

Supporting Information for

Electrodeposition of Pure Phase SnSb Exhibiting High Stability as Sodium-Ion Battery Anode

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Experimental Section

Pure phased SnSb (1:1 ratio; verified by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS)) electrodes were prepared by single-step electrodeposition process using a three-electrode setup. A platinum working electrode (BASi, 1.6mm diameter), a platinum mesh counter electrode (100 mesh, Alfa Aesar), and silver wire reference electrode were used for cyclic voltammetry. Cyclic voltammetry was done at a rate of $50 \text{ mV}\cdot\text{s}^{-1}$. A similar setup consisting of nickel foil (Sigma Aldrich) working electrode, a platinum mesh counter electrode, and silver wire reference electrode were used for the electrodeposition process. An ethaline solution, consisting of 1:2 ratio by mass of choline chloride (VWR, High Purity) and ethylene glycol (Fisher Scientific), respectively, was used as the electrodeposition solvent. Finally, 50 mM SbCl_3 (Sigma Aldrich, ACS reagent) and 50 mM $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ (Sigma Aldrich, ACS reagent) were dissolved into the ethaline to form the deposition solution. Electrodepositions were performed at 25°C with a constant potential of -0.7 V vs Ag/Ag^+ .

Electrochemical testing was performed in a Swagelok half-cell. The half-cell contains a SnSb electrode deposited onto Ni foil, polypropylene separator (MTI Corp) and glass filter (Whatman) filled with 1 M NaPF_6 (Strem Chemicals) in dimethyl carbonate (DMC) (Sigma Aldrich, anhydrous) + 5% by volume fluoroethylene carbonate (FEC) (Sigma Aldrich), and sodium metal (Sigma Aldrich). Half cells were electrochemically tested with an Arbin battery tester (BT-2000). C-rate was determined based on theoretical capacity of each electrode.

Materials Characterization

The surface morphology and composition were examined by scanning electron microscopy (SEM) (JOEL JSM-6500F operating at 15 kV) and EDS (Oxford Instrument X-Max). The EDS spectra were analyzed using AZtec software (Oxford Instrument). The crystal structure of electrodes were identified by glancing angle X-ray diffraction (GAXRD) (Bruker D8 Discover Series I,Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$). *Ex-situ* SEM and *ex-situ* XRD were performed after galvanostatically cycling the SnSb electrodes to different states of charge/discharge after set number of cycles. Electrodes were disassembled in an Argon glovebox and electrodes were cleaned using DMC prior to *ex-situ* studies.

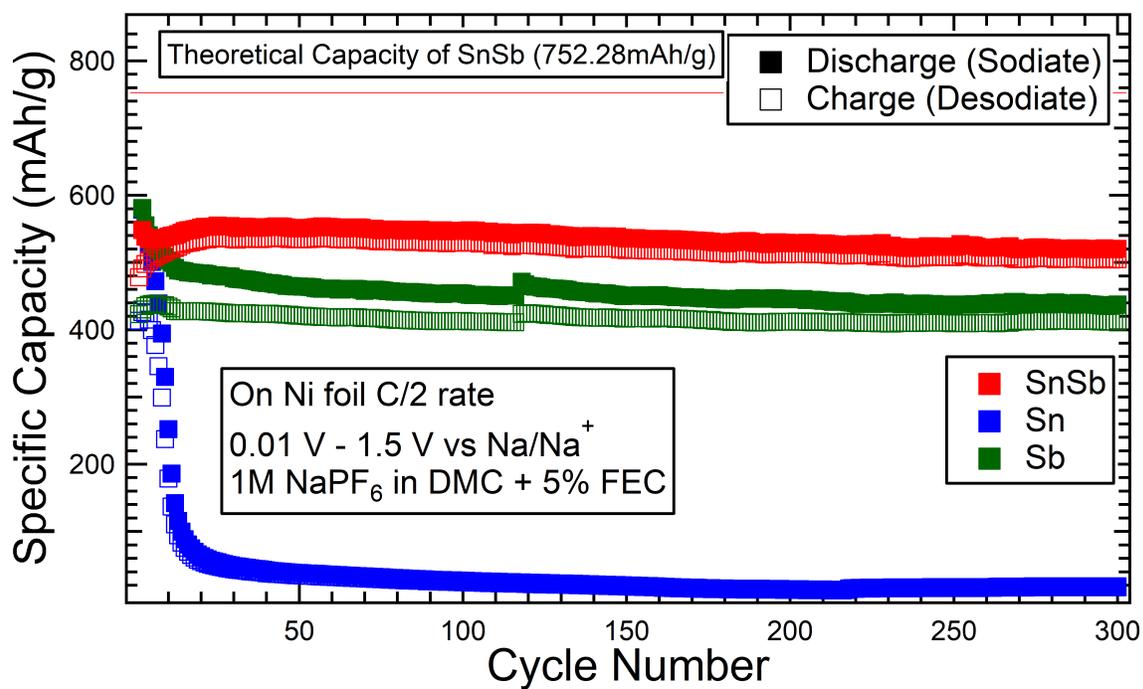


Figure S1: Galvanostatic cycling of electrodeposited SnSb, Sn, and Sb in half cells. The sudden increase in capacity at about cycle 120 of Sb is due to unexpected interruption of the ARBIN battery cycler.

