

Solution Ionic Strength Engineering as a Generic Strategy to Coat Graphene Oxide (GO) on Various Functional Particles and Its Application in High-Performance Lithium-Sulfur (Li-S) Batteries

Jiepeng Rong [†], Mingyuan Ge [†], Xin Fang [†], and Chongwu Zhou ^{‡}*

[†]The Mork Family Department of Chemical Engineering and Materials Science and [‡]Ming Hsieh Department Electrical Engineering, University of Southern California, Los Angeles, California 90089, United States

Graphene oxide (GO) synthesis

GO used in this study was prepared following a reported method.¹ Briefly, a mixture of concentrated H₂SO₄/H₃PO₄ (360:40 mL) was added to a mixture of graphite (3.0 g) and KMnO₄ (18.0 g). The reaction was kept at 50 °C for 12 h, then cooled to room temperature, and poured into ice (~400 mL) with 3 mL 30% H₂O₂. The product is centrifuged at 4000 rpm for 1 hour, and

the supernatant was decanted away. The GO in the supernatant was washed with water, 30% HCl, and water again using centrifuge.

Sulfur particle synthesis

Sulfur particles in two different sizes used in this study were prepared in different ways. Sulfur particles in the diameters between 1 μm and 10 μm (as shown in Figure 2a,b) were prepared by hand-grounding commercial sulfur powder with pestle and mortar for 5 minutes.

Sulfur particles with smaller diameter (Diameter \sim 500 nm) were synthesized by adding concentrated HCl (0.8 mL, 10 M) to an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL, 0.04 M) with the presence of Polyvinylpyrrolidone (PVP, $M_w \sim 40,000$, 0.02 wt%). After reaction for 2 hours, the sulfur particles were washed with ethanol and water, and dispersed into to an aqueous solution.

Ball-milled silicon particle synthesis

Ball-milled silicon particles were obtained by ball-milling metallurgical silicon powder. The ball-mill (MTI Inc.) was typically operated at a grinding speed of 1200 rpm for 5 hours. The ground powder has a dark-brown color.

Sulfur/GO core-shell particle synthesis

Sulfur/GO core-shell particles were synthesized in different ionic aqueous solutions (solution #4 to #9). GO and sulfur particles were first dispersed in the same kind of solution, and then sonicated for 10 minutes, respectively. The two suspensions were mixed together and stirred for 1 hour. The precipitate was collected, and washed with water and ethanol using centrifuge. The product was then dried at 60 $^{\circ}\text{C}$ in air for 12 hours, and denoted as sulfur/GO core-shell particles.

Sulfur/GO core-shell particles synthesized using different ionic solutions showed no obvious difference in morphology under SEM. To minimize the effect of solute compounds on the composition of sulfur/GO core-shell particles, SEM characterization (Figure 2), spectroscopic characterizations (Figure 3) and battery measurements (Figure 4) were all carried out on sulfur/GO core-shell particles prepared using 1 M HCl solution as dispersing medium (solution #4 in Figure 1).

Electrochemical measurements

To prepare the working electrodes, various sulfur-based materials were mixed with carbon black (Super P) and polyvinylidene fluoride binder (8:1:1 by weight) in N-methyl-2-pyrrolidinone to form a slurry. So the weight percentage of sulfur to the total mass of the electrode is about 40% without considering the mass of aluminum substrate. The slurry was then coated onto aluminum foil using a doctor blade and dried at 60 °C for 12 hours to form the working electrodes. 2032-type coin cells were assembled in an argon-filled glovebox using lithium metal as counter electrode. The electrolyte used was lithium bis(trifluoromethanesulfonyl)imide (1 M) in 1:1 v/v 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) containing 1 wt% LiNO₃. Cyclic voltammetry and galvanostatic cycling were then carried out from 1.9 V- 2.6 V versus Li⁺/Li⁰.

