## Electronic Supplementary information

# A Graphene-like Metallic Cathode Host For Long-life and Highloading Lithium-Sulfur Batteries

Quan Pang, Dipan Kundu, and Linda F. Nazar\*

Department of Chemistry and the Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Ave W, Waterloo, Ontario N2L 3G1, Canada. Email: <u>Ifnazar@uwaterloo.ca</u>

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# Experimental

### Synthesis of graphene-like Co<sub>9</sub>S<sub>8</sub> and the Co<sub>9</sub>S<sub>8</sub> /S75 composite

Microwave solvothermal methods have been used recently to prepare cathode materials such as LiFePO<sub>4</sub> and oxides for lithium ion batteries.<sup>1</sup> In this work we have used a rapid and scalable microwave solvothermal method for the synthesis of high surface area  $Co_9S_8$ . In a typical procedure, 3- 4 mmol cobalt chloride (CoCl<sub>2</sub>.6H<sub>2</sub>O) and an equivalent amount of thioacetamide (C<sub>2</sub>H<sub>5</sub>NS) were dissolved in 50 ml of a water-triethylenetetramine mixture (2:3 v/v) and transferred to a Teflon<sup>TM</sup> vessel. The sealed vessels were fitted to a rotor equipped with temperature and pressure sensors. The rotor containing the vessels was then placed in a rotating platform for uniform heating in an Anton Parr microwave synthesis system (Synthos 3000). The system temperature was raised to 160°C in 10 minutes and maintained for 90 minutes. The preset temperature was maintained automatically by continuous adjustment of the applied power (limited to 800 W). The as-synthesized product was thoroughly washed with copious amounts of water, followed by acetone, and dried at 60°C for 24 h.

The  $\text{Co}_9\text{S}_8$  /S75 sulfur composite was prepared via a simple melt-diffusion method. The  $\text{Co}_9\text{S}_8$  powder was mixed with sulfur in the desired ratio and heated under ambient atmosphere at 155 °C for 12 hours. The VC/S75 composite was prepared by the same route.

#### Synthesis of $Li_2S_4$ and $Li_2S_4$ /Co<sub>9</sub>S<sub>8</sub> composites for the interaction study

 $Li_2S_4$  was synthesized via the reaction of  $S_8$  with lithium superhydride (LiEt<sub>3</sub>BH) in the desired ratio in anhydrous tetrahydrofuran (THF) at room temperature for 1 h inside an argon glovebox. The resulting solid was washed with toluene and vacuum dried. To prepare the  $Li_2S_4/Co_9S_8$  for XPS studies, the  $Co_9S_8$  powder (20 mg) was added to a  $Li_2S_4$  solution (0.8 mg ml<sup>-1</sup>) in 1,2-dimethoxyethane, which was stirred for 6 hours, and then centrifuged. The solid was recovered and vacuum dried. All procedures were carried out in the glovebox.

#### Polysulfide adsorptivity measurements

Polysulfide adsorptivity was evaluated by electrochemical titration, which determines the amount of residual LiPS in solution after contact with the respective host cathode materials as detailed in a previous report.<sup>2</sup> Sample solutions were prepared by stirring a known mass of in a known concentration of  $Li_2S_4$  in tetraethylene glycol dimethyl ether (TEGDME). The mixtures were stirred overnight and after centrifugation, and the supernatant was collected and subjected to a titration wherein the polysulfide content was determined by electrochemical oxidation. The remaining polysulfide in solution was determined by extrapolation from a calibration curve using standard materials (see details in Ref. 2). All procedures were performed in an argon-filled glovebox.

#### **Electrochemistry measurements**

Electrodes with >1.5 mg cm<sup>-2</sup> sulfur loading were prepared by mixing sulfur composites with Super P and PVDF binder in dimethylformamide in a weight ratio of 8: 1: 1. Super P carbon was utilized only to aid in electrolyte wetting of the electrode. For the preparation of thick electrodes with high loading, sulfur composites with Super P, graphene (ACS Materials), styrene butadiene rubber aqueous binder, and carboxymethyl cellulose binder were dispersed with a weight ratio of 80: 6: 4: 3: 7 in a mixture solvent of deionized water and dimethylformamide (2:1 v/v). The slurry was doctor-blade coated onto carbon paper (AvCarb P50) to prepare the cathodes. The electrodes were dried at 60 °C overnight. Coin cells 2325 were assembled with a lithium foil anode and an electrolyte comprising 1 M bis(trifluoromethanesulfonyl)imide lithium (LiTFSI) and 2 wt% of LiNO<sub>3</sub> in a mixture of 1,2-dimethoxyethane and 1,3-dioxolane (v/v = 1:1) inside the glovebox. The cells were operated in a voltage window of 1.8-3.0 V using a BT2000 battery cycler (Arbin Instruments). A slightly larger voltage window was used for higher-rate studies (1.7-3 V and 1.6-3 V for 1C and 2C rates, respectively).

