Evolution of rGO-SnS_2 Hybrid Nanoparticle Electrodes in Li-ion Batteries

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Supporting Information

Materials

Graphite was obtained from Asbury Carbons and was used without any pre-treatment. Electrochemical grade propylene carbonate, ethylene carbonate, diethyl carbonate, N-methyl-2-pyrrolidone, polyvinylidene fluoride, and Li metal foils were purchased from Sigma-Aldrich. Carbon powder (carbon super P) were purchased from Alfa Aesar. Polypropylene layers were purchased from Cell Guard.

GITT measurement and Li-ion diffusion (D) calculation:

GITT measurements with high diffusion sensitivity were performed on the rGO-SnS_2 cells applying current pulses (~100 mA/g) for 1 minute, followed by a relaxation time for 2 min. The apparent diffusion coefficient $\widetilde{D}_{\mathrm{Li}}$ was calculated by adopting the formula reported by Wen et al[1]. The change of the electrode potential was due to stoichiometric change $\frac{dE}{dx}$. The slopes of the E vs. $\sqrt{t}$, $\frac{dE}{d\sqrt{t}}$ were derived for every pulse. From these, the diffusion coefficient was calculated at potentials, E (at the end of the relaxation time).

$$\widetilde{D}_{\mathrm{Li}} = \frac{4}{\pi}\left(\frac{iV_{\mathrm{m}}}{z_{\mathrm{A}}FS}\right)^2\left(\frac{\frac{dE}{dx}}{\frac{dE}{d\sqrt{t}}}\right)^2$$

where, z_A is the charge number (=1 for lithium); S is the effective surface area; V_m is the molar volume.

Thermogravimetric (TGA) analysis of rGO-SnS_2 hybrid

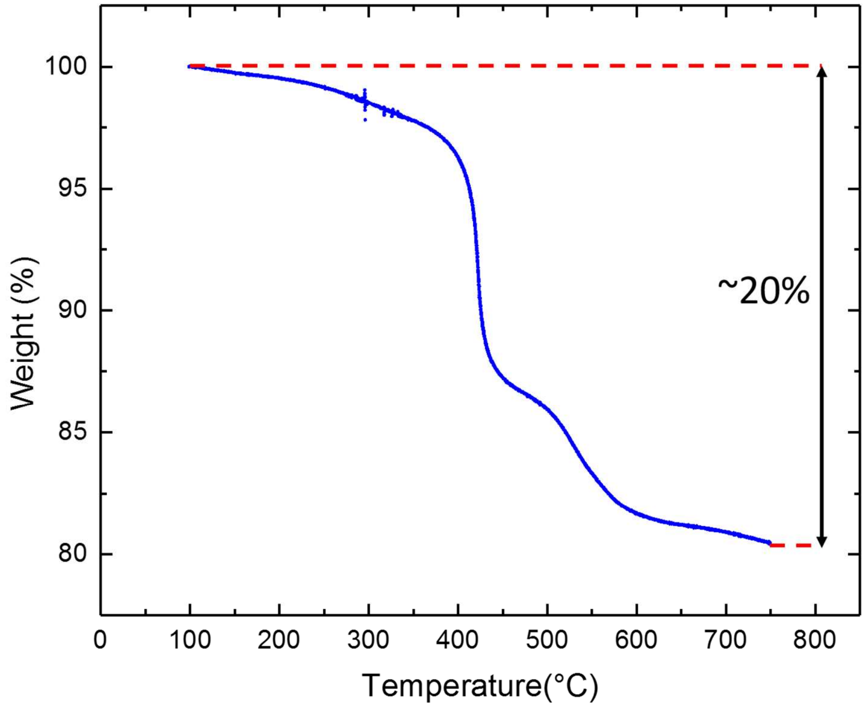

Figure S1 TGA analysis of rGO-SnS_2 hybrid material performed in air at a heating rate of 5 ºC/min. The initial weight loss (up to ~200 ºC) is due to removal of physisorbed and chemisorbed water. Subsequent weight loss is due to oxidation of SnS_2 to SnO_2 and the removal of rGO. The overall weight loss was found to be ~20%. The proportion of rGO in the hybrid is estimated to be ~5 wt%.

