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

Zhi Wei Seh,a Haotian Wang,b Nian Liu,c Guangyuan Zheng,d Weiyang Li,a Hongbin Yaoa and Yi Cui*a

With its high theoretical capacity of 1166 mA h g$^{-1}$, Li$_2$S is a promising prelithiated cathode material for applications such as vehicle electrification and grid energy storage. Herein, we demonstrate facile synthesis of Li$_2$S–graphene oxide composites for use as high-capacity and stable-cycling Li$_2$S cathodes. The wrapping of graphene oxide onto the surface of Li$_2$S through favorable lithium–oxygen interactions helps to minimize the dissolution of intermediate polysulfides into the electrolyte during cycling, which is a major reason for rapid capacity decay. Using the Li$_2$S–graphene oxide composites as a cathode material, we demonstrate a high discharge capacity of 782 mA h g$^{-1}$ of Li$_2$S (~1122 mA h g$^{-1}$ of S) with stable cycling performance over 150 charge–discharge cycles.

Introduction

There is currently a great deal of interest in the development of rechargeable batteries with high energy density and long cycle life for vehicle electrification and grid energy storage applications.1–6 Although rechargeable lithium-ion batteries are widely used today in consumer devices, their energy density is too low to render them viable for the above-mentioned applications.1–6 The major limiting factor in lithium-ion batteries today is the low theoretical capacity of conventional intercalation cathodes based on transition metal oxides and phosphates.1–6 On the other hand, Li$_2$S is a promising cathode material with a high theoretical capacity of 1166 mA h g$^{-1}$ (8Li$_2$S $\leftrightarrow$ S$_8$ + 16Li), which is ~4 times that of its transition metal oxide or phosphate counterparts.7–14 Unlike sulfur cathodes, Li$_2$S is in a fully-lithiated state and can be paired with lithium metal-free anodes (such as silicon and tin), thus obviating the safety concerns and dendrite formation associated with lithium metal.7–14 Moreover, the fact that Li$_2$S undergoes volumetric contraction in the initial delithiation process (instead of expansion as in the case of sulfur cathodes) leads to less structural damage to the entire electrode.12 Although sulfur cathodes are now under intensive study,15–20 the potential of using Li$_2$S as a starting cathode material has not received adequate attention. Similar to their sulfur counterparts, Li$_2$S cathodes are plagued with the problems of low electronic and ionic conductivity as well as the dissolution of intermediate lithium polysulfide species ([Li$_2$S$_n$]) into the electrolyte, leading to rapid capacity decay and low Coulombic efficiency.7–14 Wrapping of Li$_2$S with mesoporous carbon or carbon black has been the most common strategy used to constrain Li$_2$S$_n$ species and reduce their dissolution into the electrolyte, though the resulting cycling performance still leaves much room for improvement. This is probably because carbon, being largely non-polar in nature, does not interact favorably with the polar Li$_2$S and intermediate Li$_2$S$_n$ species involved in the cycling process.

Previous ab initio simulations have shown that oxygenated functional groups can bind strongly with Li$_2$S and Li$_2$S$_n$ species through Li–O interactions.12 Inspired by these theoretical simulations, herein we demonstrate experimentally the use of mildly-oxidized graphene oxide (GO) as an encapsulation material for Li$_2$S cathodes (Fig. 1a). The wrapping of GO onto the surface of Li$_2$S through favorable Li–O interactions helps to minimize the dissolution of intermediate Li$_2$S$_n$ species into the electrolyte during cycling, which is a major reason for rapid capacity decay. Using the Li$_2$S–GO composites as a cathode material, we demonstrate a high discharge capacity of 782 mA h g$^{-1}$ of Li$_2$S (~1122 mA h g$^{-1}$ of S) and stable cycling performance over 150 charge–discharge cycles.

Results and discussion

First, mildly-oxidized GO was synthesized using the modified Hummer’s method20,21 (ESI† Fig. S1) and then re-dispersed into anhydrous ethyl acetate. Micron-sized commercial Li$_2$S...
particles were then added (Li2S : GO = 75 : 25 by weight) followed by ultrasonication and stirring to allow wrapping of GO onto the surface of Li2S. Fig. 1b and c show scanning electron microscopy (SEM) images of the Li2S particles before and after GO coating. We can see that the surface of the Li2S particles changes to a more sheet-like appearance after GO coating (Fig. 1c; see also ESI† Fig. S2 for a low-magnification SEM image). Energy-dispersive X-ray spectroscopy (EDX) analysis in Fig. 1d shows the presence of S, C and O in the Li2S–GO composites (Li cannot be detected using EDX; the Si peak arises due to the use of a Si substrate). From the relative atomic fractions of the various elements, the Li2S content in the composite was determined to be ~76 wt% (ESI† Table S1), which is consistent with the relative amounts of Li2S and GO added during the synthesis (75 : 25 by weight). The surface coating of GO on the Li2S particles was further confirmed using Raman spectroscopy. We see that the Raman spectrum of pristine Li2S shows the characteristic T2g phonon mode of Li2S at 372 cm
1 corresponding to Li–O interaction in the Li2S–GO composites, together with their respective fitted peaks.

Fig. 2 (a) Schematic showing an example of Li–O interaction between Li2S and epoxide groups commonly found in GO. (b) XPS spectra of the Li 1s peak and (c) Raman spectra of the T2g phonon mode of Li2S in pristine Li2S and Li2S–GO composites.
Li$_2$S–GO composites. This can be explained by the strongly-electronegative O atoms in GO interacting with Li in Li$_2$S, causing the electron density along the Li–S bonds in Li$_2$S to be diminished and the bonds to be weakened, as evidenced by Raman spectroscopy.

