# **Supporting Information**

# Multivalent cationic and anionic mix redox of Sb<sub>2</sub>S<sub>3</sub> cathode contributing high-capacity aluminum ion batteries

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## **Experimental Section**

#### Synthesis of materials:

Synthesis of  $Sb_2S_3$  nanorods:  $Sb_2S_3$  nanorods are prepared by hydrothermal reaction reported <sup>[1]</sup>. The typical synthesis process is as follows: 0.913g SbCl<sub>3</sub>, 0.969g L-cysteine, 0.624g Na<sub>2</sub>S.9H<sub>2</sub>O are added to 80ml deionized water in order and stirred for 3h. The solution was then transferred to a 100ml Teflon autoclave and maintained at 180°C for 12h. After the reaction, the product was cooled to room temperature, washed several times with deionized water and ethanol, and dried under vacuum at 60° C. Finally, Sb2S3 nanorods were obtained.

*Synthesis of graphene aerogel (GA) interlayer*: Graphene oxide is prepared by the modified *Hummer*'s method from natural graphite. 100mg of graphene oxide powder was dispersed into 100ml of deionized water and ultrasonicated for 2h to obtain a uniformly dispersed GO aqueous solution. 400ml of ascorbic acid was added to the GO solution and stirred for 1h, then the above solution was divided into 20ml glass bottles and kept at 80°C for 8h to obtain a columnar aerogel. Then it was freeze-dried and kept at 400°C for 60 min under an inert atmosphere for thermal reduction to obtain GA. The obtained columnar graphene aerogel can be cut into thin sheets with a thickness of 1-2 mm and used as a battery interlayer, with an average mass of 1-1.5 mg.

#### Fabrication of electrochemical cell:

Anhydrous aluminum chloride was slowly added to the recrystallized 1-ethyl-3methylimidazole chloride in a glove box ( $O_2$ ,  $H_2O < 0.1$ ppm) at a molar ratio of 1.3:1 to obtain a light-yellow solution and stirred 12h. The preparation of cathode is to grind and mix Sb<sub>2</sub>S<sub>3</sub>, acetylene black and PVDF according to a mass ratio of 6:3:1, and use NMP as a solvent to coat on the molybdenum (Mo) current collector (the diameter is 1.1 cm.) and vacuum dry at 70°C for 12 hours. The loading of  $Sb_2S_3$  is 1.0 mg. Swagelok-type batteries are assembled with highpurity aluminum foil as the anode, glass fiber paper (Whatman, GF/D) as the separator, and GA as the interlayer. In addition, the fluffy graphene aerogel interlayer with a diameter of 1.0-1.1cm and a mass of ~1.0-1.5 mg is compacted during the battery assembly process. The cyclic voltammetry curve measures different scan rates (0.1-1.0 mV/s) in the voltage range of 0.01-1.8 V on an electrochemical workstation (CHI660E, Shanghai Chenhua Instrument corporation, China). The galvanostatic charge/discharge measurements use Wuhan LANHE battery tester. The assembled battery requires several cycles of activation to reach the maximum capacity depending on the current densities.

#### Materials characterizations:

The crystal structures of the samples were analyzed by powder X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with CuKa radiation at 40 kV and 40 mA. The microscopic morphology and microstructure of the samples were observed by field-emission scanning electron microscopy (SEM, JSM-7900F, JEOL) and high-resolution transmission electron microscopy (HRTEM, Tecnai-G2-20-S-Twin, FEI, Netherlands). X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe, ULVAC-PHI, Japan) with an Al Ka X-ray source (1486.6 eV) was used to study the surface chemical composition and valent state of the elements of the samples. The Raman spectra were recorded using a 532-nm laser excitation at room temperature on a Raman spectrophotometer (HORIBA HR Evolution). The samples used for ex-situ XPS characterization were dismantled batteries in different charge states of the 2<sup>nd</sup> cycle in a glove box, and the residual electrolyte was extruded by sandwiching the cathode between two filter papers and applying a pressure of about 3-4 MPa using a tablet press. The cathode with molybdenum current collector is then glued directly to the sample stage and transferred through the transition chamber, avoiding any contact with air and moisture. The ex-situ Raman test was performed by disassembling the cathodes and GA interlayer in a glove box and encapsulating them in cuvettes with a quartz window.

