

## Supporting Information

# Green Synthesis of the Battery Material Lithium Sulfide via Metathetic Reactions

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# 1. Experimental Section

## 1.1 Materials:

Molecular sieves (4 Å, Shanghai Ailan) were activated in a muffle furnace at 500°C for 12 hours before use. Ethanol (EtOH, Tianjin Yuanli, 99.8%) and Tetrahydrofuran (THF, Shanghai Aladdin, 99.9%) were dried with molecular sieves overnight before use. All Lithium-containing compounds (LiCl, LiBr, LiI, and LiNO<sub>3</sub>, Tianjin Xiensi, 99%) were dried under vacuum at 120°C overnight to ensure that there were no water and oxygen residuals before being transferred into the Ar-filled glove box. The raw material Na<sub>2</sub>S · xH<sub>2</sub>O (Tianjin Damao, 99.5%), whose XRD pattern is shown in **Figure S1a**, was heated under vacuum at 90°C for 2 hours and then at 220°C for 4 hours to obtain white anhydrous Na<sub>2</sub>S powder. All other chemicals were used as received.

## 1.2 Synthesis of Li<sub>2</sub>S:

Using LiCl as the model system of Li salts for metathetic synthesis of Li<sub>2</sub>S, the typical production protocol is as follows. Firstly, appropriate amounts of LiCl and Na<sub>2</sub>S at the molar ratio of 2:1 were mixed in a flask. Secondly, the needed amount of anhydrous ethanol was added into the mixture, in order to make the resulted Li<sub>2</sub>S product to be 0.5 M in the solution. Thirdly, the as-prepared solution was stirred for 30 minutes to complete the reaction. Fourthly, the reaction solution was transferred into a centrifuge tube and centrifuged at 6000 rpm for 15 minutes. Fifthly, the supernatant was filtered to prevent the byproduct NaCl precipitate from the Li<sub>2</sub>S-EtOH product solution. Finally, the ethanol was removed via distillation at 250°C to obtain the powder

production of  $\text{Li}_2\text{S}$ . Herein, all processes except the centrifugation were carried out in the Ar-filled glove box. The ethanol solvent can be collected and reused. Using a higher molar ratio of 2.10:1 between  $\text{LiCl}$  and  $\text{Na}_2\text{S}$  could enhance the removal of byproduct  $\text{NaCl}$  due to the common ion effect and produce a  $\text{LiCl}$ -containing  $\text{Li}_2\text{S}$  product. The  $\text{LiCl}$  residual could then be washed away by THF. As a result, the obtained  $\text{Li}_2\text{S}$  is highly pure, meeting the need of battery applications. The procedures of using other lithium salts like  $\text{LiBr}$ ,  $\text{LiI}$  and  $\text{LiNO}_3$  to synthesize  $\text{Li}_2\text{S}$  are similar to the above example.

### 1.3 Synthesis of $\text{Li}_6\text{PS}_5\text{Cl}$ Solid Electrolyte:

The  $\text{Li}_6\text{PS}_5\text{Cl}$  solid electrolyte powder was prepared by ball milling the house-made  $\text{Li}_2\text{S}$  with other required raw materials, followed by heat treatment. Firstly, appropriate amounts of  $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_5$  (99%, Eco Reagent), and  $\text{LiCl}$  at the molar ratio of 5:1:2 were mixed by mortar and pestle in an Ar-filled glovebox. Then, the mixture together with tungsten carbide balls was sealed into a 100-ml tungsten carbide milling jar, where the weight ratio of the milling material to the tungsten carbide balls was 1:15. Next, the jar was loaded onto a high-energy ball mixer (SPEX, Mixer/Mill 8000 M) to mechanically mill for 5 h. After that, the milled materials were sealed in a quartz tube and annealed at  $550^\circ\text{C}$  for 8 h. Finally, after crushing and granulating the annealed sample, one could obtain  $\text{Li}_6\text{PS}_5\text{Cl}$  electrolyte powder. To make  $\text{Li}_6\text{PS}_5\text{Cl}$  electrolyte pellets for measuring the ionic conductivity, 130 mg of  $\text{Li}_6\text{PS}_5\text{Cl}$  powder was placed in a polyaldehyde mold and then pressed into a pellet by applying 360 MPa pressure through two steel dies. The two dies also served as the electrical terminals for the subsequent ionic-conductivity measurements. The thickness of electrolyte pellet was measured by a spiral micrometer; and the cross-sectional area was governed by the diameter of the die (1 cm). Then, the mold was fastened with screws, which

were isolated from the steel dies through Teflon washers. After that, the complete set was placed in a sealed box and taken out of the glove box for measurements.

