEI filming of the new, by cracking created surface sites [4]. For further discussion on possible other effects on the irreversible capacity cf. Ref. [4].

The differences in the 1st cycle charge curves of both materials (Fig. 3, right) are in line with this interpretation, as they display significant "potential spikes" in the case of the NaBH₄-made Sn/SnSb, which are absent in the case of the Zn-made material. Furthermore, the shape of the charge/discharge curves reveals that the Zn-made material is apparently more crystalline than the NaBH₄-made one, as distinct plateaus are visible, which represent the Li-Sb and Li-Sn intermetallic compounds formed during uptake of lithium in the material. This indicates an in average larger particle size.

Conclusion

Reductive precipitation of metal cations with Zn in neutral aqueous solution is a feasible and comparatively cheap method for synthesis of intermetallic materials suitable as lithium storage anodes for rechargeable lithium batteries. In comparison to materials made by reduction with NaBH₄ in alkaline aqueous solution, the material apparently contains lower amounts of surface oxides, is more crystalline and the average particle size is larger. These properties have a beneficial effect on the 1st cycle irreversible capacity but a detrimental effect of the irreversible capacities in the later cycles. Future efforts will be devoted to creation of Zn-made intermetallic hosts with smaller particle sizes.

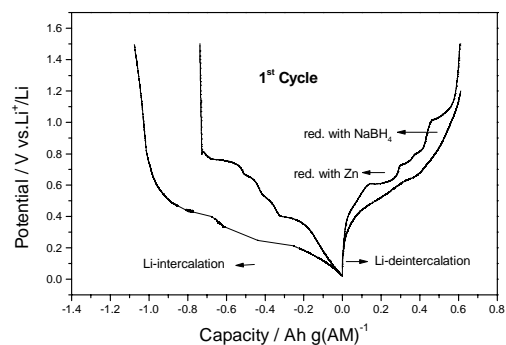
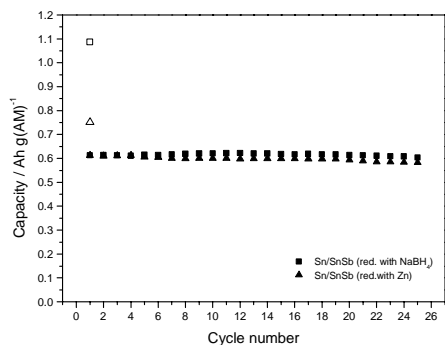


Fig. 3: (left) Constant current cycling data of Sn/SnSb materials prepared by reduction with NaBH₄ and Zn. (right) 1st charge / discharge curves of Sn/SnSb materials prepared by reduction with NaBH₄ and Zn. The curves refer to the cycling data in Fig.3, left. Current density: 0.5 mA cm⁻², potential range: 20-1500 mV, electrolyte: 1 mol L⁻¹ LiClO₄/PC

Acknowledgements

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