Supplementary Information for:

Rational design of sulphur host materials for Li-S batteries: correlating lithium polysulphide adsorptivity and self-discharge capacity loss

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Experimental

Synthesis of polysulfide standard (Li_2S_4):

In an argon filled glove box, sulfur (99.5%, Sigma-Aldrich) was dissolved in Super-Hydride® solution (1.0 M lithium triethylborohydride in tetrahydrofuran, Sigma-Aldrich) to obtain a mole ratio of 2.75:1. The resulting solution was dried under vacuum, followed by a final wash with toluene and centrifugation to isolate the yellow precipitate, Li_2S_4.

Method / Method Validation

In an argon filled glovebox, standard solutions for calibration were prepared by weighing a known mass of Li_2S_4 into 16 mL of 1.0M lithium perchlorate ($LiClO_4$, battery grade, Sigma-Aldrich) in tetraethylene glycol dimethyl ether (TEGDME) solvent. The titration of polysulfides was carried out by simple electrochemical oxidation as explained in the main text of the paper.

Sample solutions were prepared by weighing a known mass of material and adding it into a known concentration of Li_2S_4 in TEGDME. The solution was allowed to stir for 18 hours before it was centrifuged, and the supernatant was collected. The supernatant was diluted to 16 mL using 1M $LiClO_4$ in TEGDME. The oxidation potential of the sample solutions was held at

3.0V and the capacity was determined based on the integrated current passed until it reached 0 mA.

A total of 5 calibration solutions and 9 different materials were analyzed. Carbon based materials included Super P, Vulcan and FW200. Oxide materials included anatase-TiO_2 (anatase, Alfa Aesar, 99%), mesoporous-TiO_2 (meso-TiO_2, mesotech), Ti_4O_7-C[1] (contains ~15 wt% carbon), electrolytic manganese dioxide (EMD, Kerr-McGee Chemical Corporation), MnO_2 nanosheets[2] and graphene oxide (GO, ACS Materials). The capacity achieved for all calibration solutions and sample solutions are plotted in **Figure S1**. All samples analyzed had a supernatant concentration falling within the calibration curve (R^2 = 0.996), and thus these measurements were considered valid. Utilizing the achieved capacity and the calibration curve, the concentration of polysulfides in the H-cell were determined, and from this, the adsorbed polysulfide mass was calculated.

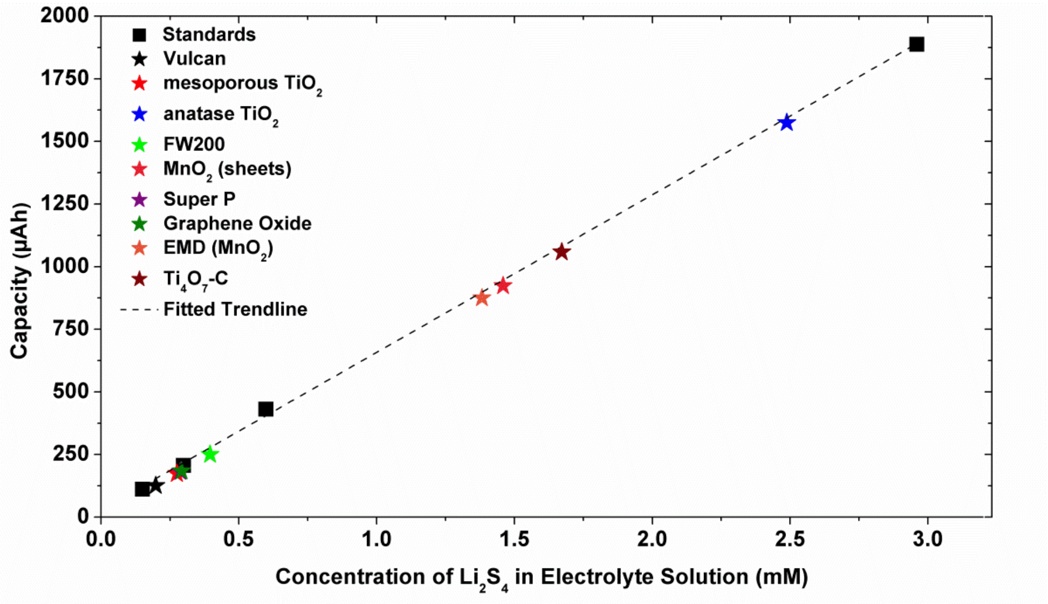

Figure S1: Calibration plot (squares) derived from the Coulombic capacity realized by oxidizing a known concentration of Li_2S_4 in TEGDME to sulfur. Experimental points (stars) were mapped on the curve for a variety of different materials using the same method, providing a measure of their polysulfide adsorptivity.

Surface Area Characterization

Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb-1 system at 77K. Surface areas were calculated using Brunauer–Emmett–Teller (BET) method. All samples were degassed at 100 °C on a vacuum line before measurement. The surface area results of each material are displayed in **Table S1**.

Table S1: Nitrogen sorption surface area measurements of all materials degassed at 100ºC

Sample	**Surface Area (m^2/g)**
Super P	67.70
Vulcan	212.1
FW200	357.7
Graphene Oxide	26.40
Non-porous anatase	54.04
Mesoporous Anatase	271.5
Ti_4O_7-C	291.2
MnO_2 sheet	103.9
EMD MnO_2	24.53

Preparation of sulfur composites:

Sulfur was infiltrated into all materials with the exception of graphene oxide using a melt infusion method at 155°C. Infiltration of sulfur into graphene oxide required an aqueous solution of 255 mg $Na_2S_2O_3$ and 278 μL concentrated HCl to be added to an aqueous dispersion of graphene oxide followed by filtration and drying at 60°C. **Figure S2** shows the thermogravimetric analysis of all sulfur composites (M/S) under a nitrogen atmosphere. All composites had similar sulfur loadings with a final content of 70 wt% sulfur.