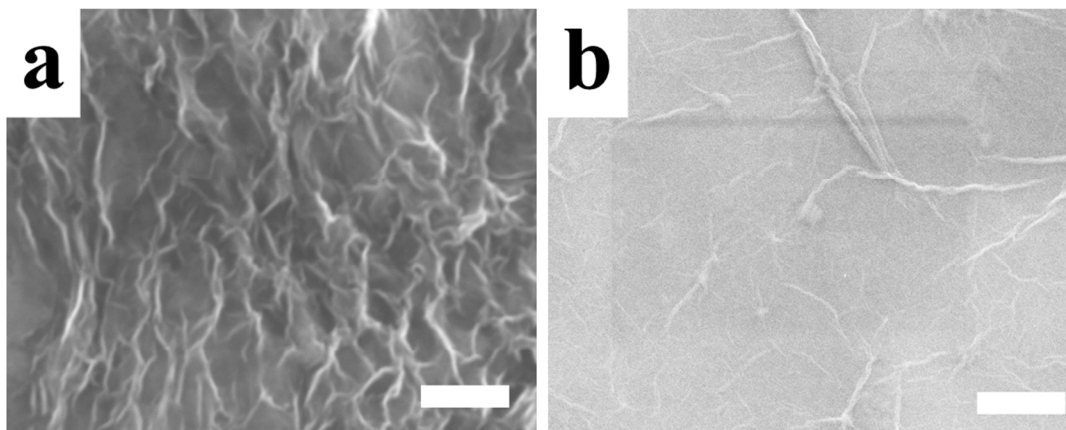


Figure S-1. SEM images of GO dried directly from (a) 1 M HCl solution, and (b) 1 M NH₃•H₂O solution. Both scale bars correspond to 1 μm.

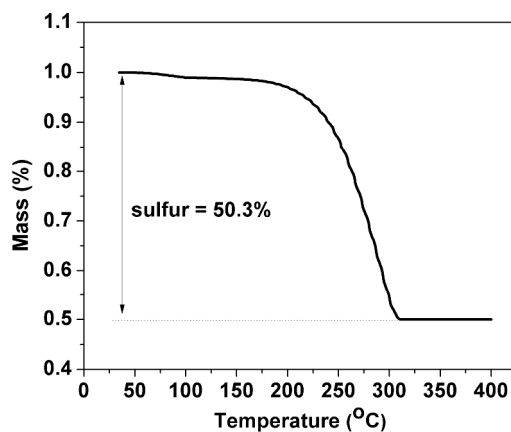


Figure S-2. Thermal gravimetric analysis (TGA) analysis curve of sulfur/GO core-shell particles recorded in the range of 35 - 400 °C at a heating rate of 1 °C/min, showing sulfur : GO ~ 1:1 by weight.

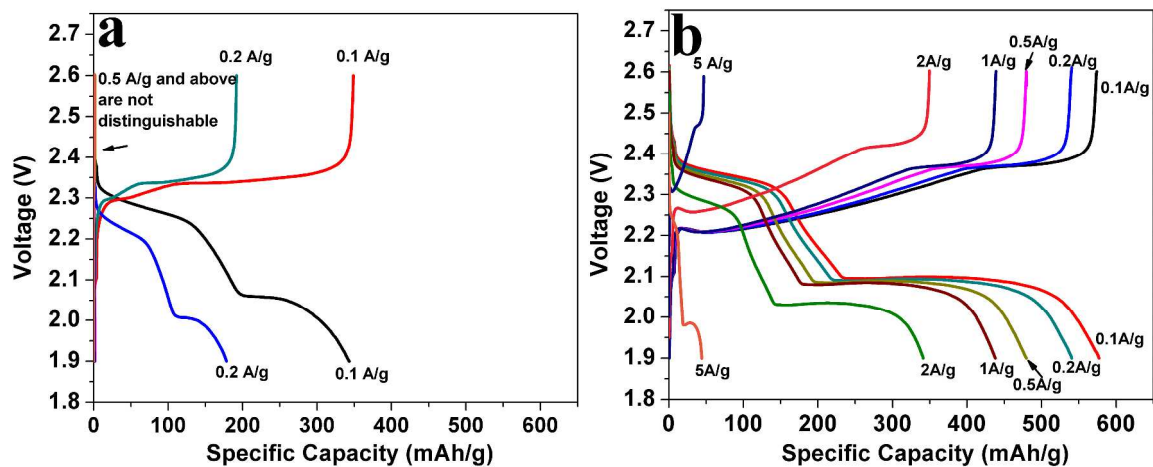


Figure S-3. Voltage profiles at different current rates of sulfur (a) and sulfur/GO (b).