## **DFT** calculation details

The spin-polarized DFT computations employed an all-electron method with the generalized gradient approximation (GGA), and the model of Perdew-Burke-Ernzerhof (PBE) functional were adopted, as implemented in the DMol3 Code.<sup>[2]</sup> Also, the double numerical plus polarization (DNP) basis set was used. The DFT-D method with the Grimme vdW correction

was employed to accurately describe the long-range electrostatic interactions.<sup>[3]</sup> Self-consistent field (SCF) calculations were performed with a convergence criterion of 10<sup>-5</sup> a.u. on the total energy, maximum force of 0.002 a.u<sup>-1</sup>, and maximum displacement of 0.005 Å.

The binding energy E is defined by eqn:

 $E_{binding} = E(substrate-SbCl_4^+) - E(SbCl_4^+) - E(substrate)$ 

#### Calculation of cell-level energy density

The methodology of calculating cell-level energy density follows *Mustain* et al. <sup>[4]</sup> The mass of the individual components, including: anode, cathode, electrolyte, separator, interlayer, and packaging, are considered when calculating the energy density of the full cell. The discharge capacity (Q = 756 mAh/g) and average voltage ( $V_{avg} = 0.8 \text{ V}$ ) are based on the discharge curve at 100 mA/g. The mass of Sb<sub>2</sub>S<sub>3</sub> is 1.0 mg and of the interlayer is 1.5 mg, while the mass of aluminum used in the anode is obtained by dividing the discharge capacity by the theoretical capacity of Al (2980 mAh/g), and the ratio of N/P is assumed to be 1.0. The mass of the electrolyte is estimated to be 3 times of Sb<sub>2</sub>S<sub>3</sub>. Finally, the mass of the separator and packaging is estimated to be 5% and 10% of the total mass, respectively. The formulas for calculating the cell-level capacity and energy density are as follows:

$$C_{cell-level} = \frac{Q}{m_{anode} + m_{cathode} + m_{electrolyte} + m_{separator} + m_{package} + m_{interlayer}}$$
(1)  
Energy density =  $C_{cell-level} \times V_{avg}$ (2)

Calculation results:

$$\begin{split} m_{cathode} &= 1.0 \ mg/0.6 = 1.67 \ mg; \\ m_{electrolyte} &= 3m_{Sb2S3} = 3.0 \ mg; \\ m_{interlayer} &= 1.5 \ mg; \\ m_{total} &= (1.67 + 0.25 + 3 + 1.5)/0.85 = 7.55 \ mg; \\ C_{cell - level} &= 756/7.55 = 100.13 \ mAh/g \end{split} \qquad ED &= 100.13 * 0.8 = 80 \ Wh/kg. \end{split}$$



Figure S1 (a) Images of Swagelok-type battery and material of each component; (b) Schematic

diagram of battery assembly.



**Figure S2** (a, b) Comparation of the charge protocol (first discharge/first charge) difference at 100 mA/g; (c) Comparison of initial discharge capacity of electrode materials with different compositions; (d) Cycling capacity of acetylene black electrode with and without GA interlayer at 100 mA/g.

Notes: (1) AB electrode, acetylene black: PVDF=9:1<sub>mass ratio</sub>; (2) AB+GA, acetylene black electrode with GA interlayer; (3) Sb<sub>2</sub>S<sub>3</sub> electrode with GA interlayer and NaAlCl<sub>4</sub> electrolyte, NaAlCl<sub>4</sub>: AlCl<sub>3</sub>: [EMIM]Cl=0.2:1.3:1.0<sub>mol ratio</sub>. The initial discharge capacity of Sb<sub>2</sub>S<sub>3</sub> cathode with GA interlayer consists of several parts: the formation of the SEI film on the surface of the carbon material (~72 mAh/g), the conductive carbon black (~22 mAh/g), the graphene aerogel interlayer (~ 36 mAh/g) and traces of Na<sub>2</sub>S left over from the preparation process (<10 mAh/g).



