Supporting Information for

Nanoporous Tin with a Granular Hierarchical Ligament Morphology as a Highly Stable Li-Ion Battery Anode

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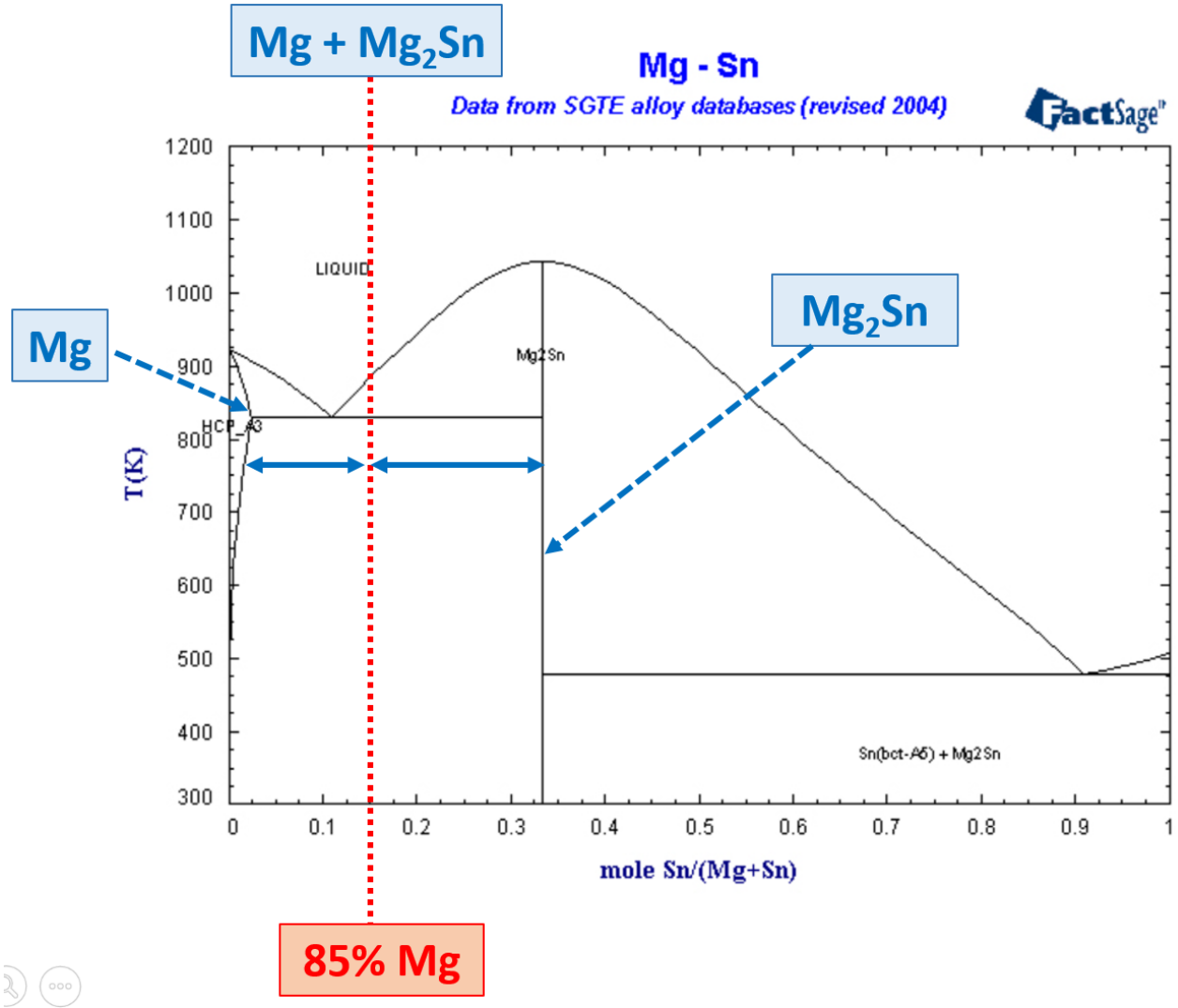

Figure S1. Sn/Mg phase diagram. When the Mg content is high (e.g. 85 at. %), the Sn/Mg alloy is heterogeneous and contains two coexisting phases: nearly pure Mg metal and the Mg_2Sn intermetallic compound. Mg removal from the intermetallic compound will result in the formation of NP-Sn. The dissolution of the nearly pure Mg metal phase will facilitate the fragmentation of the dealloyed NP-Sn into porous micrograins (i.e. into micron sized NP-Sn powders). Reproduced from '*SGTE Alloy Phase Diagrams Database'* with permission.