It is well-known that dissolution of intermediate Li$_2$S$_n$ species into the electrolyte is a major reason for rapid capacity decay in Li$_2$S cathodes. Previous \textit{ab initio} simulations have shown that oxygenated functional groups (such as those found on GO) can bind strongly with Li$_2$S$_n$ species as well, which would enable GO to constrain these polysulfide species during cycling. To verify this, working electrodes were prepared by mixing the Li$_2$S–GO composites with carbon black and binder (70 : 25 : 5 by weight) in N-methyl-2-pyrrolidinone to form a

![Fig. 3](image)

**(a)** Typical discharge and charge voltage profile showing various depths of discharge and states of charge (points 1 to 10) and (b) the corresponding percentage of sulfur measured in the electrolyte relative to the total sulfur mass on the electrode at these various points for Li$_2$S–GO and pristine Li$_2$S cathodes. Specific capacity values were calculated based on the mass of Li$_2$S.

![Fig. 4](image)

**(a)** Specific capacity and Coulombic efficiency of Li$_2$S–GO composite cathodes over 150 cycles at 0.2 C. (b) Capacity retention of Li$_2$S–GO composite cathodes cycled at 0.2 C in comparison with pristine Li$_2$S cathodes. (c) Specific capacity and (d) voltage profiles of Li$_2$S–GO composite cathodes cycled at various C-rates from 0.2 C to 2 C. Specific capacity values were calculated based on the mass of Li$_2$S.
Published on 09 December 2013. Downloaded by Stanford University on 10/02/2014 02:52:11.

To further evaluate their electrochemical performance, the Li$_2$S–GO composite and pristine Li$_2$S cathodes were cycled galvanostatically from 1.8−2.6 V vs. Li$^+$/Li. Specific capacity values were calculated based on the mass of Li$_2$S. From Fig. 4a, we see that the Li$_2$S–GO composite cathodes showed stable cycling at 0.2 C with a high initial capacity of 782 mA h g$^{-1}$ of Li$_2$S (theoretical capacity 1166 mA h g$^{-1}$). The capacity retentions achieved at the end of 50, 100 and 150 cycles were 92%, 90% and 88% respectively, relative to the initial cycle (Fig. 4b). The average Coulombic efficiency over the 150 cycles was calculated to be 97% (Fig. 4a). In comparison, pristine Li$_2$S cathodes exhibited greater capacity decay under identical testing conditions (Fig. 4b). The capacity retention of the pristine Li$_2$S cathodes was only 62% after 100 cycles (compared to 90% for Li$_2$S–GO composites), indicating a greater degree of polysulfide dissolution into the electrolyte in the former case. The stable cycling performance of the Li$_2$S–GO composite provides further evidence for the role of GO wrapping in constraining Li$_2$S$_n$ species during the cycling process.

Next, the Li$_2$S–GO composite cathodes were cycled at different C-rates to evaluate their rate capability and electrode kinetics (Fig. 4c and d). When the C-rate was increased successively from 0.2 C to 0.5 C to 1 C, the cells delivered high stabilized capacities of 695, 680 and 640 mA h g$^{-1}$ of Li$_2$S respectively (Fig. 4c). The capacities achieved at 0.5 C and 1 C correspond to 98% and 92% of the capacity that was attained at 0.2 C, indicating good reaction kinetics in the cathodes. Even at a C-rate of 2 C, a reversible capacity of 510 mA h g$^{-1}$ of Li$_2$S could be attained. When the C-rate was switched abruptly from 2 C back to 0.2 C again, the original capacity was mostly recovered (Fig. 4c), indicating the robustness and stability of the cathode material. The morphology of the Li$_2$S–GO composite cathodes was also examined after 150 cycles at 0.2 C. At the end of 150 cycles, the voltage was maintained at 1.8 V vs. Li$^+$/Li for over 20 h and the cell was disassembled in the discharged state. We see that the surface of the Li$_2$S particles retain their sheet-like appearance after cycling (ESI† Fig. S4), which indicates that the GO wrapping is intact and effective in constraining intermediate polysulfides to reduce their dissolution into the electrolyte during cycling. As a result, the solid Li$_2$S formed at the end of discharge does not precipitate randomly and irregularly all over the electrode and the original morphology is largely preserved. Finally, we note that during the cycling process, when Li$_2$S is converted to S$_8$ at the fully-charged state, the strong C−S and O−S interactions between S$_8$ and GO will help to immobilize the S$_8$ species and stabilize the electrode, contributing to the stable cycling performance as well.\(^{21}\)

### Conclusion

We have demonstrated the facile synthesis of high-performance Li$_2$S–GO composite cathodes in which the wrapping of GO onto the surface of Li$_2$S through favorable Li−O interactions helps to constrain intermediate Li$_2$S$_n$ species during cycling, hence resulting in stable cycling performance. Further work is currently ongoing to pair these stable-cycling Li$_2$S–GO composite cathodes with lithium metal-free anodes (such as silicon or tin) to achieve a full-cell configuration. This work provides insight on the use of suitable encapsulation materials that bind strongly with Li$_2$S cathodes, for the future development of high-capacity and long-lasting rechargeable batteries.

### Acknowledgements

This work was supported as part of the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the US Department of Energy, Office of Science, Basic Energy Sciences. Z.W.S. and G.Z. acknowledge the support of an A*STAR National Science Scholarship.

### References

21 L. Ji, M. Rao, H. Zheng, L. Zhang, Y. Li, W. Duan, J. Guo, B. Zhang, X. Qin, G. R. Li and X. P. Gao,