## 1.4 Materials characterization:

X-ray diffraction (XRD, Rigaku Smartlab9KW, Japan,) was employed to characterize crystalline phases in solid materials, using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). Typically, the XRD samples were prepared in the glove box by spreading sample powders onto glass substrates covered with dome-like polyimide films. Morphological and elemental analyses were performed on field emission scanning electron microscope (FESEM, FEI Apreo S LoVac, Czech) with the EDS function and transmission electron microscope (TEM, FEI Talos F200X, American) with the electron diffraction function. To measure the possible existence of ethanol residual in Li<sub>2</sub>S samples, the thermal-desorption mass spectrometer (Hiden Analytical, HPR20) was employed to online monitor the exhausting gas out of heated quartz tubes holding 10 mg of Li<sub>2</sub>S samples. The detection mode was temporal analysis of the ethanol fragment at the m/z of 31, using a secondary electron multiplier (SEM) detector. The X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, English) was employed to determine the identities and oxidation states of elements. Before taking the XPS spectra, the sample surfaces were bombarded with Ar<sup>+</sup>-ions to etch the top layer of 30 nm.

The ionic conductivity of Li<sub>6</sub>PS<sub>5</sub>Cl solid electrolytes was measured at TUT. The sealed box holding the assembled electrolyte set was put inside a thermostatic oven whose temperature was controlled in the range of 30 – 120°C. Then the electrical terminals were connected to a PARSTAT MC (PMC) electrochemical workstation to measure the electrochemical impedance spectra (EIS). The spectra were measured in the frequency range of 1 Hz to 10 MHz

with the voltage amplitude of 10 mV. The ionic conductivity ( $\sigma$ ) was calculated according to the equation of  $\sigma = d/AR$ , where  $d$  was the pellet thickness,  $A$  was the pellet area and  $R$  was the pellet resistance.

## 2. Supporting Figures and Video

**Table S1:** Thermodynamic analysis for metathetic synthesis of  $\text{Li}_2\text{S}$  according to the reaction of  $2\text{LiY} + \text{Na}_2\text{S} \rightarrow \text{Li}_2\text{S} + 2\text{NaY}$ ; ( $\Delta G^\circ_{\text{r,m x}} < 0$ )

LiY	LiCl	LiBr	LiI	LiNO <sub>3</sub>	Li <sub>2</sub> SO <sub>4</sub>
$\Delta G^\circ_{\text{r,m}} \text{ (kJ/mol)}$	-62	-78	-96	-36	-12
K	$1.63 \times 10^{11}$	$4.63 \times 10^{13}$	$6.60 \times 10^{16}$	$2.03 \times 10^6$	$1.27 \times 10^2$

**Table S2:** The solubility of all the involved reactants in ethanol

LiY	LiCl	LiBr	LiI	LiNO <sub>3</sub>	Li <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> S
S(mol/L)	1.81	2.49	2.81	2.14	0.086	0.84

