Supplementary Information

A long-life, high-rate lithium/sulfur cell: a multi-faceted approach to enhancing cell performance

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Methods

Synthesis of CTAB-modified S-GO nanocomposites.

0.58g of sodium sulfide (Na₂S, anhydrous, Alfa Aesar) was dissolved in 25ml ultrapure water (Millipore) to form a Na₂S solution, then 0.72g elemental sulfur (S, sublimed, 99.9%, Mallinckrodt) was added to the Na₂S solution and stirred with a magnetic stirrer for 2 hours at room temperature. The color of the solution changed slowly from yellow to orange as the sulfur dissolved. After dissolution of the sulfur, a sodium polysulfide (Na_2S_x) solution was obtained. Commercial graphene oxide (GO) water dispersion (10mg/ml, ACS Material) was used for the deposition of S onto GO by a chemical precipitation method in an aqueous solution. 18ml of GO solution was taken by an auto pipette and diluted with ultrapure water (162ml) to form a GO suspension (180mg of GO in 180ml of ultrapure water). Different amounts (0~5mM) of cetyltrimethyl ammonium bromide (CTAB, CH₃(CH₂)₁₅N(Br)(CH₃)₃, Sigma Aldrich) were added to the GO suspension and stirred for 2 hours. Then, the Na_2S_x solution was added to the prepared GO-CTAB blended solution drop-wise using a glass pipette while stirring. Then, the Na_2S_x -GO-CTAB blended solution was stirred for 16 hours (overnight). Next, the as-prepared Na_2S_x -GO-CTAB blended solution was slowly added to 100ml of 2M formic acid (HCOOH, 88%, Aldrich) using a burette while stirring. The resulting mixture was stirred for 0.5 hours or 2 hours for elemental S to be precipitated onto the GO. Finally, the CTAB-modified S-GO composite was filtered and washed with acetone and ultrapure water several times to remove salts and impurities. Then, the CTAB-modified S-GO composite was dried at 50°C in a vacuum oven for 24 hours. The as-synthesized CTAB-modified S-GO composite was heat-treated in a tube furnace under flowing argon with a controlled flow rate of 100cc/s at 155°C for 12 hours. In order to control the S content, 0.5hours was also used.

Materials characterization.

A scanning electron microscope (SEM, Zeiss Gemini Ultra-55) was operated at an accelerating voltage of 3 kV to examine the morphology of the CTAB-modified S-GO nanocomposites. An energy dispersive X-ray spectrometer attached to the SEM (JEOL JSM-7500F) was used to conduct elemental analysis of sulfur and the distribution with an accelerating voltage of 10 kV. Thermogravimetric analysis (TGA, TA Instruments Q5000) was used to determine the weight of the S on the GO using a heating rate of 10°C/min in N₂. Fourier transform infrared spectroscopy (FT-IR, PerkinElmer Spectrum One) was used to examine the presence of CTAB on the S-GO surface. Raman spectroscopy (Horiba LabRAM ARAMIS) was used to investigate the interaction between CTAB and sulfur.

Cell assembly and electrochemical characterization.

The sulfur electrodes were fabricated by mixing the S-GO nanocomposite, carbon black (Super P) with a binder (either PVDF or SBR/CMC 1:1 by weight) at a weight ratio of 70:20:10 in N-methyl-2-pyrrolidone (NMP) solvent for PVDF or ethanol/water (1:1 by volume) solution for SBR/CMC to form a slurry using an ultrasonicator. The resulting slurry was uniformly spread via a doctor blade (Elcometer 3540 Bird Film Applicator) on pure aluminum foil. The solvent was allowed to evaporate at room temperature for 24 hours. The electrodes were then dried in a vacuum oven at 50°C for 48 hours to fully eliminate any solvent residue. The electrode was punched into circular pieces with a diameter of 12.7 mm for cell assembly. The average sulfur loading of the electrodes was ~0.8mg/cm².

For the electrolyte, 1 mol/kg lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, Sigma-Aldrich) in (n-methyl-(n-butyl) pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14TFSI, Sigma-Aldrich)/polyethylene glycol dimethyl ether (PEGDME, Sigma-Aldrich) mixture (1:1, by weight) was prepared and used for evaluation of the electrochemical performance of electrodes with different sulfur loadings, CTAB amounts, and heat-treatments. For the long-term cycling test and rate capability measurements, a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) was introduced to PYR14TFSI to form 1 M LiTFSI in PYR14TFSI/DOL/DME mixture (2:1:1 by volume). 0.1M or 0.5M LiNO₃ was used as an additive in the electrolyte.

