Supporting Information

Spatially-confined lithiation/delithiation in highly dense nanocomposite anodes towards advanced lithium-ion batteries

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Experimental Section

Sample preparation: A novel pulsed-deposition technique, pulsed-spray evaporation chemical vapor deposition (PSE-CVD), was applied for the deposition of various electrodes. The SnCl₄·5H₂O and Fe(acac)₃ precursors were dissolved in ethanol at a concentration of 0.015 and 0.010 mol L⁻¹, respectively, and used as liquid feedstocks. For the deposition of SnO₂-Fe₂O₃-Li₂O (59.0:36.6:4.4 of weight ratio, the primary nanocomposites in the work) and SnO₂-Fe₂O₃-Li₂O (70.0:25.6:4.4 of weight ratio), the concentration of LiNO₃ precursor in ethanol is 15 mM, while it is 60 mM in the preparation of SnO₂-Fe₂O₃-Li₂O (50.2:31.1:18.7 of weight ratio). These liquid feedstocks were injected into the evaporation section in a pre-set pulsed sequence (Scheme S1). For all the depositions, the pulse width for every injection was 10 ms and the spacing interval between two injections is 990 ms. During the deposition of pure SnO_2 or Fe_2O_3 , only the ethanol solution of $SnCl_4 \cdot 5H_2O$ or $Fe(acac)_3$ was injected into the reactor (Scheme S1a). While for the preparation of SnO₂-Fe₂O₃ or SnO₂-Li₂O composite, SnCl₄·5H₂O and Fe(acac)₃ or LiNO₃ liquid precursors were introduced into the evaporation section alternately in a sequence mode shown in Scheme S1b. Scheme S1c, d and e demonstrate the sequences (time) for the fabrication of SnO₂-Fe₂O₃-Li₂O (59.0:36.6:4.4 of weight ratio), SnO₂-Fe₂O₃-Li₂O

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(70.0:25.6:4.4 of weight ratio) and SnO₂-Fe₂O₃-Li₂O (50.2:31.1:18.7 of weight ratio) electrodes. Glass slides and stainless steels were used as substrates, which were maintained at 350 °C in all depositions. In this set-up, the evaporation zone and transport zone were set above the CVD chamber, the temperatures of which were kept at 180 °C and 210 °C, respectively. N₂ (nitrogen, 800 sccm) was used as carrier gas. The working pressure in the reactor during deposition processes was stabilized at 400 Pa.

Sample characterization: The identification of the crystalline phase was performed using X-ray diffraction (XRD) on a Rigaku D/Max-2550pc diffractometer equipped with Cu K α radiation ($\lambda = 1.5406$ Å), with a scan range of 20–80°. To study the electronic structure and understand the compositional behavior in the compounds, Xray photoelectron spectroscopic (XPS) measurement was performed with an ESCALAB 250 X-ray photoelectron spectrometer, using excitation energy of 1486.6 eV (Al K α). The exact percentage composition was confirmed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS INTREPID II XSP).The structure and morphology were characterized by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, FEI Tecnai G²F20microscope) and scanning transmission electron microscopy (STEM, Titan G2 80-200 w/ ChemiSTEM, FEI). HAADF imaging and EDS mapping were carried out with a probe-corrector, and this microscope was operated with an acceleration voltage of 200 kV. The selected area electron diffraction (SAED) patterns were carried out using a FEI Tecnai G²F20 microscope. The accelerating voltage was set to 200 kV.

In Situ Electrochemical Experiments: The in situ TEM experiments were carried out using a Nanofactory scanning tunneling microscopy (STM) holder in a JEOL-2100 TEM. Briefly, the electrochemical setup consisted of SnO_2 -Fe₂O₃-Li₂O composite as the working electrode, a layer of Li₂O solid electrolyte, and a bulk Li metal as the counter electrode. When the SnO_2 -Fe₂O₃-Li₂O composite electrode is biased (usually to -3 V in this experiment), Li ions flow through the solid electrolyte and are reduced working electrode. Delithiation was performed by using a bias of +3 V. These potentials are larger than those used in actual Li-ion batteries; these values are necessary to drive the Li⁺ ions through the solid electrolyte in these experiments.

Electrochemical test: All the films were deposited by PSE-CVD for 3 h on stainless steel and glass (used for XRD characterization) substrates that were maintained at 350 °C during deposition processes. The mass of the active layers were calculated by weighing the mass of the stainless steel substrates with a microbalance (accuracy of 0.002mg, Sartorius CPA26P, Germany) before and after the deposition directly. The mass loading is about 0.15-0.25 mg/cm², corresponding to 300-500 nm in thickness. The PSE-CVD-derived films on stainless steel were used as the electrodes of electrochemical cells (*vs*.Li/Li⁺) with 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (EC-DMC, 1:1 v/v) as the electrolyte. All the cells (CR2025 coin type) were assembled in an argonfilled glove box, where both moisture and oxygen levels were less than 1 ppm. They were charged and discharged galvanostatically at a range

of 0.005-3 V (*vs*.Li/Li⁺) on a battery test system (Neware BTS-5). Cyclic voltammetry (CV) tests were conducted on aCHI604D electrochemistry work station between 0.005 and 3.0 V (*vs*.Li/Li⁺) at a scan rate of 0.1 mV s⁻¹. All the electrochemical measurements were carried out at room temperature.



Scheme S1. Sequences (time) used for the deposition of (a) SnO_2 (or Fe_2O_3), (b) SnO_2 - Fe_2O_3 and SnO_2 - Li_2O , (c) SnO_2 - Fe_2O_3 - Li_2O (59.0:36.6:4.4 of weight ratio, the primary nanocomposites in the work), (d) SnO_2 - Fe_2O_3 - Li_2O (70.0:25.6:4.4 of weight ratio) and (e) SnO_2 - Fe_2O_3 - Li_2O (50.2:31.1:18.7 of weight ratio) electrodes.