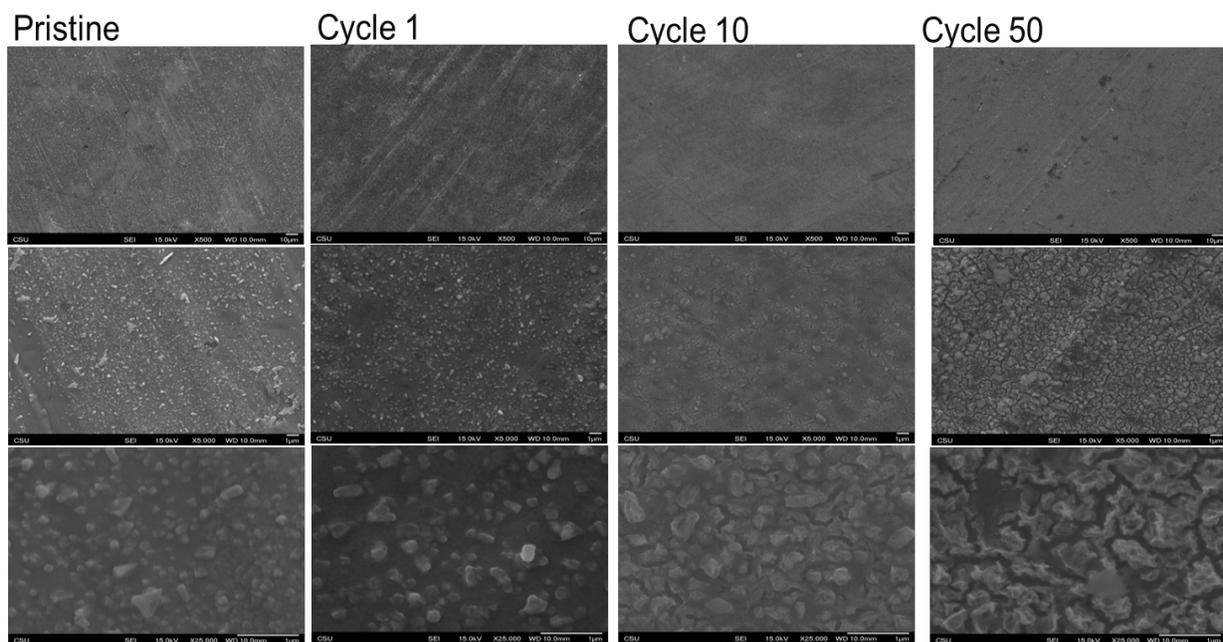


Figure S2: Images of SnSb electrode surfaces after different electrochemical conditions using the scanning electron microscope. Images were taken at x500, x5k, and x25k magnification.