CR2032-type coin cells were assembled by sandwiching two separators (Celgard 2400) between a lithium metal foil (99.98%, Cyprus Foote Mineral) and a sulfur electrode fabricated with the S-GO composite in a glove box filled with high-purity argon gas. Cyclic voltammetry was performed using a potentiostat (Biologic VSP) with a voltage range of 1.5 to 2.8V for 10 cycles at a constant scan rate of 0.01 mVs^{-1} . Galvanostatic discharge and charge testing of the coin cells was performed using a battery cycler (Maccor Series 4000) at different rates between 1.5 and 2.8V. The cell capacity was normalized both by the weight of sulfur and total electrode weight. Electrochemical impedance spectroscopy was performed with amplitude of 5mV in the 1 MHz to 0.1Hz frequency range on a Maccor battery cycler to monitor how the impedance changed during cycling. Before all electrochemical characterizations, the cells were held at open circuit at room temperature for 24 h. All electrochemical characterizations were performed inside a chamber (TestEquity TEC1) maintained at 30 °C.

Supplementary Discussion



Figure S1. Cycling performance of Li/S cells fabricated with S-GO composites of different sulfur content: 50 wt.% and 80 wt.% of sulfur in the S-GO composites. Cells were cycled at a constant current rate of 0.1C after two cycles at 0.02C. PVDF binder was used to fabricate composite S-GO cathodes. The capacity is normalized by the weight of sulfur only. The average sulfur loading of the electrodes is 0.8mg/cm². For the electrolyte, 1 mol/kg LiTFSI in PYR14TFSI/PEGDME mixture (1:1 by weight) was used.



Figure S2. FT-IR spectra of S-GO nanocomposites prepared (a) with 5mM CTAB, (b) 2.5mM CTAB, (c) 0.14mM CTAB and (d) without CTAB. The figures on the right side show an enlarged view of the FTIR spectra between 3200 and 2500 cm⁻¹ for the figures on the left side. The peaks at 2918 and 2848 cm⁻¹ can be attributed to two different C-H vibratioal bands of CTAB. Figure S2 shows that the S-GO surface was well modified with CTAB.



Figure S3. TGA curves of S-GO nanocomposites prepared with different amounts of CTAB before and after heat-treatment at 155° C for 12 h in Ar. The deposition time was 30 minutes for samples (a~c) and 2 hours for sample (d).



Figure S4. Cycling performance of Li/S cells fabricated with S-GO composites prepared with different amounts of CTAB added during the synthesis of S-GO nanocomposites: (a) CTAB ~ 5mM, (b) CTAB ~ 0.14mM, and (c) no CTAB. Cells were cycled at a constant current rate of 0.1C after two cycles at 0.02C. PVDF binder was used to fabricate the composite S cathodes. The capacity is normalized by the weight of sulfur only. For the electrolyte, 1 mol/kg LiTFSI in PYR14TFSI/PEGDME mixture (1:1 by weight) was used.



Figure S5. Cycling performance of Li/S cells fabricated with S-GO composites prepared with different heat-treatment time (12 hours and 0.5 hours) under Ar atmosphere at 155°C. Cells were cycled at a constant current rate of 0.1C after two cycles at 0.02C. PVDF binder was used to fabricate these composite S cathodes. The capacity is normalized by the weight of sulfur only. The average sulfur loading of the electrodes is 0.8mg/cm². For the electrolyte, 1 mol/kg LiTFSI in PYR14TFSI/PEGDME mixture (1:1 by weight) was used.



Figure S6. (a) SEM image, (b) a selected area for elemental mapping of (c) carbon and (d) sulfur by energy dispersive X-ray spectroscopy of S-GO nanocomposites with 80% sulfur loading.



Figure S7. FT-IR spectra of S-GO nanocomposites after 10 and 100 cycles. The peaks at 2918 and 2848 cm⁻¹ can be attributed to two different C-H vibratioal bands of CTAB. Figure S7 shows that CTAB remains intact with reduced peak intensities after cycling.