Figure S1. SEM images of the as-deposited SnO₂ (a) and SnO₂-Fe₂O₃-Li₂O (b) films



Figure S2. (a) Wide survey XPS of the SnO_2 -Fe₂O₃-Li₂O. Detailed XPS of Sn 3d (b), Fe 2p (c) and Li 1s (d).



Figure S3. XRD patterns of SnO₂ and SnO₂-Fe₂O₃-Li₂O films.



Figure S4. (a) Low magnification TEM image of SnO_2 -Fe₂O₃-Li₂O. Inset: the corresponding selected area electron diffraction (SAED) patterns, indicating the amorphous nature of SnO_2 -Fe₂O₃-Li₂O. (b) and (c) High magnification TEM image of the blue rectangle areas of (a). (d) The SAED patterns corresponding to (c).



Figure S5. Element mapping images of SnO_2 -Fe₂O₃-Li₂O



Figure S6. TEM characterization of pure SnO₂: (a) Low magnification TEM image.(b) The SAED patterns corresponding to (a). High magnification TEM images of pure SnO₂ (c) and (d).



Figure S7. Galvanostatic discharge/charge profiles of pure SnO_2 at a constant current density of 200 mA g⁻¹.



Figure S8. Capacities vs. cycle number of the bare substrate steel.



Figure S9. Cycling performance of (a) Fe₂O₃, (b) SnO₂-Fe₂O₃ and (c) SnO₂-Li₂O.



Figure S10. Cycling performance of SnO₂-Fe₂O₃-Li₂O electrodes at virous current densities.



Figure S11. Cycling performance of (a) SnO_2 -Fe₂O₃-Li₂O(70.0:25.6:4.4 of weight ratio) and (b) SnO_2 -Fe₂O₃-Li₂O (50.2:31.1:18.7 of weight ratio) electrodes .



Figure S12. XPS of SnO_2 -Fe₂O₃-Li₂O that first discharge to 0.005 V and then charge to 1.5V:(a) Fe 2p and (b) Sn 3d.



Figure S13. *In-situ* TEM characterization of lithiation and delithiation processes: (a) 3rd cycle, (b) 4th cycle, (c) 5th cycle and 6th cycle.

Samples	Volumetric	Voltage	Current density	Cycle	Mass loading
	capacities	range (V)		numbers	(mg cm ⁻²)
	(mAh cm ⁻³)				/Thickness
SnO ₂ -Fe ₂ O ₃ -Li ₂ O	6034.5	0.005-3	200 mA/g	200	0.15-0.25
(This work)					/300-500 nm
SnO ₂ -Se ^[1]	4831	0.01-3	15 μAcm ⁻²	100	0.05/80 nm
$Ga_2Se_3^{[2]}$	712.4	0-3	$2 \mu \text{Acm}^{-2}(0.1\text{C})$	100	0.025/200 nm
ZnO-Se ^[3]	2110	0.01-3.5	$5\mu Acm^{-2}(0.1C)$	50	0.04/80 nm
Cu ₆ Sn ₅ -TiC-C ^[4]	~1200	0-2	100 mA g ⁻¹	70	-
SiC@Pb@C ^[5]	1586	0.005-1	100 mA g ⁻¹	600	-
InSe ^[6]	2275(2 rd	0.01-3	0.05mAcm ⁻² (50mA/g)	-	-
	cycle)				
MnO ^[7]	3484(2 rd	0.01-3	6.3µAcm ⁻² (0.125C)	-	0.04/132 nm
	cycle)				
carbon nanotubes ^[8]	1420	0-3	50 mA g ⁻¹	100	-
Zn-Al ₂ O ₃ -C ^[9]	1800	0-2	100 mA g ⁻¹	100	-
Fe ₃ O ₄ /SWNT ^[10]	2000	0.005-3	1C(872 mA g ⁻¹)	100	-
CoMnSb ^[11]	1930(1 st)	0.01-1.5	0.2 mA cm ⁻²	-	-
SnO ₂ ^[12]	<4000	0.01-1.5	0.05C	30	-/800 nm
Si ^[13]	2000	0.01-1	0.4 A/g(0.2C)	900	0.02-0.1/-
SnO ₂ /Graphene ^[14]	1482	0.01-2.5	100 mA g ⁻¹	200	1/6 µm
Co ₃ O ₄ ^[15]	5800	0.02-3	0.22C	70	0.023/40 nm
TCO ^[16]	2200	0.1-1.2	-	-	-
Zn-SnO ₂ ^[17]	1376	0-1.7	10µAcm ⁻²	50	-
Fe ₃ O ₄ /carbon ^[18]	252	0.005-3	390 mA g ⁻¹	100	1.5/-
Sn/SnO ₂ ^[19]	1200	0.005-2	1000 mA g ⁻¹	100	-
Co ₃ O ₄ ^[20]	2100	0-3	C/20	50	-/347 nm
Sn/C ^[21]	<2875.5	0.02-3	200 mA g ⁻¹	130	1/-
Si/graphene/UGF ^[22]	381	0.01-2.2	400 mA g ⁻¹	100	0.4/-
t-Si@G-NW ^[23]	1500	0.02-2	0.2C (840 mA g ⁻¹)	200	1/-
SiNP-PANi ^[24]	808.8	0.01-1	1 A g ⁻¹	1000	0.2-0.3/-
alginate-based	1520	0.01-1	140 mA g ⁻¹	-	-
nano-Si ^[25]					

Table S1. Comparison of volumetric capacities between references and present work

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