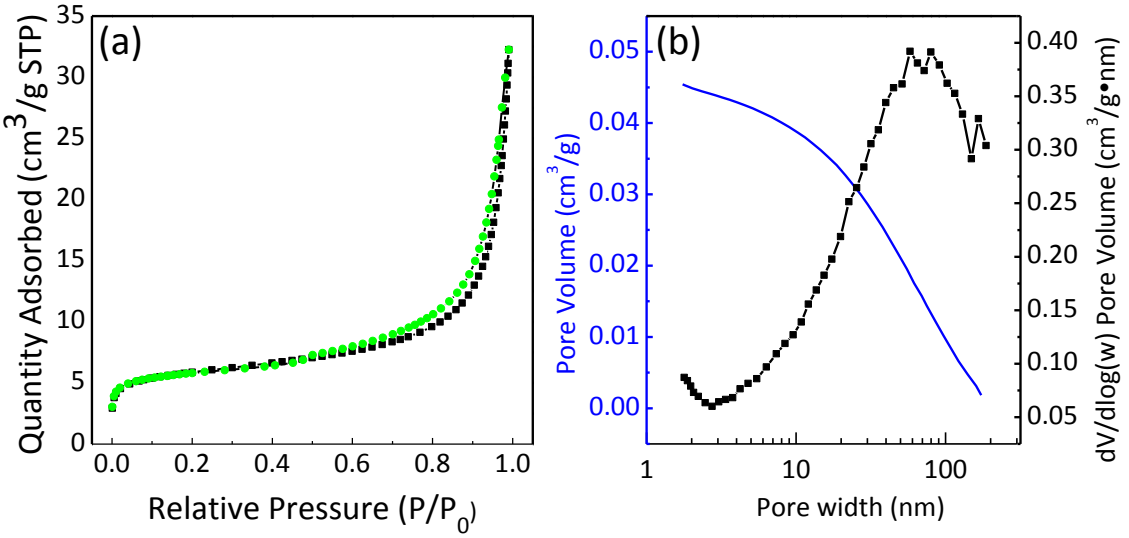

Figure S2. (a) Nitrogen adsorption and desorption isotherm for NP-Sn. This data was used to calculate a surface area of 19 m^2/g using the Brunauer-Emmett-Teller (BET) method. Since the surface area is normalized by mass, this value appears somewhat low compared to other high surface area materials with lower intrinsic density (porous silica, metal oxides, carbons, etc.). However, considering the high density of tin (7.31 g/cm^3), the total surface area for this material is actually quite large. (b) Cumulative pore volume (blue) and Barrett-Joyner-Halenda (BJH) pore size distribution (black) calculated from the adsorption branch of the nitrogen isotherm. The average pore size is ~70 nm and the total pore volume is 0.045 cm^3/g. Using the total pore volume value, the porosity of NP-Sn is calculated to be ~25%.

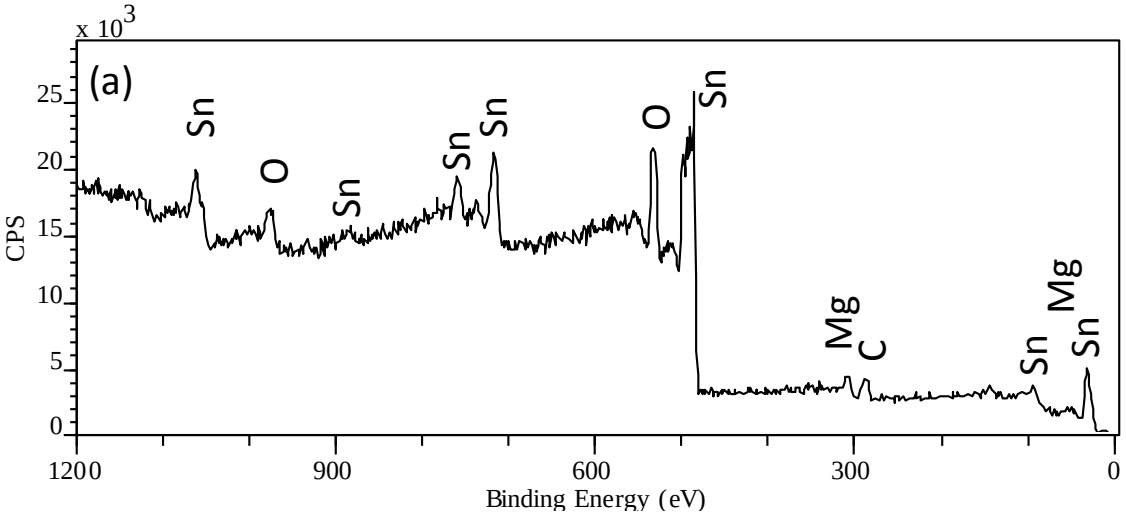

Figure S3: XPS survey scan of NP-Sn from 0-1200 eV. This data shows that the elements present at the surface of the material are Sn, O, Mg, and C.

