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Supporting Information for

3D Graphene Frameworks Supported Li_2S coated with ultra-thin Al_2O_3 films: Binder-

free Cathodes for High-Performance Lithium Sulfur Batteries

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1. Electrolyte testing

Sulfur content measurement. The method of analyzing sulfur content in the electrolyte referred to the work of Cui et al.¹ First of all, a sulfur-free electrolyte is required, which composes of 1 M LiClO₄ in DME/DOL (1:1, v/v) solution with 1 wt% LiNO₃ (50 μ L in each cell). The assembly process of these cells is the same as that described above. These cells are charged to 3.8 V at 0.05 C and then cycled with a voltage range of 1.8-2.6 V at 0.2 C. At the given discharge or charge potential state, the cells were disassembled in an Ar-filled glove box and the contents (including cathode, anode and separator) were washed several times with DOL and collected the polysulfide-containing solution. For testing, the solution was oxidized by concentrated HNO₃ until the solution was colorless, and finally diluted with distilled water. An inductively coupled plasma-optical emission spectroscopy (ICP-OES, iCAPTM 7400) was used to analyze the sulfur content.

Electrolyte composition measurement. The Al₂O₃-Li₂S-GS cells were disassembled immediately in an Ar-filled glove box at selective charge/discharge voltages after cycling at 0.2 C, such as firstly charging to 3.8 V, and then discharging to 2.3, 2.1, 2.05 and 1.8 V respectively. The Al₂O₃-Li₂S-GS cathodes and Li anodes were prepared without washing and dried naturally in glove-box to take XPS, Raman and XRD characterization. The separators were washed using 2 mL fresh electrolyte, then measured by using UV-vis. absorption spectroscopy with sealable quartz cuvettes to avoid contacting with air during transfer and measurement process. The fresh electrolyte serves as reference solution. The range of wavelength is 200-800 nm.

2. Proof of formula

The association between charge-transfer resistance (R_{ct}) of the cell and the apparent activation energies (E_a) of the electrochemical reactions can be calculated by the following equations^{2, 3}:

$$i_0 = RT/nFR_{ct} \tag{1}$$

$$i_0 = Aexp(-E_a/RT) \tag{2}$$

Where i_0 is the exchange current, R is the gas constant, T is the absolute temperature, n is the number of transferred electron, F is the Faraday constant, A is the temperature-independent coefficient. Therefore, the E_a is proportional to $\ln R_{ct}$:

$$E_a \propto \ln R_{ct} \tag{3}$$

3. Additional figures and tables



Figure S1. (a) Low and high-magnification SEM images of GS framework show the welldefined and interconnected 3D porous structure of GS framework. (c) Nitrogen adsorptiondesorption isotherms of GS framework shows that the high specific surface area ($256.5 \text{ m}^2 \text{ g}^{-1}$), calculated using the Brunauer-Emmett-Teller (BET) method, is in favor of the absorbing sulfur species. (d) Pore size distribution of GS framework possesses an abundant mesoporous and microporous, offering a good pathway for the electrolyte.



Figure S2. (a) Low and (b) High-magnification SEM images of $Li_2SO_4 \cdot H_2O$ -GS composites illustrate that the 3D porous structure of GS framework is maintained after loading $Li_2SO_4 \cdot H_2O$, moreover, no obvious $Li_2SO_4 \cdot H_2O$ bulk is observed. (b) Line scanning with SEM is measured to investigate the distribution of $Li_2SO_4 \cdot H_2O$. It can be seen that sulfur (d, yellow) elements distribute evenly on the surface of GS framework, from the elements distribution at the bottom (carbon in c).



Figure S3. (a) XRD pattern of Kapton tape and (b) Raman spectrum of glass holder used to protect samples from reacting with moisture in air atmosphere during characterization.



Figure S4. (a) Low and (b) high-magnification SEM images of Li_2S -GS composites show that the morphology of Li_2S -GS composites alters due to the consumption of carbon with the generation of Li_2S , compared to GS framework. However, the 3D porous structure is still maintained in Li_2S -GS composites.