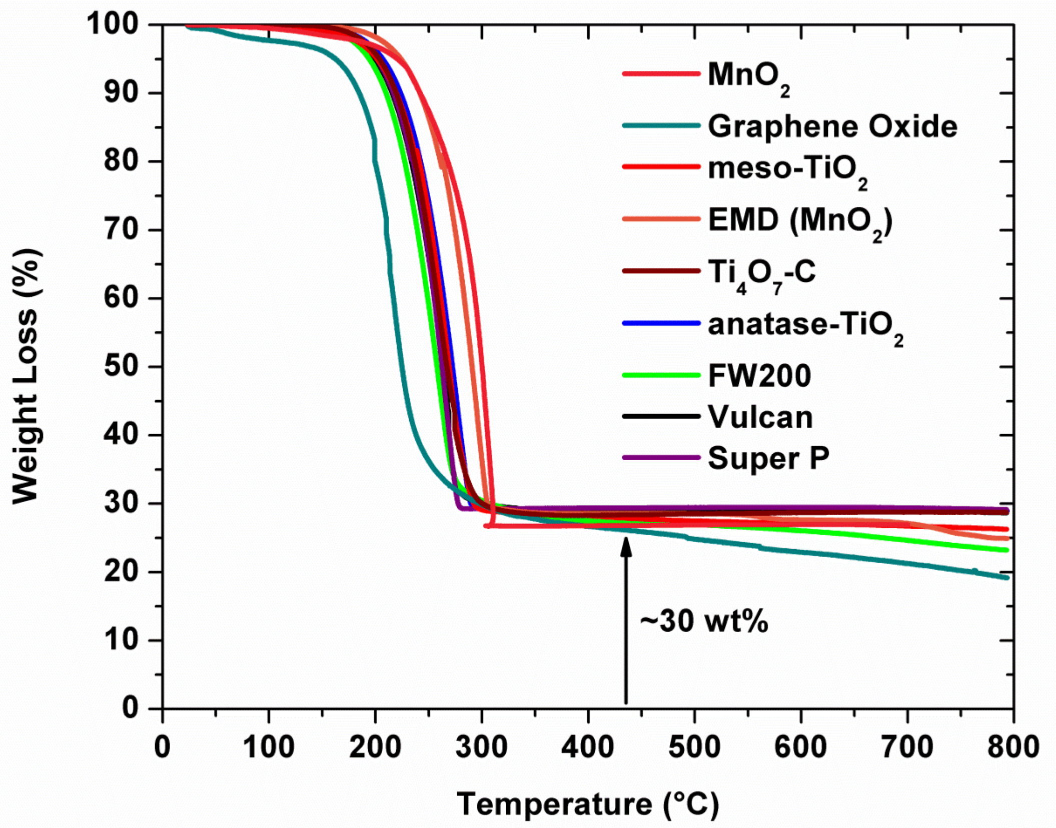

Figure S2: Thermogravimetric analysis of all sulfur composites studied

Electrochemical analysis:

Positive electrodes were prepared by mixing a uniform distribution of the sulfur composite, Super P carbon, and poly(vinylidene fluoride-co-hexafluoropropylene) in a 80:10:10 mass ratio in dimethylformamide (DMF) by sonication; drop-casting the slurry onto P50 carbon paper (AvCarb, Fuel Cell Earth) current collector; and drying the electrode at 60ºC overnight. The only exception was graphene oxide/sulfur material, where the components were ball milled to ensure no agglomeration of graphene oxide occurred. This mixture was stirred (not sonicated) in DMF prior to being drop-cast onto P50 carbon paper.

To minimize any electrochemical differences resulting from cathode composition, the sulfur loading for all electrodes was kept constant at 0.9 mg±1%/cm^2. Each positive electrode was tested in a 2325 type coin cell using 50 µL of an electrolyte comprised of 1M lithium bis(trifluoromethanesulfonyl)imide in a 1:1 v/v ratio of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) with 2 wt% $LiNO_3$. Lithium metal foil was used as the negative electrode, and was physically isolated using 2 sheets of Celgard 3501 separators. For long-term cycling, cells were cycled between 1.8 and 3.0V using a BT2000 Arbin battery cycler at room temperature at a discharge/charge rate of C/2 (1C = 1675 mA/g) which corresponds to a current density of 0.625 mA/cm^2. The results of the long-term cycling are summarized in **Table S2**.

Table S2: Capacity retention of galvanostatically cycled cells at C/2 rate

Material	Initial Discharge Capacity (mAh/g)	Capacity Retention from 1st Cycle (%)	Capacity Retention from 20th Cycle (%)
MnO_2 (sheets)	941.1	86.1	95.2
Graphene Oxide	1012.4	71.2	96.8
Mesoporous TiO_2	1095.6	82.1	99.3
EMD	1025.3	81.3	98.1
Ti_4O_7-C	1081.4	76.3	93.8
anatase	1161.9	71.6	90.2
FW200	1018.1	83.3	82.5
Vulcan	1141.9	67.7	84.6
Super P	1188.1	52.1	75.1

Self-discharge experiments were conducted for each material in 2325 type coin cells fabricated as described above. Galvanostatic cycling at a C/2 rate for 9 cycles allowed for stabilization and on the 10th discharge cycle, cells were stopped at 2.1V (before supersaturation) to rest for three days. After resting, cells resumed discharge to 1.8V, where normal galvanostatic cycling continued.

References

1 Q. Pang, D. Kundu, M. Cuisinier, and L.F. Nazar, *Nat. Commun.*, 2014, 5:4759.
2. X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss and L. F. Nazar**,** *Nat. Commun* in press, 2014.