#### Materials characterization

Powder X-ray diffraction was performed on a Bruker D8-Advance powder diffractometer equipped with a Vantec-1 detector, using Cu-K $\alpha$  radiation ( $\lambda$ = 1.5405Å) in the range from 5° to  $80^{\circ}$  (20) at a step size of 0.025° using Bragg-Brentano geometry. The morphology of the sample was examined by field-emission SEM (FE-SEM, LEO 1530) and HRTEM (FEI Titan 80-300). For TEM, samples were dispersed in isopropanol by ultrasonication and loaded onto a carbon coated copper grid. Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb-1 system at 77K. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method and the pore size distribution was derived from the desorption branch of isotherm using the Barrett-Joyner-Halenda (BJH) model. TGA analysis was conducted at a heating rate of 10 °C/min under a N<sub>2</sub> flow, using a TA Instruments SDT Q600. XPS analysis was performed on Thermo ESCALAB 250, where a monochromatic or non-monochromatic Al K $\alpha$  source was used for conductive and non-conductive materials, respectively. All spectra were fitted with Gaussian-Lorentzian functions and a Shirley-type background. For S 2p spectra with  $2p_{3/2}$  and  $2p_{1/2}$  doublets, constraints of 1.2 eV splitting, peak area ratio of 2:1 and equal full width half maximum were applied. The  $2p_{3/2}$  and  $2p_{1/2}$  doublets in Co 2p spectra maintain a ~15 eV difference and thus only the  $2p_{3/2}$  component is fitted. The binding energy values were all calibrated using the C 1s peak at 284.8 eV.

#### **Computational methods**

First-principle calculations were performed using the plane wave-based VASP code. Projector augmented wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (CGA) were applied to describe electron-ion interactions and the electronic exchange correlation effect.<sup>3,4</sup> Spin-polarized calculation was employed. A cut-off energy of 400 eV was used for the plane wave basis set to ensure convergence. Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S<sub>4</sub> were employed as the representative lithium polysulfides. A four-layer slab model with the two bottom layers frozen was applied to model the three Co<sub>9</sub>S<sub>8</sub> surfaces. A two-layer  $6\times 6$  slab with the bottom layer frozen was use for graphite, so that Co<sub>9</sub>S<sub>8</sub> and carbon were close in supercell volume. A vacuum layer of 20 Å was used in the vertical direction to avoid the interaction between the layer and its images. The conjugate-gradient algorithm was used for ionic relaxation. The binding energy (E<sub>b</sub>) of Li<sub>2</sub>S, Li<sub>2</sub>S<sub>2</sub>, or Li<sub>2</sub>S<sub>4</sub> on the substrates is defined as:

$$E_b = (E_{sub} + E_{ps} - E_{sub+ps})$$

where  $E_{sub}$ ,  $E_{ps}$  and  $E_{sub+ps}$  represent the ground-state energies of the substrate, polysulfide and substrate-polysulfide. A larger positive value means greater binding ability.

#### Calculation of volumetric energy density

The volumetric energy density of the cathode side can be estimated and compared with a hypothetical graphene oxide based electrode. The assumption was made that both have the same sulfur loading (4.5 mg cm<sup>-2</sup>) and areal specific capacity (2.7 mA h cm<sup>-2</sup>) at a rate of C/5 (1.51 mA cm<sup>-2</sup>) as in our study, with a sulfur fraction of 75 wt% in the composite. The volumetric density Ev can be calculated as:

$$Ev = \frac{Q * U}{V} = \frac{Q * U}{A * d}$$

where Q is the capacity obtained based on the cathode only, U is the average voltage of the cell (2.1 V here), and d is the thickness of the cathode materials, A is the electrode area. The components included are sulfur, sulfur host materials, carbon additives. The volume of polymeric binder is disregarded in this back-of-the-envelope comparison. Therefore,

$$V = V_S + V_H + V_C = A * (d_S + d_H + d_C)$$

where  $V_{s}$ ,  $V_{H}$ ,  $V_{c}$  is the volume of sulfur, sulfur host and carbon additive, respectively. The density of sulfur, Co<sub>9</sub>S<sub>8</sub>, graphene oxide, and Super P is estimated at 2.07, 5.35 (crystallographic densities), 0.98 (Aldrich), 1.00 g cm<sup>-3</sup> respectively.