Figure S5. The elemental mapping from EDX for Li_2S -GS composites confirms the presence of carbon, sulfur and oxygen. The carbon and sulfur elements correspond to remaining rGO sheets and Li_2S based on the XRD pattern, respectively. The oxygen spectrum is detected derived from the oxygen-containing groups of rGO and the oxidation of Li_2S during transferring Li_2S -GS composites from poly/foil bag to the SEM chamber.



Figure S6. Elemental mapping by TEM of Li_2S -GS composites coincided with carbon region (red) surrounding the sulfur region (light blue) of Li_2S , showing the distribution of Li_2S particles on graphene sheets. The oxygen spectrum is also detected because of the oxygen-containing groups of rGO and the oxidation of Li_2S during transferring Li_2S -GS composites from poly/foil bag to the TEM chamber.



Figure S7. Elemental mapping by TEM of Al₂O₃-Li₂S-GS composites, including carbon (red), oxygen (green), sulfur (light blue) and aluminum (white), further confirming the distribution of

 Li_2S particles on graphene sheets. The Al map further verifies that Al_2O_3 preferentially grows on the surface of Li_2S particles than graphene.



Figure S8. (a) Digital photos of Al_2O_3 - Li_2S -GS cathodes, showing that Al_2O_3 - Li_2S -GS cathodes recover their original shape after compression. (b) SEM images of cross section of Al_2O_3 - Li_2S -GS electrode.



Figure S9. XPS spectra of Li₂S-GS and Al₂O₃-Li₂S-GS composites, inset showing the XPS spectrum of Al 2p and a single fitted peak.



Figure S10. Cyclic voltammetry curves at the initial charge process of Li_2S -GS and Al_2O_3 - Li_2S -GS cells at a scan rate of 0.05 mA s⁻¹. The first charge peaks of Al_2O_3 - Li_2S -GS and Li_2S -GS cells are observed at a similar voltage site of 3.5-3.6 V.



Figure S11. SEM image of original Li metal foil.



Figure S12. EIS spectra of Li_2S -GS and Al_2O_3 - Li_2S -GS cells after 150 cycles at discharge state. Compared with the results before cycling, the impedance spectra of Al_2O_3 - Li_2S -GS and Li_2S -GS cells after 150th discharge test at 0.2 C show the lower resistance, indicating the formation

of a stable interface allows the fast charge transfer during cycling. The R_{ct} value of Al₂O₃-Li₂S-GS cells is 69.9 Ω lower than that of Li₂S-GS cells (98.5 Ω), indicating its better charge-transfer kinetics after 150 cycles. This result further confirms that the ultrathin Al₂O₃ films coated on Li₂S particles are able to limit the dissolution of Li₂S_n species.



Figure S13. Comparison of electrochemical performance at various rate of Al_2O_3 -Li₂S-GS cathodes and previous Li₂S work in literatures, showing showing that Al2O3-Li₂S-GS cathodes can deliver a competitive performance as comparing with recently reported studies about Li₂S cathodes.



Figure S14. Morphology and electrochemical performance of the various Li₂S content of Li₂S-GS composites with (a) ~40 wt%, (b) ~58 wt% and (c) ~73 wt% Li₂S, shows the increasing size of Li₂S particles with the increasing Li₂S content. Scale bars, 10 μ m in (a-c) and 5 μ m in (a-c, inset). Specific capacities based on (d) Li₂S and (e) cathode of the Li₂S-GS cathodes with these various Li₂S content cycled with a voltage window of 1.8-2.6 V at 0.2 C. The Li₂S-GS composites with ~40 wt% Li₂S shows a high specific capacity, but shows a fast capacity decay and a low capacity based on cathode due to its very low loading of active material. On the other hand, the capacity of Li₂S-GS composites is too poor to maintain its structure under the volume change during repeatedly cycling. Among the various amounts of Li₂S in the Li₂S-GS cathodes, the cathodes with ~58 wt% Li₂S shows a considerable capacity not only based on Li₂S but also based on the cathode. Therefore, we choose the Li₂S-GS composites with 58 wt% as the substrate to deposit Al₂O₃ films.