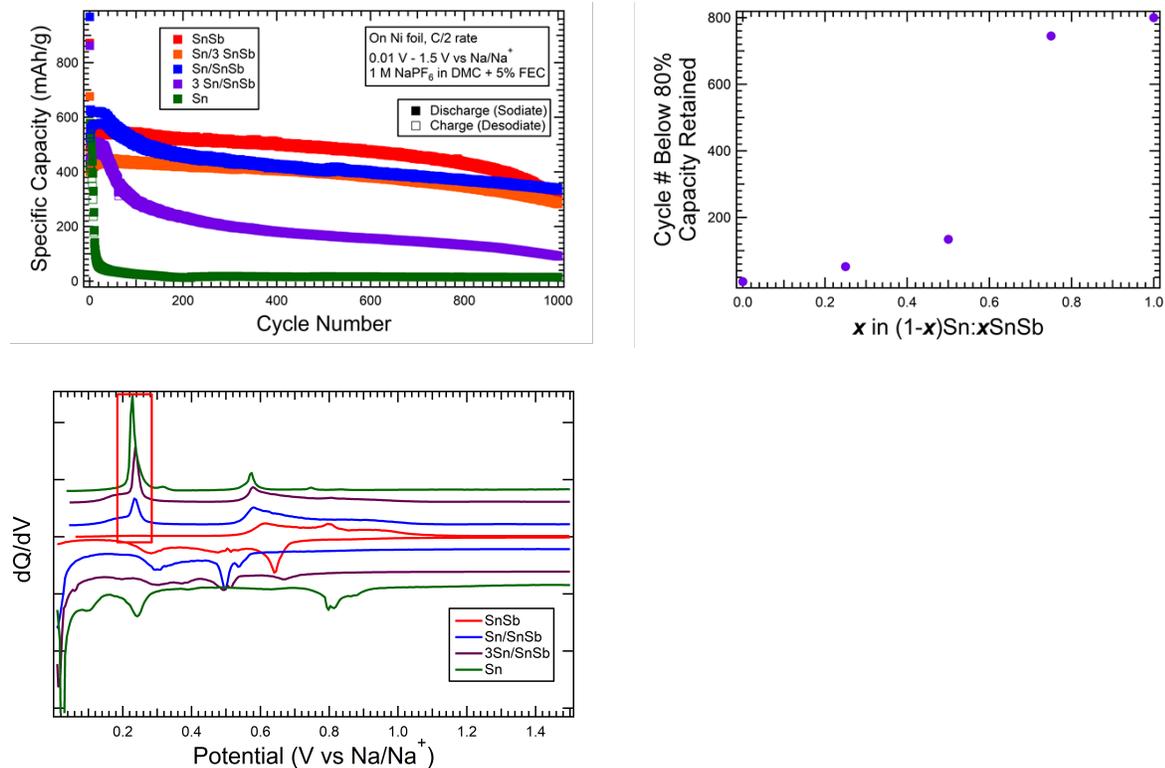


Figure S3: (Top left) Galvanostatic cycling of electrodeposited SnSb and different Sn-SnSb compositions leading to pure Sn. (Top right) Graph extrapolated from galvanostatic cycling showing when the different composition electrodes fall below 80% capacity retention. Electrodepositions of the Sn:SnSb compositions were done using different Sn:Sb concentrations in ethaline and verified using EDS. (Bottom) dQ/dV graph extrapolated from the galvanostatic cycling showing the sodiation and desodiation events present for different Sn:SnSb electrodes. The red box highlights the presence of a new electrochemical activity at this rate that grows proportionally with the increase of Sn content, suggesting this event is unique to non-SnSb tin.

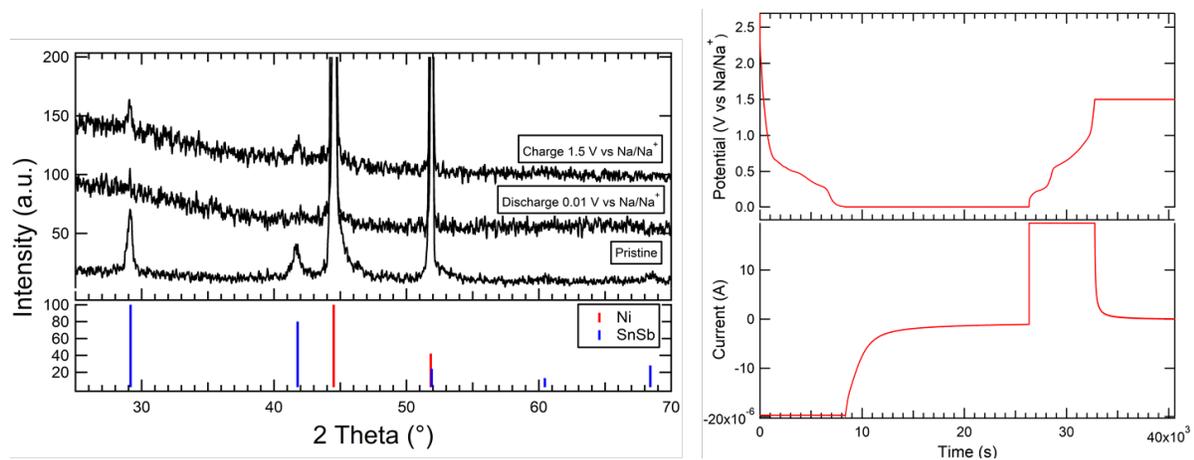


Figure S4: *Ex-situ* X-ray diffraction patterns (left) taken pristine SnSb, after sodiation, and after the first desodiation. The SnSb was cycled galvanostatically to 0.01 V vs Na/Na⁺, held potentiostatically for 5 hours or when current reaches nA, and galvanostatically charged to 1.5V vs Na/Na⁺, then held potentiostatically for 5 hours or when current reaches nA. This test was done to verify crystalline SnSb does reform during desodiation after becoming amorphous during sodiation.