

Sb-Based Nanocomposite Alloy Anodes for Li-ion Batteries

E. Allcorn and A. Manthiram
Materials Science and Engineering Program
The University of Texas at Austin
Austin, TX 78712

Introduction

Lithium-ion batteries have been a major contributor to the widespread proliferation of portable electronics over the past two decades due to their high volumetric and gravimetric energy storage capabilities. The graphite anode used in most commercial Li-ion batteries is the source of a number of issues that are hampering the application of Li-ion to other desirable fields like transportation and stationary storage. Graphite has a relatively low specific capacity of 372 mAh g^{-1} and a low tap density of roughly 1.0 g cm^{-3} , limiting both its gravimetric and volumetric storage capabilities. In addition, the reaction potential of lithium with graphite is very close to that of Li/Li^+ , and above the LUMO of the typically used organic solvent based electrolytes. This causes the formation of a solid-electrolyte interphase (SEI) layer on graphite surface, restricting the rate capability. The low operating potential is also a safety hazard as it can lead to lithium plating on the electrode surface, resulting in dendrite growth and short circuiting of the cell.

Lithium alloying materials – such as Sb, Sn, or Si – offer a promising alternative to graphitic anodes. These materials offer significantly higher theoretical capacities (e.g. 660 mAh g^{-1} for Sb) and some of them have reaction potentials well above that of Li/Li^+ , so SEI formation could be mitigated and lithium plating could be avoided. The primary issue with these materials is that they undergo massive volume change during lithiation/delithiation, which leads to crumbling and failure of the electrode, generally within a few cycles¹. Despite its lower specific capacity relative to other lithium alloying materials, our work has focused on the use of Sb as an anode due to its high density, high reaction potential vs Li/Li^+ , and flat potential curve². We have addressed the volume change issue through the use of a composite electrode composed of an intermetallic compound of active Sb combined with an electrochemically inactive buffer phase of Al_2O_3 and conductive carbon. We employ a single step synthesis route of high energy mechanical milling (HEMM) to produce a desirable nanocomposite morphology composed of very small ($< 20 \text{ nm}$) active particles of NiSb well-dispersed within an inactive matrix. The resulting anode demonstrates good specific and volumetric capacities as well as excellent rate capability and cycle life.

Experimental

Our anode material was synthesized by high energy mechanical milling (HEMM) of a mixture of Ni powder, Al powder, and Sb_2O_3 powder in stoichiometric ratios along with 20 wt % acetylene black carbon in order to induce the mechanochemical formation of active NiSb and Al_2O_3 . Milling was carried out for 36 h at 500 rpm under an argon atmosphere at room temperature with a Pulverisette 6 Planetary Mill and hardened steel vial. After synthesis, phase analysis was performed on the final NiSb- Al_2O_3 -C material with X-ray diffraction (XRD). Microstructure, morphology, and composition analysis was performed with scanning electron microscopy (SEM)

and transmission electron microscopy (TEM). The electrodes were prepared by coating Cu foil with a slurry composed of 70 wt. % active material, 15 wt. % Super P carbon, and 15 wt. % PVDF binder using NMP as the solvent. CR 2032 coin cells of our material were assembled with lithium foil as the counter and reference electrode and 1 M LiPF_6 in EC / DEC (1:1 v/v) as the electrolyte. Electrochemical cycling was then carried out at 0 – 2.0 V vs Li/Li^+ at 100 mA g^{-1} .

Results and Discussion

XRD analysis of the as-synthesized NiSb- Al_2O_3 -C showed the presence of crystalline NiSb. No other crystalline phases were observed but XPS analysis confirmed the presence of amorphous Al_2O_3 as in our previous work³. Fig. 1 shows the morphology as observed with TEM. Crystalline particles of active NiSb on the order of 10 nm are dispersed within an amorphous Al_2O_3 and carbon matrix. This nanostructured morphology is believed to mitigate strain from volume change, inhibit active particle agglomeration, and minimize lithium diffusion distances.

Fig. 2 demonstrates the superior cycle life of the nanocomposite anode material relative to both the intermetallic and a composite containing only carbon as the buffer and conductive material. Both NiSb and NiSb-C suffer from rapid capacity fade in early cycling. NiSb- Al_2O_3 -C, while suffering a large first cycle capacity loss, retains a stable capacity of $\sim 300 \text{ mAh g}^{-1}$ through 1000 cycles. NiSb- Al_2O_3 -C has also shown very high rate capability, retaining 90% of its storage capacity even up to 10C rate.

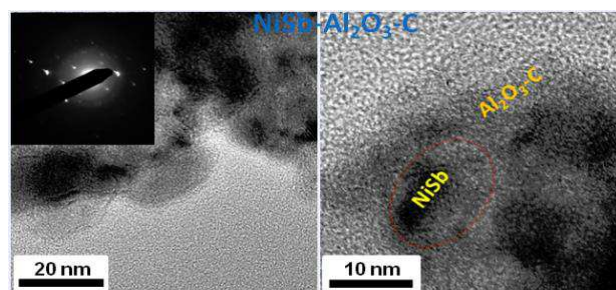


Fig. 1. TEM images of nanostructured morphology with the small active NiSb particles dispersed in amorphous Al_2O_3 and carbon matrix.

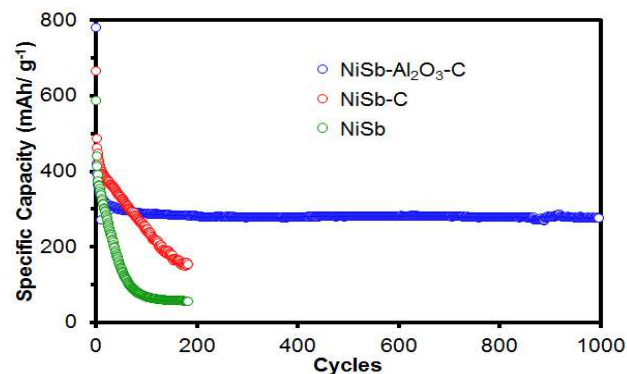


Fig. 2. Cyclability of NiSb- Al_2O_3 -C electrode material relative to similar systems without a buffer matrix or conductive carbon.

References

1. W.-J. Zhang, J. Power Sources, **196**, 1 (2011).
2. J. Wang, I. D. Raistrick and R. A. Huggins, J. Electrochem. Soc., **133**, 3 (1986).
3. D. Applestone, S. Yoon and A. Manthiram, J. Mater. Chem., **22**, 7 (2012).