Figure S15. EDX line scan spectra by SEM and electrochemical performance of the various ALD-Al₂O₃ cycles of Al₂O₃-Li₂S-GS composites. (a-c) SEM images of Al₂O₃-Li₂S-GS composites with (a) 5, (b) 10 and (c) 30 ALD cycles, where carbon (red), sulfur (cyan), oxygen (green) and aluminum (pink), showing the preferentially growth of Al₂O₃ on the surface of Li₂S particles. Scale bars, 5 μ m in (a-c). (d-f) Charge/discharge profiles of Al₂O₃-Li₂S-GS composites with (d) 5, (e) 10 and (f) 30 ALD cycles at selected cycles, showing two discharge plateaus and two charge plateaus. However, the charge/discharge overpotential of the cathodes with 30 ALD cycles is much higher than others, indicating the large polarization of the cells. Moreover, the discharge plateaus change into the long-sloping plateaus. (e) Specific capacities of Al₂O₃-Li₂S-GS composites with these various ALD cycles tested with a voltage window of 1.8-2.6 V at 0.2 C. With the increasing ALD cycles, the cycling stability of cathodes increases,

nevertheless, the capacity decreases at 30 ALD cycles. Overall, Al_2O_3 films grown by ALD technology on Li_2S -GS composites can improve its cycling stability; however, thick Al_2O_3 films will enlarge the polarization and lower the capacity of the cells because of the electrochemical inactivity and insulating nature of Al_2O_3 .



Figure S16. Charge/discharge profiles of (a) Al₂O₃-Li₂S-GS and (b) Li₂S-GS cells at first five cycle and (c) the first cycle after initial charge.



Figure S17. (a) UV-vis. spectra of the electrolyte from Al₂O₃-Li₂S-GS cells at different charge/discharge states and (b) with the increasing depth of discharge (from 3.8 V to 1.8 V). All the spectra show two sharp absorbance bands in the UV region, similar to the absorption

spectrum of S₈ in electrolyte, which is induced by the transition of double bond π to π antibonding orbital $(\pi \rightarrow \pi^*)$.⁴ Additionally, the absorbance bands at ~300 nm generate a blue shift (Figure S15b) with the increasing depth of discharge (from 3.8 V to 1.8 V), revealing that the resonance of π -system weakens in polysulfide mainly due to the decreasing nonbonding electron of their sulfur atoms. Therefore, this blue shift demonstrates that the polysulfide chain shortens during discharge process. At the end of initial charge (3.8 V), strong absorption bands are observed at ~458 nm (S_6^{2-}) and 538 nm (S_8^{2-}), and weaker bands around 407 nm (S_4^{2-}) and 603 nm (S_3^{-1}) .⁵ The presence of S_8^{2-} and S_6^{2-} in the electrolyte indicates that the Li₂S in Al₂O₃-Li₂S-GS cathodes are not completely converted to elemental sulfur, and they trigger a disproportionation reaction to generate S_4^{2-} and S_3^{--} ($S_8^{2-} \leftrightarrow S_4^{2-} + 1/2S_8$, $S_6^{2-} \leftrightarrow 2S_3^{--}$). As discharging to 2.3 V, the absorbance ratio between the bands at 458 nm and 538 nm strongly increases, revealing the increasing amount of S_6^{2-} in electrolyte during this process. It is obvious that the consumption of sulfur and the formation of S_6^{2-} occur during this discharge step. Further discharging to 2.1 V, the 458 nm band linked to S_6^{2-} is decreasing, while two absorption bands are emerging markedly at ~407 nm and ~603 nm, attributed to S_4^{2-} and S_3^{-5} Continuously discharging to 2.05 V, the absorbance ratio between the 407 nm band and 530 nm band decreases, indicating the decreasing amount of S_4^{2-} in electrolyte at the 2.05 V stage. At the end of discharge (1.8 V), besides the 603 nm bands, the absorption bands at 407 nm, 458 nm and 538 nm nearly disappear, implying that polysulfide species in electrolyte precipitate again.