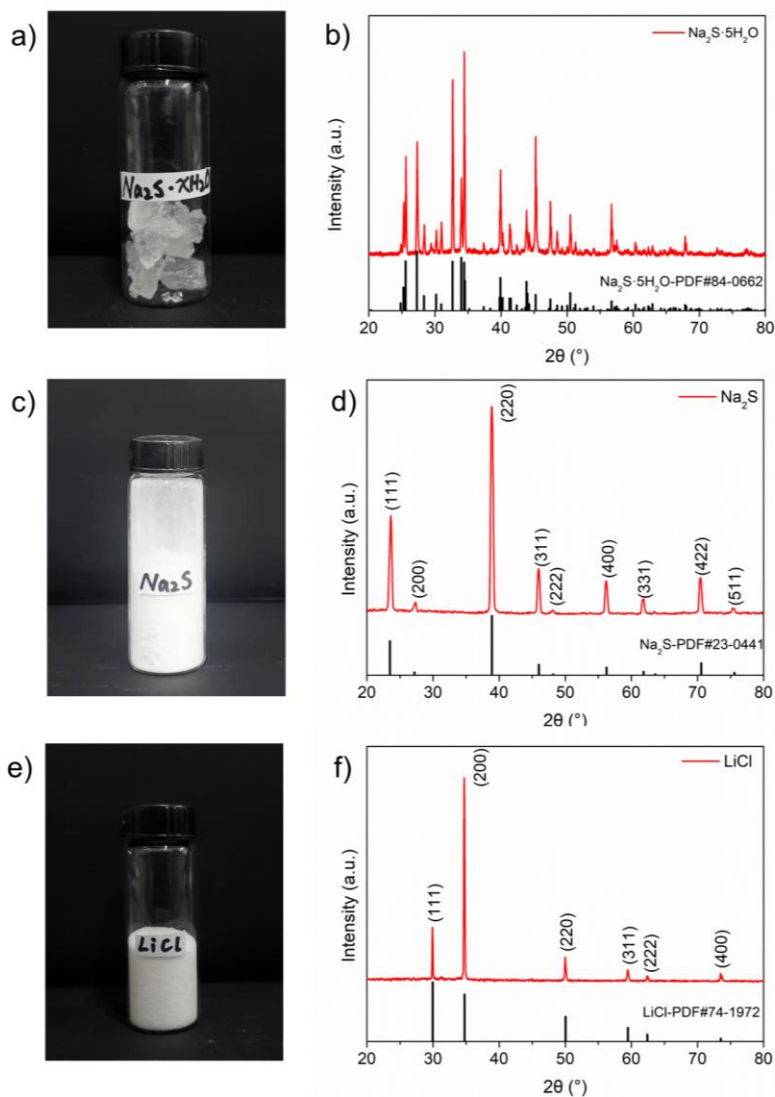
**Table S3:** Comparisons of the properties of recent  $\text{Li}_6\text{PS}_5\text{Cl}$  electrolytes.

Reference	Ionic conductivity (mS/cm)	Activation Energy (eV)
This work	3.86	0.26
1	1.21-0.331	0.29-0.30
2	~1	~0.45
3	0.11	0.35
4	—	0.33
5	1.58	0.26
6	0.46	0.33

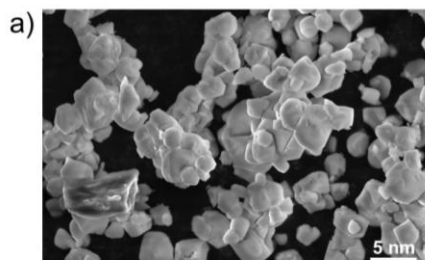


LiCl+Na<sub>2</sub>S.mp4

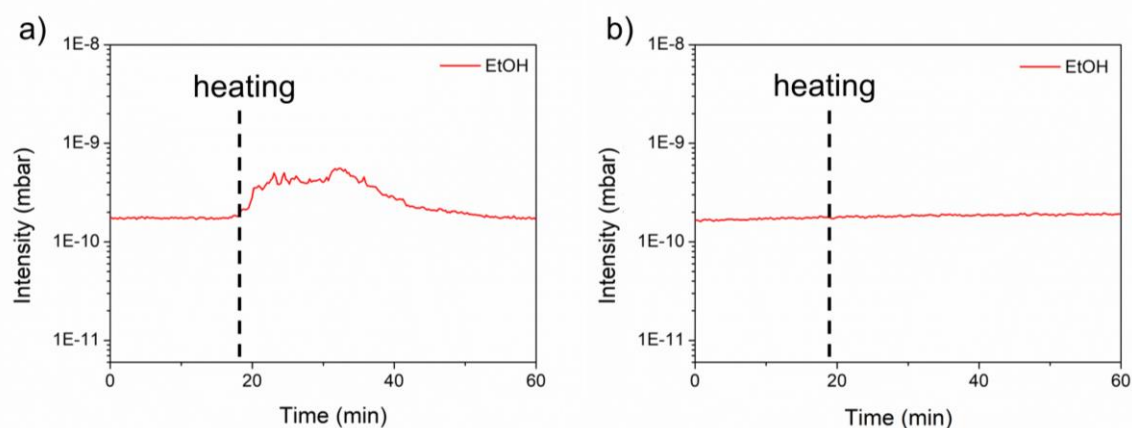
**Video S1:** Demonstration of the metathetic synthesis of Li<sub>2</sub>S by mixing the respective ethanol solutions of Na<sub>2</sub>S and LiCl.