Figure S8. Electrochemical impedance spectra (EIS) collected on electrodes fabricated with PVDF and SBR/CMC binder after 100 cycles between 1.5 and 2.8V at rates of 1C and 0.5C for discharge and charge, respectively. The diameter of the semicircle represents the charge transfer resistance at interface. These spectra were measured at fully charged state.



Figure S9. Comparison of electrochemical performance up to 200 cycles for Li/S cells employing CTAB-modified S-GO nanocomposite electrodes with and without ionic liquid (PYR14TFSI) in 1M LiTFSI in DOL/DME (1/1 by volume) with 0.1M LiNO₃. (a) Cycling performance of CTAB-modified S-GO composite cathodes at rates of 1C and 0.5C for discharge and charge, respectively. (b) Coulombic efficiency of Li/S cells as a function of cycle number. The S-GO composite contained 80% S and elastomeric SBR/CMC binder was used.



Figure S10. Coulombic efficiency of Li/S cells as a function of cycle number. Coulombic efficiencies were 98.8%, 97.8% and 96.3% after 500, 1000, and 1500 cycles at rates of 1C and 0.5C for discharge and charge, respectively. SBR/CMC binder was used to fabricate these composite S-GO cathodes. The S-GO composite contained 80% S, and the electrode composition was 70% S-GO, 20% Super P, and 10% SBR/CMC. For the electrolyte, 1 M LiTFSI in PYR14TFSI/DOL/DME mixture (2:1:1 by volume) with 0.1M LiNO₃ was used.



Figure S11. Voltage profiles of CTAB-modified S-GO nanocomposite cathodes, cycled between 1.5 and 2.8V at a constant rate of 0.05C after (a) 200 cycles, (b) 400 cycles, (c) 650 cycles, and (4) 1000 cycles at 1C for discharging and 0.5C for charging. Constant voltage was applied after constant current charging until the current drops below 5% of the initial charging current. SBR/CMC binder was used to fabricate these composite S cathodes. The S-GO composite contained 80% S, and the electrode composition was 70% S-GO, 20% Super P, and 10% SBR/CMC. The capacity is normalized by the weight of sulfur only. The average sulfur loading of the electrodes is 0.8mg/cm². For the electrolyte, 1 M LiTFSI in PYR14TFSI/DOL/DME mixture (2:1:1 by volume) with 0.1M LiNO₃ was used.



Figure S12. Discharge voltage profiles of CTAB-modified S-GO nanocomposite cathodes, cycled between 1.5 and 2.8V at constant rates of 0.02C and 0.05C after 1500 cycles at the 1C rate for discharging and 0.5C rate for charging. SBR/CMC binder was used to fabricate the composite S cathodes. The S-GO composite contained 80% S, and the electrode composition was 70% S-GO, 20% Super P, and 10% SBR/CMC. The capacity is normalized by the weight of sulfur only. The average sulfur loading of the electrodes is 0.8mg/cm^2 . For the electrolyte, 1 M LiTFSI in PYR14TFSI/DOL/DME mixture (2:1:1 by volume) with 0.1M LiNO₃ was used.



Figure S13. Estimated cell-level specific energy plot. Cell specific energy curves are estimated using the weight of all components except the cell housing and shown as a function of the specific capacity and content of sulfur in the electrode. The data of this work is indicated by the solid stars. Details of the calculation are provided in Table S1.

Design Parameters for Calculations of Cell Specific Energy	
Cell part	Weight of Material for Li/S cell (mg/cm ²)
Cu Foil (5 microns thick)	4.5
Lithium Electrode (100% excess)	3.6
Electrolyte and separator (50 microns thick)	5
S Electrode (including binder/additives)	6
Al Foil (5 microns thick)	1.4
Total weight	20.5

Table S1. Data for estimation of the Li/S cell-level specific energy

Cell design parameters used to estimate the cell-level specific energy (including all components except cell-housing) are shown in Table S1. A sulfur electrode loading of 6 mg/cm² is assumed to calculate the cell specific energy curves shown in Figure 5. A 100% excess of lithium is assumed with respect to the theoretical amount required for the full conversion of S to Li₂S. For the electrolyte, two layers of separator (polypropylene, porosity 50%, density = 0.9 g/cm^3) and organic solvent (average density = 1.1 g/cm^3) are assumed.



Scheme S1. Molecular structure of cetyltrimethyl ammonium bromide (CTAB)