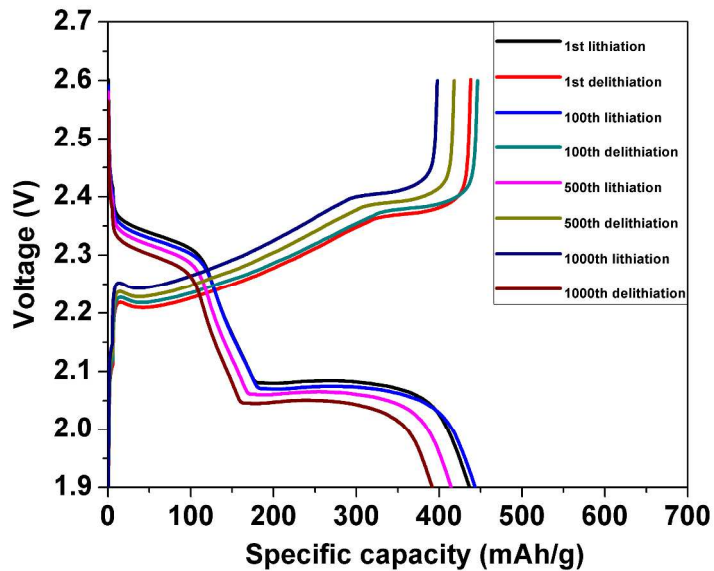


Figure S-4. Voltage profile of sulfur/GO core-shell at 1 A/g of the 1st, 100th, 500th, and 1000th cycle.

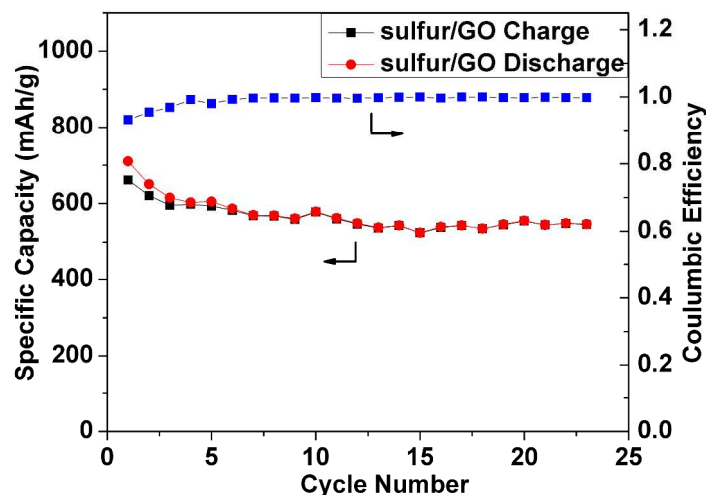


Figure S-5. Galvanic charge-discharge performance and Coulombic efficiency of sulfur/GO at 50 mA/g for 23 cycles.