**Figure S3 (a)** Galvanostatic charge/discharge curve of  $Sb_2S_3$  at 100 mA/g and **(b)** cycle performance curve at 500 mA/g; (c) Cycling performance of  $Sb_2S_3$  electrodes with different loadings (2.6 mg, 4.5 mg, 7.5 mg) at 1 A/g. (Notes: The area loads are 2.74, 4.74, 7.89 mg/cm<sup>2</sup>)



Figure S4 Comparison of cycling performance in different voltage ranges at 1000 mA/g.



Figure S5 Comparison of galvanostatic charge-discharge curves in different voltage ranges.

Cathode Material	Initial Discharge Capacity(mAh/g)	Current Density (mA/g)	Cycle Number	Retention Capacity (mAh/g)	Discharge Potential (V)	active material loading(mg)	Reference
	756	100	25	574	0.8	1.0	
Sb <sub>2</sub> S <sub>3</sub>	494	1000	220	363	0.8	1.0	This Work
	185	1000	200	175	0.75	7.5	
CoS2@CNFs	170	200	500	~80	0.8	6.0	5
a-TiS4	206	180	1000	200	0.9	unknown	6
FeS <sub>2</sub> @C/CNT	~285	100	100	~250	0.9	1.0	7
$WS_2$	~240	1000	500	119	0.5	1.1	8
$VS_4$	~140	400	120	129	0.7	1.5	9
FeS <sub>2</sub> @C	120	1000	1000	120	0.4	1.0	10
SnS	~320	100	1000	227	1.1	unknown	11
Co3S4	290	50	150	~90	0.6	1.1	12
C09S8@CNT- CNF	315	100	200	~300	0.8	1.0	13
CuS@C	250	20	100	100	0.6	unknown	14
$G-SnS_2$	270	200	100	70	0.7	1.6	15
Ni <sub>3</sub> S <sub>2</sub> @Graphene	350	100	100	60	1.0	3.6	16

 Table S1 Comparison of electrochemical performance of metal sulfide cathodes.



Figure S6 Comparison of CV curves of  $Sb_2S_3$ , S at 1.0 mV/s.



Figure S7 TEM images and corresponding element mapping images of initial, fully charged and fully discharged  $Sb_2S_3$  cathode at  $2^{nd}$  cycle.



Figure S8 TEM images of fully charged Sb<sub>2</sub>S<sub>3</sub>.



Figure S9 (a) Construction of the in situ XRD battery. Beryllium (Be) sheets are used as cathode current collectors and windows for X-ray irradiation; (b, c) Images of the assembled in-situ cell and test scene.



Figure S10 (a) In-situ XRD patterns of  $Sb_2S_3$  electrodes coated on the beryllium (Be) current collector and (b) in pristine and fully charged status.



Figure S11 Comparison of the XPS reference peaks of  $Sb_2S_3$ , S and various Sb-based compounds reported in literatures (Reference 18-22) and this work. Notes: Unit: eV.



**Figure S12** (a) Image of the transition compartment for XPS and Schematic diagram of sample seal transfer; (b) XPS spectra Sb  $3p_{5/2}$  of washed and unwashed electrolyte-impregnated initial Sb<sub>2</sub>S<sub>3</sub> electrodes.; (c, d) Ex-situ XPS spectra of Sb 3d and S 2p of Sb<sub>2</sub>S<sub>3</sub> electrodes etched by argon ion in different charge/discharge states.

