Abstract

The invention of Li-ion batteries paved the pathway for the development of modern day portable electronics. With an increasing dependency on high energy sources for the portable equipment and devices, a simultaneous development of the compatible Li-ion battery with a high energy density is necessary. However, the present commercially available Li-ion battery based on graphite anodes fails to meet this increasing demand owing to their lower theoretical capacity (372 mAh/g). Therefore, there is an urgent need for a new anode material with a theoretical capacity of at least twice than that of graphite.

The Sn and Sb based alloys are well known for high volumetric and gravimetric capacity (7214.14 mAh/cc; 993 mAh/g), and they are emerging as a potential replacement for graphite (Winter and Besenhard, 1999). However, Sn suffers enormous volume expansion (260 %) (Winter and Besenhard, 1999) during lithiation and undergoes a large volumetric stress, leading to pulverization (Huggins R. A. 2009).

Use of “active-active” and “active-inactive” alloys has long been adopted to minimize the volumetric strain. The refined particle size reduces lithium diffusion length allowing a faster lithiation/delithiation and the nanocrystalline structure helps to accommodate the strain. The “active-active” alloys (alloys consisting of two or more lithium active elements), such as Ag_4Sn, SnSb, lithiate under different voltage plateaus (characteristic to each element) reducing the volumetric stress on lithiation (Li H. et al., 2001; Mukaibo H. et al. 2004). Examples of the “active-inactive” principle include intermetallics, such as Ni_3Sn_4, Cu_2Sb, and Cu_6Sn_5, which lithiate (and expand) at a unique potential with the ejection of the conductive inactive phase (Ni, Cu, Fe) which buffer the volume expansion (Hou X. et al. 2009; Sharma S. et al. 2003).

The objective of this thesis is to develop a Sn-Sb-Cu ternary alloy (with a target capacity of ~700-800 mAh/g) composed of two lithium-active (Sn and Sb) and one lithium inactive component (Cu) as negative electrodes for the Li-ion battery. It combines all the aforementioned strategies and to correlate the lithiation mechanism with the various degradation mechanisms in this ternary anode, and proposes a viable solution to mitigate them. The reason for selecting Sb as the second active element over others is that the lithiation range of Sb is 0.87-0.91 V and that of Sn is 0.66-0.38 V; far apart from each other. Thus, the lithiation of Sn and Sb takes place independently without interfering with each other. The reason for selecting Cu as the inactive element is that Cu is ductile and may arrest the volumetric stress by undergoing plastic deformation itself.

From the processing point of view, the Sn-Sb-Cu alloys have been prepared using various synthesis techniques like ball milling, reductive co-precipitation, and electrodeposition. Among them electrodeposition is a suitable bottom-up method which can be used to synthesize metals and alloys in a wide range of nanostructures or microstructures with a variety of compositions (Nithya C. et al. 2013; Wang F. et al. 2008; Arpacık M. et al. 2013; Jiang Q., Xue R., Jia M. 2012; Yang R. et al. 2010). The method is cheap, fast, simple, and environmental friendly. Binder-free Sn based anodes can easily be electrodeposited with various morphologies and varying compositions. Synthesis of such 3D anodes using electrodeposition offers the flexibility in preparing appropriate microstructures, which are not offered by other synthesis techniques.

A Sn-Sb-Cu alloy electrode, having a phase mixture of SnSb, Cu_6Sn_5 and Sn, with a target capacity of ~700-800 mAh/g (at 200 mA/g charge-discharge rate) has been prepared using electrodeposition. In spite of the strategies employed, the electrode has faded after delivering 672 mAh/g till the 22nd cycle. In order to provide a more physical buffering, a foamy electrode has been deposited followed by incorporation of reduced graphene oxide (RGO). The RGO reinforced foamy sample delivers ~600 mAh/g till the 55th cycle. However, the capacity drops to 272 mAh/g only after 80 cycles.

In order to identify the exact mode of failure, a study on the phase transformation during lithiation has been carried out with the help of the X-ray diffraction technique. It has been found that Li reacts with Cu_6Sn_5 to form Li-Sn intermetallic and free Cu. Because of this the interfacial bonding weakens, and the electrode fails owing to the delamination from the current collector (Cu), but not due to pulverization.

The problem has been rectified with four different strategies. In the first strategy, the problem has been partially solved by employing an Ag current collector, where the intermetallic interface (Ag_3Sn) reacts at a lower voltage than Sn. By cutting off the cycling before the intermetallic interface reacts, the problem of delamination is solved while still obtaining a high specific capacity.

In the second strategy, instead of a Sn rich alloy a Sb-rich ternary alloy has been used. It is found that $Sn_{35}Sb_{55}Cu_{10}$ outperforms $Sn_{75}Sb_{15}Cu_{10}$ owing to a better mechanical stability. This superiority of $Sn_{35}Sb_{55}Cu_{10}$ electrode can be attributed to more number of lithiation voltage plateaus which produce better buffering against volumetric strain. Moreover, in the $Sn_{35}Sb_{55}Cu_{10}$ electrode, Cu in its elemental form is present throughout the lithiation cycle and performs as a more effective buffer than the Cu in $Sn_{75}Sb_{15}Cu_{10}$ electrode. Because of these structural advantages, $Sn_{35}Sb_{55}Cu_{10}$ delivers 377 mAh/g at 200 mA/g charge-discharge rate even after the 100th cycle.

The third strategy is to replace the conventional Cu current collector (foil) with the Cu/Ni foam. This Cu/Ni foam is prepared by electrodeposition utilizing the in-situ hydrogen evolution as a dynamic template. The porous Ni scaffolded Sn-SnSb-Ni_3Sn_4 alloy lithiates at five different potentials inside the 3D Ni scaffold, and thereby avoids mechanical disintegration and loss of the electrical connectivity owing to the stress accommodation during cycling. The as-synthesized binder-free electrode delivers a high reversible capacity of 506 mAh/g after the 100th cycle and it undergoes only a capacity loss of 16% in the last 50 cycles at a rate of 0.5 C. It shows an exceptional rate performance of 380 mAh/g at 1C rate.

In the fourth strategy, pure Sn has been electrodeposited on Ni-foam followed by isothermal holding at 300 ^{o}C for 1 hr. This process melts Sn which completely impregnates the Ni-foam resulting in the formation of Sn-Ni and Sn-Cu intermetallics within the Ni-scaffold. This active-inactive Sn:Sn-Cu/Ni intermetallic, impregnated into Ni-scaffold assembly, delivers a specific capacity of 587.9 mAh/g at a rate of 500 mA/g (0.5 C) after the 100th cycle and superior rate capability delivering 463 mhA/g at a rate of 2 A/g (2 C).