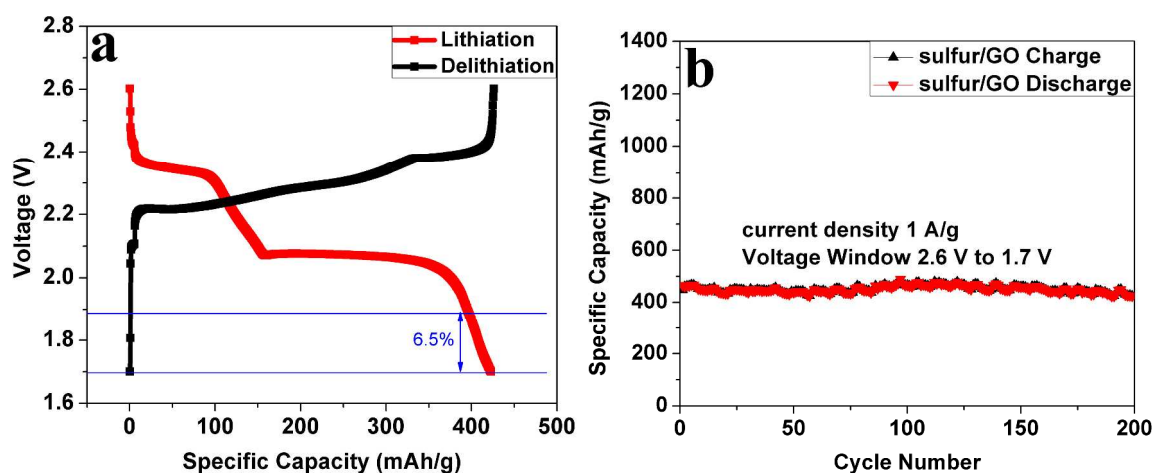


Figure S-6. (a) Voltage profile between 2.6 V and 1.7 V of sulfur/GO core-shell particles at 1 A/g current density. The results show specific capacity contribution from 1.9V-1.7V in discharge is only 6.5%. In this paper, we used 2.6 V-1.9 V as voltage window for all electrochemical measurements unless otherwise specified. (b) Galvanic charge-discharge performance of sulfur/GO at 1 A/g between 2.6 V to 1.7 V. Specific capacity calculated based on the total weight of sulfur/GO.

Self-discharge Test

We cycled a battery using sulfur/GO core-shell particles as cathode for 9 cycles. Then the battery was rest for one week, and open circuit voltage was continuously measured. After

that, the battery was continued for charge/discharge test. Based on the results, the specific capacity in the 9th discharge is 429 mAh/g, and that in the 10th discharge is 382 mAh/g. The self-discharged capacity in one week is calculated to be $(429-382)/429=11\%$. Open circuit voltage after one week is decreased from 2.6 V to 2.35 V.

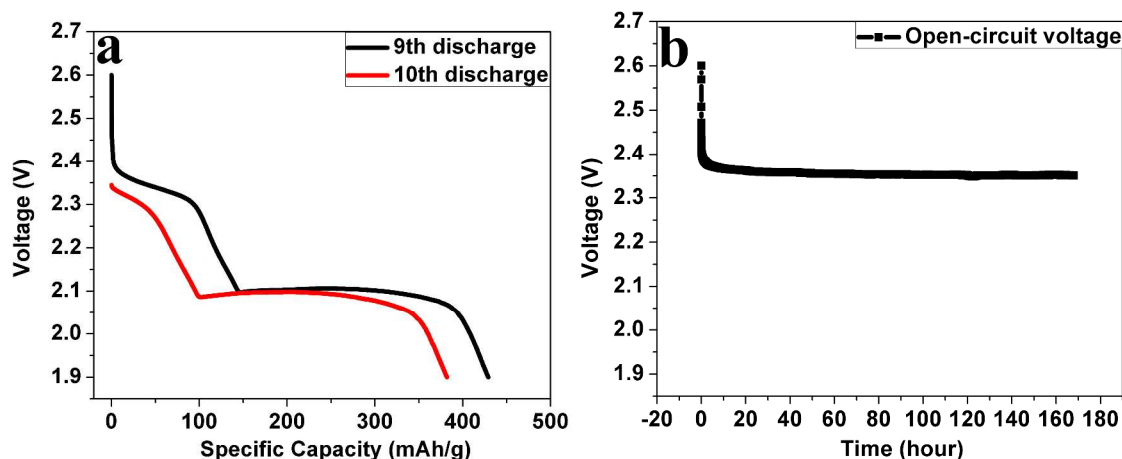


Figure S-7. (a) Voltage profile of sulfur/GO core-shell particles as Li-S battery cathode materials in the 9th and 10th discharge. (b) Open circuit voltage measured over one week between the 9th and 10th cycle.

REFERENCES

- (1) Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z. Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. *ACS Nano* **2010**, *4*, 4806.