Figure S18. (a) Raman spectra of Al₂O₃-Li₂S-GS cathodes at different charge/discharge states; (b) the strong Raman activity of sulfur species under 600 cm⁻¹. Except for the Raman peaks of glass and the D-band and G-band of GS, the Raman peaks of sulfur species are also detected. At 3.8 V, S_8^{2-} and S_6^{2-} are detected in Raman spectra, corresponding to the broad peak at ~360 cm^{-1.6} On the other hand, the cathodes present the characteristic peaks of sulfur at 154, 217, and 473 cm⁻¹, demonstrating the formation of sulfur during the initial charge process. The intensity of sulfur notably reduces after discharging to 2.3 V, moreover, the Raman peak corresponding to S_6^{2-} at 360 cm⁻¹ becomes stronger. Additionally, the Raman peaks of sulfur, S_8^{2-} and S_6^{2-} are scarcely detected. Continuously discharging to 2.1 V, several new peaks at 235 and 534 cm⁻¹ contributed by S_4^{2-} and S_3^{--} (formed from the disproportionation of S_4^{2-}) highlight, as well as a shoulder peak at ~450 cm⁻¹ caused by S_3^{2-} and $S_4^{2-.6}$ From 2.1 V discharge to 1.8 V, the intensity of S_3^{2-} , S_4^{2-} and S_3^{--} Raman peaks weakens obviously, and a new peak at 367 cm⁻¹ induced by Li₂S, confirming the precipitation of Li₂S at the end of discharge.⁷



Figure S19. XRD pattern of Al_2O_3 - Li_2S -GS cathodes after charge at 3.8 V, in which the sharp peaks of crystalline sulfur are legible. Thus, the conversion of Li_2S into sulfur is generated during the initial charge process.



Figure S20. Proposed discharge reaction mechanism showing major electrochemical reactions and Li_2S_n compounds. The crystalline sulfur in cathodes is formed, and S_8^{2-} and S_6^{2-} are still detected in the electrolyte owing to the incomplete conversion of Li_2S to sulfur, after initially charging to 3.8 V. Discharging to 2.3 V, S_6^{2-} are the main product in the Al₂O₃-Li₂S-GS cells. The first step of the discharge reaction is described as $S_8 + 2Li^+ + 2e^- \rightarrow Li_2S_8$ and $Li_2S_8 \rightarrow Li_2S_6 + 1/4S_8$. Further discharging to 2.1 V, the electrochemical reaction of $2Li_2S_6 + 1/4S_8$.

 $2\text{Li}^+ + 2e^- \rightarrow 3\text{Li}_2\text{S}_4$ occurs, and thus S_4^{2-} is the main product during the second step. Then lithium polysulfide gradually precipitates with the increasing depth of discharge from 2.1 V to 1.8 V, involving the electrochemical reactions: $3\text{Li}_2\text{S}_4 + 2\text{Li}^+ + 2e^- \rightarrow 4\text{Li}_2\text{S}_3$, $2\text{Li}_2\text{S}_3 + 2\text{Li}^+ + 2e^- \rightarrow 3\text{Li}_2\text{S}_2$ and $\text{Li}_2\text{S}_2 + 2\text{Li}^+ + 2e^- \rightarrow 2\text{Li}_2\text{S}$. It should be pointed out that S_3^{--} can be observed even at the end of discharge because of the disproportionation of polysulfide ($\text{S}_n^{2-} = [(2n-2)/5]$] $\text{S}_3^{--} + [(6-n)/5] \text{S}^{2-}).^4$



Figure S21. XPS spectra of Al₂O₃-Li₂S-GS cathodes at different charge/discharge states.



Figure S22. S 2p XPS peaks over 168 eV of Al₂O₃-Li₂S-GS cathodes at (a) 3.8 V, (b) 2.3 V, (c) 2.1 V, (d) 2.05 V and (e) 1.8 V, showing the existence of LiTFSI salt in cathodes.



Figure S23. Li 1s XPS spectra and their fitted results of Al₂O₃-Li₂S-GS cathodes at (a) 3.8 V, (b) 2.3 V, (c) 2.05 V and (d) 1.8 V, showing the stable presence of Li-O binding throughout charge/discharge process.

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