Post-mortem SEM characterisation of rGO-SnS_2 battery electrode

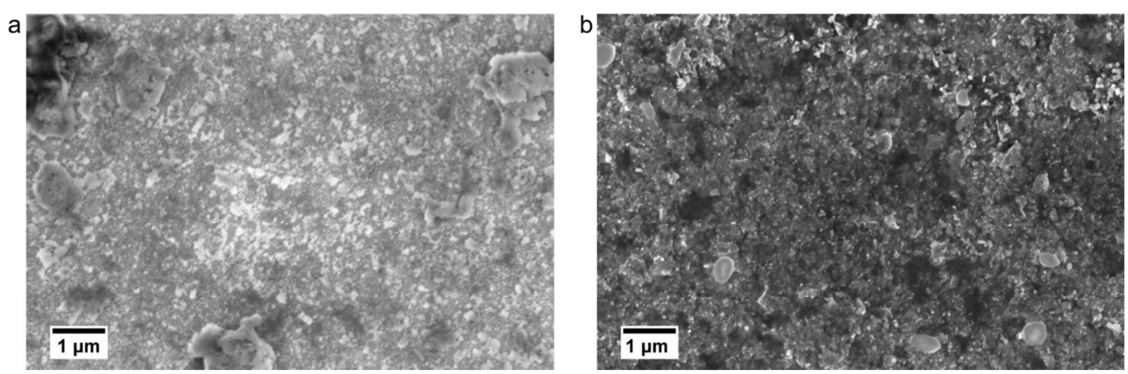

Figure S2 SEM images of cycled electrodes a) 50 cycles at 1000 mAg^{-1} ; b) 100 cycles at 100 mAg^{-1}. Agglomerates were observed on these cycled electrodes in de-lithiated state, indicating a rapid growth of amorphous phases originating from the electrode reactions, with larger agglomerates forming on electrodes that were cycled at a faster rate.

XRD and Raman data of rGO-SnS_2 from the initial cycles.

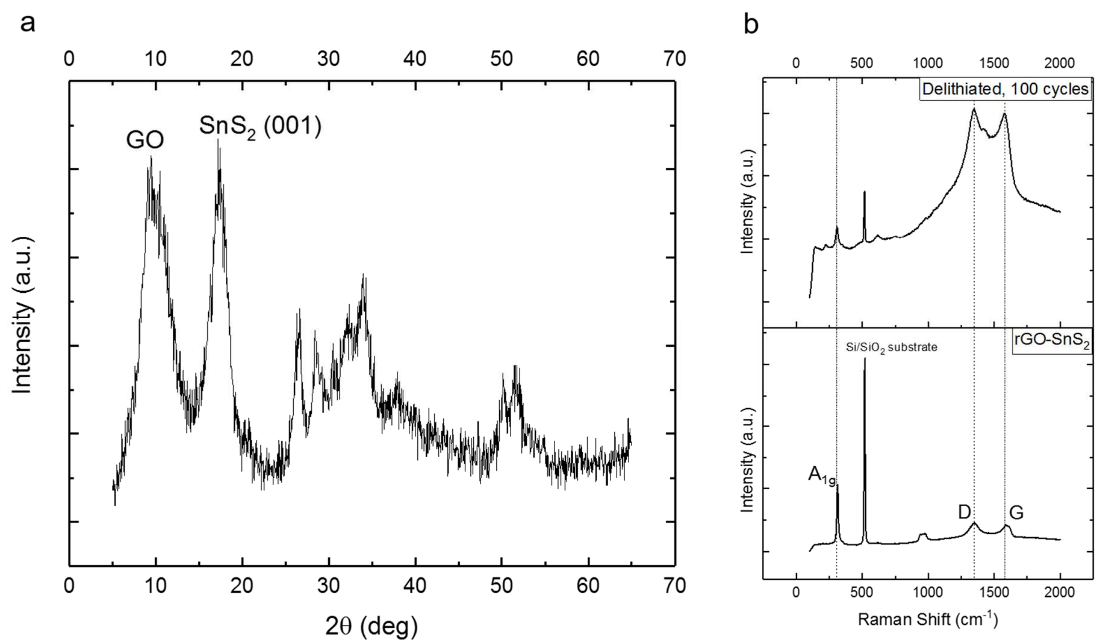

Figure S3 rGO-SnS_2 electrodes after 100 cycles at 100 mAh/g. a) XRD data from the battery electrode shows a peak associated with GO and a broadened and shifted SnS_2 peak b) Raman spectra shows the presence of the SnS_2 A_{1g} peak as well as the D and G peaks of graphene oxide.