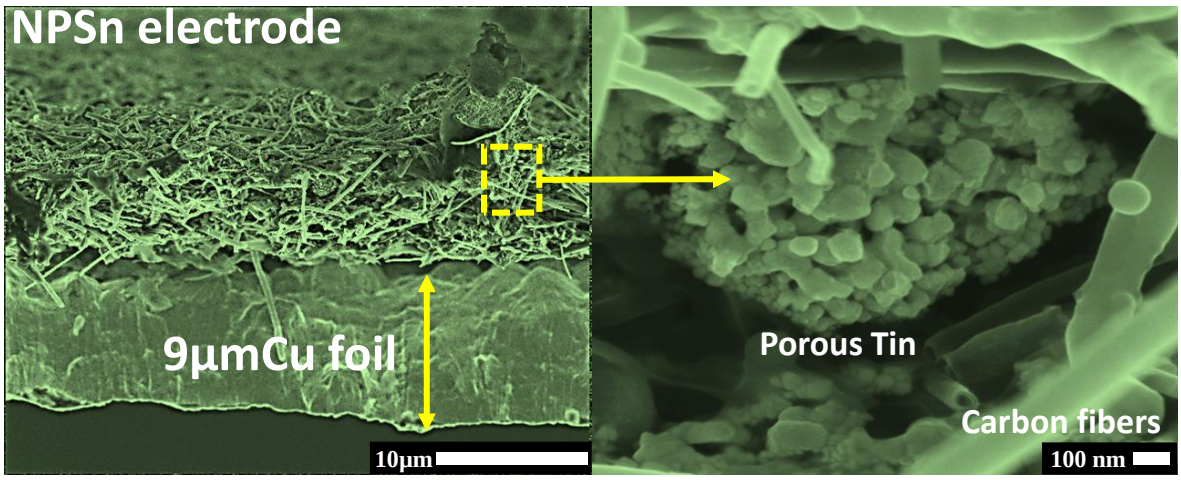

Figure S4: Scanning electron microscopy cross sectional images of the composite NP-Sn electrode. The thickness of the electrode is 8 – 10 µm. Tin metal has a low melting point (232°C), which can be depressed further in nanostructured samples. Therefore, it was important to verify that the NP-Sn grains did not coarsen or melt during the electrode fabrication process. The higher magnification image shows that, indeed, the NP-Sn grains retain their nanoscale architecture after the ball milling and drying (70°C) procedures used to fabricate the composite electrodes.

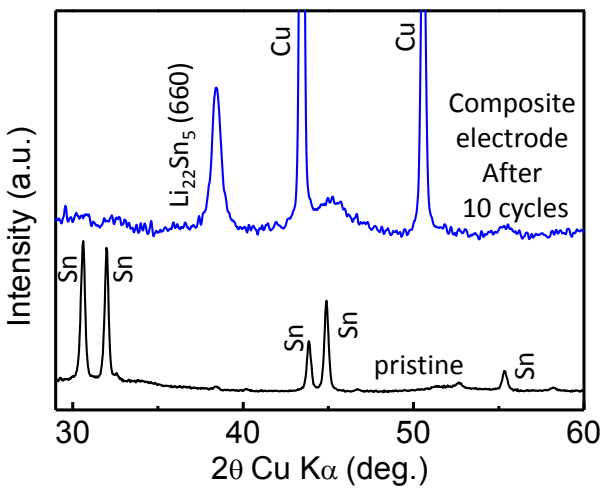

Figure S5: Ex-situ XRD of NP-Sn at 0.07V after 10 charge/discharge cycles between 1 - 0.07 V (protected in a polyimide tape pouch). This XRD data shows that the low density $Li_{22}Sn_5$ (2.05 g/cm^3) phase is formed in NP-Sn, despite these samples not reaching full theoretical capacity. This data suggests that the improved cycle lifetime overserved in this material results from its unique nanoscale architecture, and not by preventing formation of the $Li_{22}Sn_5$

Table S1: Parameters used to calculate electrode level volumetric charge density. The electrode thickness was obtained from Figure S4. The NP-Sn electrodes fabricated in this study have two-

Sample Name	**Measured or calculated value**	**Reference**
Areal capacity NP-Sn	0.693 mAh/cm^2	This work
Electrode thickness NP-Sn	8 µm	This work
Volumetric capacity NP-Sn	870 mAh/cm^3	This work
Theoretical volumetric capacity bulk $Li_{22}Sn_5$	1991 mAh/cm^3	1
Commercial graphite electrode volumetric capacity	400 – 470 mAh/cm^3	1

fold higher volumetric capacity compared to commercial graphite electrodes.

TXM Tomography Movies Available for Download:

Movie S1. 3D rendering of pristine NP-Sn before cycling. The file is labeled: Movie S1_Pristine 3D

Movie S2. 3D rendering of NP-Sn after the first lithiation, which corresponds to a voltage of 70 mV *vs.* Li/Li^+. The file is labeled: Movie S2_Lithiated

Movie S3. 3D rendering of NP-Sn after lithiation and delithiation, which corresponds to a final voltage of 1.2 V *vs.* Li/Li^+. The file is labeled: Movie S3_Delithated_After 1 cycle

References

(1) Nitta, N.; Yushin, G. High-Capacity Anode Materials for Lithium-Ion Batteries: Choice of Elements and Structures for Active Particles. *Part. Part. Syst. Charact.* **2014**, *31*, 317–336.