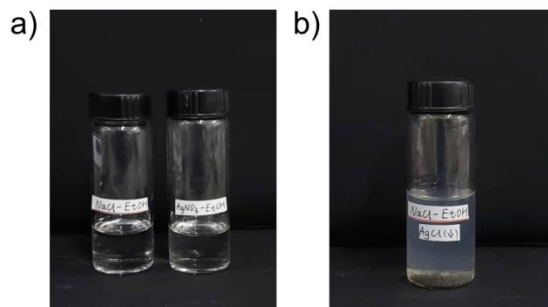
**Figure S1:** Optical images (a, c, and e) and XRD data (b, d, and f) of raw materials of  $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$  before (a and b) and after (c and d) drying, and anhydrous  $\text{LiCl}$  (e and f).



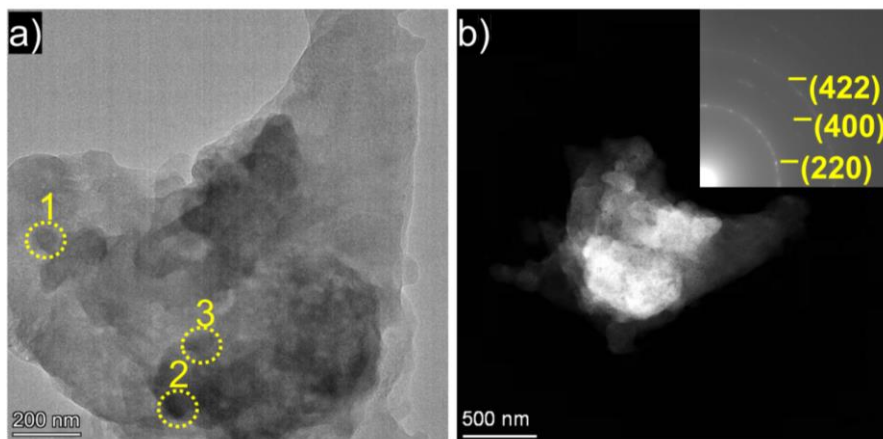
**Figure S2:** An SEM image of the  $\text{NaCl}$  byproduct.



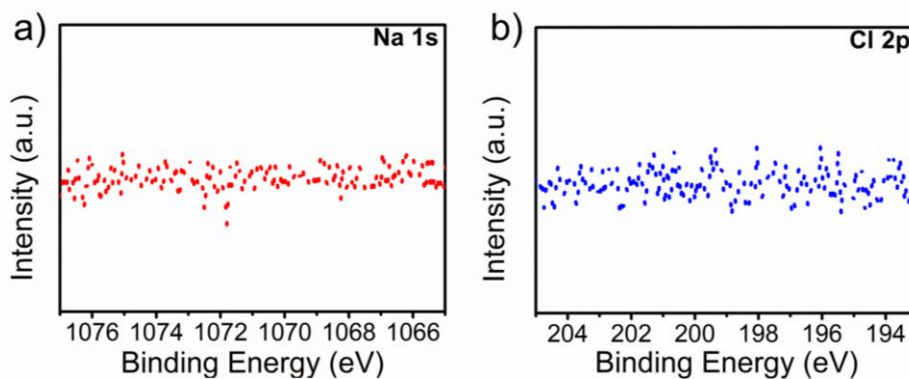
**Figure S3:** The thermal-desorption mass spectrometric plots monitoring the ethanol trace for the  $\text{Li}_2\text{S}$  samples further post-annealed at  $500^\circ\text{C}$  for 4 h treatment (a) and further post-annealed at  $700^\circ\text{C}$  for 4 h (b).



**Figure S4:** An optical image of clear ethanol solutions of  $\text{AgNO}_3$  and  $\text{NaCl}$  before mixing (a) and an optical image showing the generation of cloudy precipitates ( $\text{AgCl}$ ) after mixing (b).