The performance of the pure SnS_2 electrodes reported in the literature.

No	Electrode	1st cycle	2nd cycle	Cycling capacity	Current max	Reference
1	SnS_2 nanosheets in 100-200 nm agglomerates	~1600 mAh/g at 100 mA/g	~600 mAh/g at 100 mA/g	>~ 10 mAh/g after 40 cycle at 100mA/g	N/A	Chuanxin Zhai et al; *ACS Appl. Mater. Interfaces* 2011, 3, 4067-4074
2	SnS_2 nanoparticle ~80nm	~1580 mAh/g at 50 mA/g	~620 mAh/g at 50 mA/g	~ 293 mAh/g after 50 cycles at 50 mA/g	~100 mAh/g at 1C	Hyun Sik Kim et al; *Electrochimica Acta* 54 2009, 3606-3610
3	SnS_2 nanoparticles ≥ ~0.5 µm	1104.5 mAh/g	~400 mAh/g at 100 mA/g	~290 mAh/g after 50 cycles at 100 mA/g	~100 mAh/g at 800 mA/g	Dongsheng Guan et al; *Journal of Alloys and Compounds* 658 (2016) 190-197
4	SnS_2 powder	~1300 mAh/g at 200 mA/g	~600 mAh/g at 200 mA/g	~600 mAh/g at 200 mA/g after 5 cycles	~200 mAh/g at 1000 mA/g	Zhi Xiang Huang et al; *2D Mater.* 2 (2015) 024010
5	SnS_2 flower-like (≥ ~0.5 µm)	1540 mAh/g at 100mA/g	560 mAh/g at 100 mA/g	~417 mAh/ g after 50 cycles at 100 mA/g	N/A	Manoj K. Jana et al; *CrystEngComm*, 2014, 16, 3994-4000
6	SnS_2 nanoplates of a lateral size of 100-150 nm	1438 mA h/ g at 100 mA/g	579 mA h/ g at 100 mA/g	521 mA h/ g at 100 mA/g after 50 cycles	136-340 mAh/g at 3000 mA/g	Lingyan Wang et al; *Electrochimica Acta* 112 (2013) 439- 447
7	SnS_2 NPS	1600 mAh/g at 50 mA/g	~550 mAh/g at 50mA/g	~310 mAh/g at 50 mA/g after 30 cycles	~1.9 mAh/g at 1000 mA/g	Xin Jiang et al; *Journal of Power Sources* 237 (2013) 178-186
8	SnS_2 (1 micron) interconnected agglomerates	1602.9 mAh /g at 100 mA/g	850 mAh/g at 100 mA/g	282.2 mAh/ g at 100 mA/g after 50 cycles	~0 mAh/g at 1000 mA/g	Jianping Li et al; *Electrochimica Acta* 111 (2013) 862- 868
9	SnS_2 powder	600 mAh/g at 0.2 mA/cm^2	500mAh/g at 0.2 mA/cm^2	~120-160 mAh/g at 3.2 mA /cm^2 after 20 cycles	>~50-70 mAh/g at 25.6 mA/cm^2	Shuangyu Liu et al; *ACS Appl. Mater. Interfaces* 2013, 5, 1588–15
10	SnS2 nanorods	~1050 mAh/g at 160 mA/g	~850 mAh/g at 160 mA/g	~400 mAh/g at 160 mA/g after 50 cycle	-	Alok M. Tripathi et al; *RSC Adv.*, 2015, 5, 23671-23682

Table S1: Some pure SnS_2 battery electrodes performance reported in literature.

Reference:

(1) Wen, C. J.; Boukamp, B. A.; Huggins, R. A.; Weppner, W. Thermodynamic and Mass Transport Properties of "LiAl." *J. Electrochem. Soc.* **1979**, *126*, 2258.