## Supporting Information

Integration of Sn/C Yolk-Shell Nanostructures into Free-standing Conductive Networks as Hierarchical Composite 3D Electrodes and the Li-ion Insertion/Extraction Properties in a Gel-type Lithium-ion Battery Thereof

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**Figure S1.** Large-scale SEM images of tin nanoparticles encapsulated elastic hollow carbon spheres (TNHCs) integrated in flexible carbon nanofibers texture (FCNFs).



**Figure S2.** TEM images of the Sn@C nanostructures after long-time exposure to high-intensity electron beam, leaving a nanoporous, cellular carbon shell aggregation behind.



Figure S3. The pore size distribution plots calculated based on a) adsorption and b) desorption isotherms.



**Figure S4.** TGA curves in air atmosphere for a list of Sn@C samples prepared by the pyrolysis process of  $SnO_2@PAN$  under hydrogen atmosphere with varied time and temperature. The mass content of Sn in the Sn@C nanocomposite is calculated by the Equation 1 in Supporting Information.

## Composition analysis from TGA results:

From TGA data of Sn@C composite (air atmosphere)

 $m_{(\text{SnO2})}/m_{(\text{Sn+C})} = \text{R}, \ m_{(\text{SnO2})} = m_{(\text{Sn}+2\text{O})}$  (Equation 1)  $\Rightarrow m_{\text{Sn}}/m_{(\text{Sn+C})} = \text{R} \times (118.7/150.7) = 44.0 \text{ wt.\%} (e.g., \text{R} = 55.8 \text{ wt.\%})$ 

i.e., the mass fraction of Sn in Sn@C composite is calculated to be 44.0 % for the sample with weight loss of 55.8 wt.% in Figure S4.



Figure S5. SEM image of the PVDF microporous separator membrane.



**Figure S6.** The discharge/charge capacity profiles of the Sn@C composite (with 44 wt.% Sn) in 2–0.01 V voltage window (*vs.* Li/Li<sup>+</sup>) with a current density of 50 mA  $g^{-1}$ .



Figure S7. Nyquist plots of the Sn/C yolk-shell free-standing composite network as anode. E = 2.6 V, 10 mHz < f < 100 kHz.



**Figure S8.** The typical galvanostatic potential-specific capacity curve of  $LiCoO_2$  as cathode active material with lithium foil as anode and reference electrode. The current density for charge and discharge is 50 mA g<sup>-1</sup>.



**Figure S9.** SEM of the Sn@C yolk-shell 3D nanofibrous structure synthesized by pyrolysis of their precursor SnO<sub>2</sub>@PAN (SnO<sub>2</sub>/PAN mass ratio of 1:1.3) in nitrogen atmosphere at 800 °C for 30 min.



Figure S10. Thermogravimetry analysis of the as-prepared Sn/C yolk/shell free-standing composite film in air atmosphere, as well as that of the related precursor samples such as PAN and SnO<sub>2</sub>/PAN composite networks in nitrogen atmosphere with a heating rate of 20 °C min<sup>-1</sup>. The mass fraction of Sn in Sn@C composite is calculated 77.9 % 98.9 be for the sample with weight loss of wt.%. to



**Figure S11.** a) Cyclic voltammogram of the Sn/C free-standing nanocomposite network by pyrolysis in nitrogen (sample in Figure S9), with a scanning rate of 0.1 mV s<sup>-1</sup>, over the potential range of 3–0 V vs. Li/Li<sup>+</sup>. b) Galvanostatic voltage–specific capacity profiles of the Sn/C composite network with lithium foil as counter electrode and reference electrode. c) Galvanostatic voltage–specific capacity profiles of the Sn/C composite network with LiCoO<sub>2</sub> as counter electrode (positive electrode).



**Figure S12.** SEM images of a–c) the hollow SnO<sub>2</sub>/PAN core-shell free-standing network with higher SnO<sub>2</sub> content, which is electrospun from the slurry (SnO<sub>2</sub>/PAN mass ratio of 3:1). d–h) SEM images and i) schematic illustration of the resulted Sn/C yolk-shell free-standing network with higher tin content, i.e., with higher Sn@C yolk/shell density on a string and more exposed tin microspheres by pyrolysis in a nitrogen atmosphere. The mass fraction of Sn in Sn@C composite is calculated to be 92.7 wt.% for the sample with weight loss of 117.7 wt.% in air atmosphere.

**Note S1.** The Sn component seems inclined to exhibit a series of sharp peaks in the CV scanning loops as the anode material of Li-ion batteries, however, the carbon-coated Sn anode materials seem to show suppressed peaks (i.e., smooth peaks), as a typical instance, Prof. Cho's group [Ref S1] has shown <u>the related features</u>, which showed that the amorphous carbon-coated Sn anodes had a smooth differential capacity with a suppression of the sharp peaks indicative of phase changes during the alloying/dealloying reaction with lithium, and the phase transition voltage of the coated Sn was quite different from those in pure Sn metal. And this may be attributed to the overall change in phase-change rate influenced by the amorphous carbon coating layer.

Furthermore, the lithium-tin voltage profile during the alloying and removal of lithium from a tin negative electrode material varies as the phases of Li-Sn that are present in the electrode change, which has been researched by Prof. Dahn et al. The voltage profile of an electrochemical cell with Sn as anode active material is shown in Figure Sx(a), which is corresponding to the volume expansion of alloy materials (i.e. the lithiation ratio) as shown in Figure Sx(b). From these figures, it can be derived that the voltage plateaus in our case may be corresponding to the sequent reaction stages as shown in the following formula,

$$Sn \leftrightarrow Li_2Sn_5 \leftrightarrow LiSn \leftrightarrow Li_5Sn_2(Li_{13}Sn_5) \leftrightarrow Li_7Sn_2 \leftrightarrow Li_{22}Sn_5$$
(Formula S1)



Figure Sx. a) The experimental (solid line) and calculated (dashed line) voltage profile for the lithiation of tin. b) The volume per mole of host atoms of tin, as a function of its lithium content. Phases occurring in the binary phase diagram of tin with lithium are indicated. After 'Fig 3&4 in Ref S2' by Prof. Dahn et al.

- Ref S1. M. Noh, Y. Kwon, H. Lee, J. Cho, Y. Kim and M. G. Kim, Chem. Mater., 2005, 17, 1926-1929.
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- Ref S4. M. Obrovac, L. Christensen, D. B. Le and J. Dahn, J. Electrochem. Soc., 2007, 154, A849-A855.