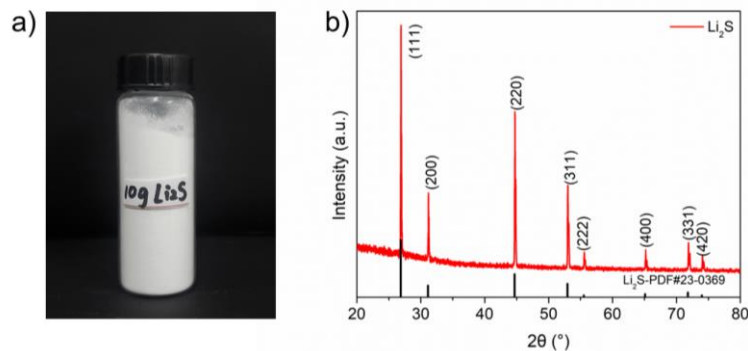


**Figure S5.** (a) bright field TEM image and (b) dark field TEM image of further thermally-treated  $\text{P}_{2.10\_THF}$  sample, wherein the inset is the electron diffraction patterns.

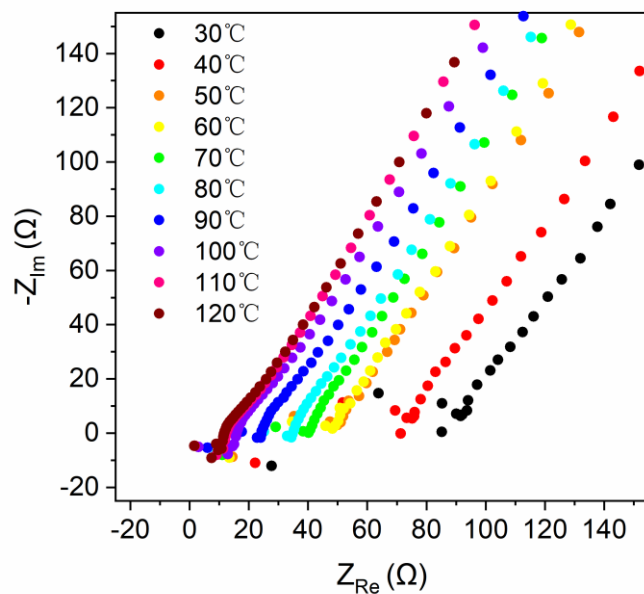


**Figure S6.** XPS spectra of the house-made  $\text{Li}_2\text{S}$  product for elemental analyses of Na (a) and Cl (b).

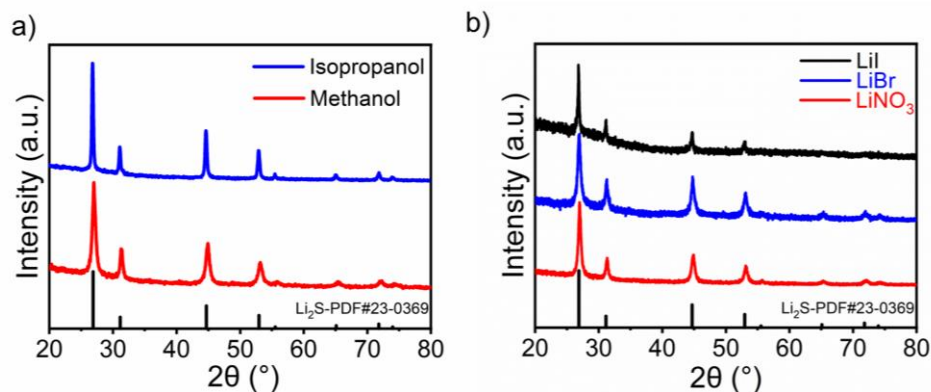




**Figure S7:** An optical image (a) and XRD data of 10g  $\text{Li}_2\text{S}$  (b).



**Figure S8:** The electrochemical impedance spectra (EIS) of solid electrolyte based on the house-made  $\text{Li}_2\text{S}$  in the temperature range of 30 – 120°C.



**Figure S9.** Generality of this metathesis method for synthesizing  $\text{Li}_2\text{S}$  by using different alcohols and different lithium salts. (a) XRD patterns of the obtained  $\text{Li}_2\text{S}$  samples by using the  $\text{LiCl-Na}_2\text{S}$  pair and methanol (red) or isopropanol (blue) as the solvent. (b) XRD patterns of the obtained  $\text{Li}_2\text{S}$  samples by using ethanol as the solvent and  $\text{LiBr}$  (red),  $\text{LiI}$  (blue), or  $\text{LiNO}_3$  (black) as the Li source.

### 3. Reference

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