Notes: (1) DMC, dimethyl carbonate. The peak positions of O 1s is highly overlapped with Sb  $3p_{5/2}$ . The electrodes would be inevitably oxidized in the process of washing and vacuum drying, which will affect the valence analysis of Sb (Sb<sub>2</sub>O<sub>3</sub>, Al (OH)<sub>3</sub>, H<sub>2</sub>O, et al). (2) the etching depth is 5 nm. To reduce errors, we performed peak shift correction by comparing the as-synthesized Sb<sub>2</sub>S<sub>3</sub> powder with the electrolyte-impregnated pristine Sb<sub>2</sub>S<sub>3</sub> electrode. (3) The XPS results of Figure 3b, c and Figure S12c, d is both measured with unwashed electrodes transferred by transition compartment.



Figure S13 The cyclic voltammetry curve of  $Sb_2S_3$  cathode at 0.1 mV/s, and the correlation between each redox peak and chemical reaction.



Figure S14 (a) Schematic diagram of the laboratory preparation of  $SbCl_5$ ; (b) physical diagrams of  $SbCl_3$  and  $SbCl_5$ ; (c) synthesis mechanism of  $Cl_2$  and  $SbCl_5$ .



**Figure S15** Raman spectra of (a) pure SbCl<sub>5</sub> and (b) SbCl<sub>5</sub> dissolved in a certain amount of electrolyte (AlCl<sub>3</sub>/[EMIM]Cl 1.3<sub>mol ratio</sub>).

Cathodag	Deastion	Defenence
Cathodes	Reaction	Reference
$Sb_2S_3$	$Sb_2S_3 \rightarrow [SbCl_4]^+ + S$	This work
Sb	Sb→SbCl <sub>3</sub> +SbCl <sub>5</sub>	17
Sb <sub>2</sub> Te <sub>3</sub>	$Sb_2Te_3 \rightarrow [TeCl_3]^+ + SbCl_3$	18
FeSe <sub>2</sub>	$FeSe_2 \rightarrow FeCl_2 + Se + FeCl_{n-2}Se_2 + Fe(AlCl_4)_mSe_2$	19
NiSe <sub>2</sub>	$NiSe_2 \rightarrow NiCl_2 + Se + NiCl_{n-2}Se_2 + Ni(AlCl_4)_mSe_2$	20
S	$S \rightarrow [SCl_3]^+$	21, 22
S	$Al_2S_3 \rightarrow S \rightarrow [SCl_3]^+$	23
Se	Se $\rightarrow$ SeCl <sub>2</sub> /[SeCl <sub>3</sub> ] <sup>+</sup> /Se <sub>2</sub> Cl <sub>2</sub>	24, 25
Se	$Al_2Se_3 \rightarrow Se \rightarrow [SeCl_3]^+$	26
Te	$Te \rightarrow [TeCl_3]^+$	27, 28

Table S2 Summaries of the energy storage mechanisms of various reported cathodes



Figure S16 Electrochemical equilibrium reaction equation of Al-Sb<sub>2</sub>S<sub>3</sub> battery



Figure S17 galvanostatic charge/discharge curve of GA at current density of 100 mA/g.



Figure S18 (a) The galvanostatic charge/discharge curve and (b) the cycle performance curves of  $Sb_2S_3$  cathode without GA interlayer at the current density of 1 A/g.



Figure S19 SEM images of graphene aerogel (GA) interlayer.



Figure S20 Morphologies and corresponding element mapping of  $Sb_2S_3$  electrodes after different charge-discharge cycles at 1000 mA/g. (a) Pristine; (b) 50 cycles; (c) 200 cycles.



**Figure S21** Morphologies and corresponding element mapping of GA interlayer after different charge-discharge cycles at 1000 mA/g. (a) pristine; (b) after 200 cycles. Notes: Al, Cl, Sb, S elements on pristine GA can be determined as allowable errors.



Figure S22 (a) IR and (b) XPS spectra of GA.



**Figure S23** Self-discharge performance of Al-Sb<sub>2</sub>S<sub>3</sub> batteries using GA interlayers. (a) galvanostatic charge-discharge tests at different resting times (1, 2, 6, 12, 24, 48 h) at 1000 mA/g; Comparison of (b) galvanostatic charge-discharge curves and (c) cycle performance curves at different resting times.

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