Electronic Supplementary Information

High-capacity Li$_2$S–graphene oxide composite cathodes with stable cycling performance

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Experimental Methods

Materials synthesis. Mildly-oxidized graphene oxide (GO) was synthesized using the modified Hummer’s method$^1$ (Fig. S1) and re-dispersed into anhydrous ethyl acetate. Commercial Li$_2$S particles was then added (Li$_2$S: GO = 75: 25 by weight), followed by ultrasonication for 10 min and stirring in an argon-filled glove box. The as-synthesized Li$_2$S–GO composite was collected by centrifugation and allowed to dry in the glove box.

Characterization. To prevent moisture contamination of Li$_2$S, special precautions were taken during characterization. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using a FEI XL30 Sirion SEM. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI 5000 VersaProbe. For SEM, EDX and XPS, the samples were first tightly sealed in foil/poly bags before being transferred into the chamber via an argon-filled glove bag. Raman spectra were obtained using a WITEC Raman spectrometer (531 nm excitation laser) after the samples were tightly sealed in a glass holder.
**Electrochemical measurements.** Due to the sensitivity of Li$_2$S to moisture, all the electrode preparation and cell assembly procedures were carried out in an argon-filled glove box with moisture and oxygen levels below 0.5 ppm. The Li$_2$S–GO composites were ground with conductive carbon black (Super P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70: 25: 5 using a mortar and pestle, followed by dispersion in N-methyl-2-pyrrolidinone (NMP) to form a slurry. After overnight stirring, the slurry was then coated onto aluminum foil (carbon-coated; Exopack) using doctor blade and dried at 60°C to form the working electrode. For comparison, pristine Li$_2$S cathodes were also prepared in the same way by mixing Li$_2$S with Super P and PVDF binder in a weight ratio 70: 25: 5. 2032-type coin cells were assembled using lithium foil as the counter electrode. The electrolyte used was a freshly-prepared solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1 M) in 1:1 v/v 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) containing LiNO$_3$ additive (1 wt%). Galvanostatic cycling was carried out using a 96-channel (Arbin Instruments) or a 8-channel (MTI Corporation) battery tester. The cathodes were first activated at C/20 (1C = 1,166 mA g$^{-1}$) by charging to a high cutoff voltage of 3.8 V vs. Li$^+/\text{Li}$ to overcome the initial potential barrier (Fig. S3), followed by discharge to 1.8 V. Galvanostatic cycling was then carried out from 1.8 - 2.6 V vs. Li$^+/\text{Li}$. The typical mass loading of Li$_2$S was ~1 mg cm$^{-2}$ and specific capacity values were calculated based on the mass of Li$_2$S.
**Electrolyte testing.** For analysis of sulfur content in the electrolyte, a sulfur-free lithium salt of LiClO₄ (1 M) in 1:1 v/v DME/DOL solution with LiNO₃ (1 wt%) was used as the electrolyte (25 μL in each cell). All other cell assembly procedures are the same as that described above. The cells were disassembled at various points during a discharge/charge cycle, after which the contents (cathode, anode and electrolyte-soaked separator) were washed with DOL solution. This polysulfide-containing solution was then oxidized with concentrated HNO₃ and diluted with deionized water for analysis of sulfur content using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Thermo Scientific ICAP 6300 Duo View Spectrometer).³

**References:**


Fig. S1 (a) SEM image and (b) X-ray diffraction (XRD) pattern of as-synthesized mildly-oxidized GO, showing the characteristic peaks of GO.\(^4\) XRD was performed using a PANalytical X’Pert Diffractometer using Cu K\( \alpha \) radiation.

Fig. S2 Low-magnification SEM image of the as-synthesized Li\(_2\)S–GO composites.
Table S1. Elemental composition of the Li$_2$S–GO composites determined using large-area EDX analysis, showing the measured at% of the various elements (except Li which cannot be measured by EDX). The wt% of Li was calculated from the at% of S based on the empirical formula Li$_2$S. From the results, we can determine the overall Li$_2$S content in the Li$_2$S–GO composites to be ~76 wt%. This is consistent with the relative amounts of Li$_2$S and GO added during the synthesis process (75: 25 by weight).

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<th>Li</th>
<th>S</th>
<th>C</th>
<th>O</th>
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<td>16.0</td>
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<tr>
<td>Composition</td>
<td>76.0 wt% Li$_2$S</td>
<td>24.0 wt% GO</td>
<td></td>
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Fig. S3 Typical activation charge profile of the Li$_2$S–GO composite cathodes. A high cutoff voltage of 3.8 V vs. Li$^+$/Li was used to overcome the initial potential barrier associated with micron-sized Li$_2$S particles as described in previous work.$^2$
**Fig. S4** Morphology of the Li$_2$S–GO composite cathodes after 150 cycles at 0.2C. The cell was disassembled in the discharged state after the voltage was maintained at 1.8 V vs. Li$^+$/Li for over 20 h.