Supporting Information

Direct Evidence of conversion mechanism in NiSnO₃ anode for lithium ion battery application

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Experimental Section:

Preparation of NSO electrode: Commercial nickel tin oxide (NiSnO₃· 2H₂O, Sigma Aldrich) powders were dried at 100 °C for 72 h under vacuum to get rid of the water in the molecular, then dried NiSnO₃ was mixed with super P, and poly(vinylidene) fluoride in the N-methylpyrrolidinone (NMP) solvent with a weight ratio of 8:1:1. The obtained slurry was casted onto a copper foil and dried in vacuum at 80 °C overnight. The electrode was cut into pellets with diameter of 8 mm and used as the working electrode in the cell. Lithium metal was used as counter and reference electrodes. 1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 was used as electrolyte. The cell was assembled in an Ar-filled atmosphere.

Characterization: The morphology and EDX of the prepared samples was investigated with scanning electron microscopy (SEM, JEOL, Tokyo). The structure of NiSnO₃ was recorded by X-ray diffraction (XRD) (Philips) using Cu Kα radiation.

Electrochemical performance evaluation: Cyclic voltammetry measurement was carried out using a Voltalab 80 electrochemical workstation with scan rate at 0.1 mVs⁻¹. The galvanostatic charge-discharge profiles were recorded using an Arbin MSTAT battery test

station in the potential range of 0.005-3 V vs. Li⁺/Li with current at 100 mA g⁻¹. For the *ex*situ examination, the galvanostatic measurement was stopped at certain potentials at 1st and 20th cycle, respectively. The cell was dissembled in the glove box and the electrode was washed with dimethyl carbonate (DMC) to remove the LiPF₆ from electrolyte. The cleaned electrode materials were dispersed in DMC by ultra sonication for 1 day to get a fully homogeneous dispersion of the reaction products. The material drop was dipped onto the copper grid for TEM measurements. All procedures were conducted under Ar atmosphere except few second air-exposure when transferring the copper grid to the TEM. Two to four samples from different cells were prepared and tested for each of the potential point investigated depending on the quality of the TEM images.

Transmission electron microscopy: Bright-field TEM images and selected area electron diffraction (SAED) patterns were acquired at 120 kV on a Zeiss EM912 microscope with an Ω -type energy filter. High–resolution TEM images were obtained at 400kV on a JEOL 4000FX microscope. All TEM data was further processed with Digital Micrograph software (Gatan, USA). The SAED patterns are recorded in the scale of 500 nm.



Figure S1. XRD pattern of NiSnO₃.



Figure S2. SEM image of NiSnO₃ before cycling.



Fig. S3. Low (a) and high (b) -resolution TEM images of original NiSnO₃; Low-resolution TEM images of reduced product of NiSnO₃ at different potentials during the first cycle (c) 0.9 V; (d) 0.6 V; (e) 0.02 V; (f) 1V; (g) 2.2 V vs. Li/Li⁺. The yellow and red circles in Fig. S2c emphasize the discharged products with particle size of ~ 5 and 30 nm, respectively; The brown circles in Fig. S3e indicate that some of the discharged products remain small particle size (5-10 nm) after discharged to 0.02 V.



A (big aggregation):



Fig. S4 SEM image of the NAS electrode after first cycle and the energy-dispersive X-ray spectra (EDX) at different areas of the electrode. The distribution of Ni and Sn is inhomogeneous for the NAS electrode.



A (big agglomerates):



Fig. S5 SEM image of NSO electrode after 1 cycle and the Energy-dispersive X-ray spectra (EDX) at different areas of the electrode. The distribution of Ni and Sn elements is homogeneous for NSO electrode.

Electrode	Peak location				
Licenoue	I cak location		Reaction	Ref	
Materials	(V vs. Li ⁺ /Li)				
NiO	Lithiation	0.75 V	0.75 V Formation of Li _{0.5} NiO		
		(1 st cycle)	SEI film formation	2	
		0.6 V	Decomposition of NiO to Ni	3	
		(1 st cycle)	and Li ₂ O		
		~ 1.2 V	Decomposition of NiO in the		
		(2nd cycle on)	following cycles	3	
	Delithiation	~ 1.5 V	Decomposition of SEI film	4	
		~ 2.2 V	Decomposition of Li2O and	3	
			formation of NiO		
Sn	Lithiation	< 0.5 V	Formation of Li _x Sn	5	
	Delithiation	0.5 V, 1.2 V	Dealloy of Li _x Sn	5	

Table S1. Assignment of redox peaks of NiO and Sn during reactions with lithium.

d-spacing [nm]	Assignment	d-spacing [nm]	Assignment
0.292	Sn (200)	0.176	Ni (200)
0.279	Sn (101)	0.166	Sn (301)
0.266	Li ₂ O (111)	0.163	Li ₂ O (220)
0.241	NiO (111)	0.146	Sn (400)
0.231	Li ₂ O (200)	0.139	Li ₂ O (311)
0.209	NiO (200)	0.125	Ni (220)
0.206	Sn (220)	0.115	Li ₂ O (400)
0.204	Ni (111)		

Table S2. Assignment of the Bragg reflections based on *d*-values from SEAD patterns and space group for Sn, Li₂O, Ni, and NiO.

Substance	Space group	a [nm]	b [nm]	c [nm]	Reference
NiO	Fm-3m	0.418	0.418	0.418	6
Ni	Fm-3m	0.353	0.353	0.353	7
Sn	I41/amd	0.583	0.583	0.318	8
Li ₂ O	Fm-3m	0.461	0.461	0.461	9

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