For the  $Co_9S_8$  based electrode:

$$d = d_{S} + d_{H} + d_{C} = \frac{4.5 \ mg/cm^{2}}{2.07 \ g/cm^{3}} + \frac{\frac{4.5}{3} \ mg/cm^{2}}{5.35 \ g/cm^{3}} + \frac{\frac{4.5}{6} \ mg/cm^{2}}{1.00 \ g/cm^{3}} = 0.003190 \ cm = 31.90 \ \mu m$$

$$Ev = \frac{Q * U}{A * d} = \frac{2.7 \ mAh * 2.1 \ V}{1 \ cm^{2} * 31.90 \ \mu m} = 1777 \ Wh/L$$

Similarly, for the graphene oxide based electrode:

 $d = 44.5 \ \mu m, Ev = 1274 \ Wh/L$ 

This demonstrates that by using a higher-density sulfur host material ( $Co_9S_8$ ), the cathode can achieve 40% higher volumetric energy density than the graphene oxide based cathode, although they possess the same gravimetric energy density. While this is not the volumetric energy density for a full cell, and does not take into account additional porosity needed for electrolyte egress, it simply illustrates the advantage in utilizing a denser cathode host when the same sulfur content (75 wt%) can be sustained. Furthermore, for the  $Co_9S_8$  based electrode, the volume of electrolyte needed to wet the electrode would also be lower, further contributing to higher volumetric energy density.

### Supplementary figures and tables



**Figure S1.** a) Top views and b) bird-views of the fully relaxed geometry of the substrate slabs (without  $Li_2S_2$ ) after first-principle calculation for the three surfaces of cubic  $Co_9S_8$ ; c, d) the other two meta-stable (local minima in free energy) configurations of  $Li_2S_2$  binding on the three surfaces, with their binding energy value labelled. Brown, blue, green and yellow 3D spheres represent C, N, Li and S (of  $Co_9S_8$ ) atoms, respectively and 2D yellow circles represent S of lithium polysulfides. In our calculations, three (or more) different starting sets of coordinates were used for the initial configurations for geometry optimizations for each surface, which usually yields multiple local minima.

![](_page_5_Figure_0.jpeg)

**Figure S2.** The fully relaxed binding geometry of  $Li_2S$  and  $Li_2S_4$  molecules on the three  $Co_9S_8$  surface substrates after first-principle calculations, with their binding energy value labelled accordingly. Brown, blue, green and yellow 3D spheres represent C, N, Li and S (of  $Co_9S_8$ ) atoms, respectively and the two-dimensional yellow circles represent the S atoms of the lithium polysulfides.

![](_page_6_Figure_0.jpeg)

**Figure S3.** High-resolution XPS spectra of S 2p of a) the pristine  $Li_2S_4$ , b) the pristine  $Co_9S_8$  and c) the  $Co_9S_8$ -Li\_2S\_4 composite. Black circles and solid lines represent the experimental and overall fitted spectra, respectively. The S 2p has  $2p_{3/2}$  and  $2p_{1/2}$  doublets for each distinct component, and only the value of  $2p_{3/2}$  is noted. The S 2p of  $Li_2S_4$  consists of two components, attributed to the terminal ( $S_T$ -1,161.5 eV) and bridging sulfur ( $S_B^0$ ,163.1 eV).<sup>5</sup> The broad peak at 166.2 eV in b)  $Co_9S_8$  is due to a minor oxidation species formed during manipulation of the sample. The S 2p spectrum of  $Co_9S_8$ -Li\_2S\_4 is fit with two sulfur components. The peak at 161.4 eV includes multiple sulfur species as explained in the main text, whereas the peak at 166.2 eV derives from the oxidation species in  $Co_9S_8$  explained above.

![](_page_7_Figure_0.jpeg)

**Figure S4.** a) TGA curve of  $Co_9S_8/S-75$  and VC/S-75 under an Ar flow with a ramp rate of 10 °C/min; representative SEM images of b) the  $Co_9S_8/S-75$  composite, c) VC-S75 composite, d) the high-loading thick  $Co_9S_8/S-75$  electrode surface.

![](_page_7_Figure_2.jpeg)

**Figure S5.** a) The first-cycle voltage profile and b) capacity retention of a pure  $Co_9S_8$  electrode (without any sulfur) cycled vs. lithium metal at a current of 83 mA g<sup>-1</sup>.

![](_page_8_Figure_0.jpeg)

**Figure S6**. Nyquist plots of the  $Co_9S_8$  electrodes in their pristine state and after cycling (cycles 1, 20, 40 shown) at a discharged state; b) is the enlarged plot of the box shown in a).

### References

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