

Supporting information

Experimental section

Preparation of Li_2S using active carbon as the carbon source by mixer-milling:

First, the $\text{Li}_2\text{SO}_4@\text{C}$ precursor was prepared by a mixer mixing using $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and activated carbon as the raw materials. The $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and activated carbon were weighed and put into the mixing-bottle together with the zirconia balls (diameter of 10 mm), and then the assembled bottle was placed on the roller mixer and mixed for 12 h with 120 r/min. The weight ratio of zirconia balls and mixed materials is 1: 4. Then, the mixture was placed in a corundum crucible with a diameter of 7 cm and pre-sintered in air at 240 °C for 6 h to obtain the $\text{Li}_2\text{SO}_4@\text{C}$ precursor. Afterwards, 1 g of the $\text{Li}_2\text{SO}_4@\text{C}$ precursor was pressed in the PEEK die under 100 MPa to process the precursor wafer. Finally, the precursor wafer was sintered at 825 °C for 5 h under flowing argon to obtain pure Li_2S products.

Preparation of Li_2S using active carbon as the carbon source by ball-milling:

$\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and activated carbon were mixed by ball-milling with a speed of 600 r/min for 3 h to obtain the $\text{Li}_2\text{SO}_4@\text{C}$ mixture. $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and activated carbon were weighed with a molar ratio of 1: 3.4 and put into the ball-milling tank together with the zirconia balls, and the weight ratio of zirconia balls and mixed materials is 1: 30 (the ratio of large balls with a diameter of 10 mm to small balls with a diameter of 3 mm is 1: 1). The mixture was then pre-sintered in air at 240 °C for 6 h to dehydrate, and later 1 g of the $\text{Li}_2\text{SO}_4@\text{C}$ precursor was pressed in the PEEK die under 100 MPa and subsequently sintered at 825 °C for 5 h under flowing argon to obtain pure Li_2S .

Preparation of $\text{Li}_{6-x}\text{PS}_{5-x}\text{Cl}_{1+x}$:

The $\text{Li}_{6-x}\text{PS}_{5-x}\text{Cl}_{1+x}$ solid-state electrolyte (LPSC_{1+x}) was synthesized by high-energy ball-milling using Li_2S , P_2S_5 (99%, Aladdin), and LiCl (99%, Aladdin) as raw materials, and the molar rate of Li_2S , LiCl and P_2S_5 is $(2.5-x): (1+x): 0.5$. The raw materials were weighed under the argon atmosphere in the glove box and were assembled in the zirconia ball milling tank together with the zirconia balls, and the mass ratio of zirconia balls and raw materials was 30:1 (the ratio of large balls with diameter of 10 mm to small balls with diameter of 3 mm is 1: 1). Whereafter, the assembled ball milling tank was placed in the planetary ball-milling apparatus for two-stage ball milling (200 r/min for 1 h and 600 r/min for 1 h). In the middle of the two stages, the tank was taken out of the ball-milling apparatus and opened in the glove box filled with argon atmosphere to shovel off the adhering materials. The ball-milled material was subsequently pressed into wafers by the homemade mold and then sintered at 550 °C for 8 h in the argon-filled glove box to obtain the final S-SE.

Materials characterization:

The crystal structure of Li_2S and S-SE was characterized via X-ray diffraction (XRD, Rigaku D/MAX-2500, Japan) with $\text{Cu K}\alpha$ radiation in a 2θ range of 5°–90°. Field emission Scanning electron micrographs (FESEM, JSM-IT700HR, Japan) and energy dispersive spectral (EDS, Xplore 30-Oxford, UK) mapping images were employed to observe the morphologies. X-ray photoelectron spectroscopy (XPS; PHI Versa Probe 4, Al target, Japan) was utilized to analyze the chemical states and the binding energy was measured precisely relative to the C 1s peak at 284.8 eV.

The electrochemical station (Auto-lab, Switzerland) was applied to measure the AC electrochemical impedance spectroscopy (EIS) of S-SEs with an amplitude of 10 mV in a frequency range from 0.1 Hz to 10^6 Hz. Then, the ionic conductivities of S-SEs were calculated

through equation $\sigma=L/SR$, where L (1.53 cm) represented the thickness of S-SEs; S (0.785 cm²) was the area of the wafer; and R was the total resistance of S-SEs. Before the measurement, S-SEs powders (120 mg) were cold pressed into wafers under 300 MPa in a PEEK die with a diameter of 10 mm and sandwiched by two stainless steel (SS) wafers. Meanwhile, the galvanostatic polarization curves of these S-SEs were also tested by the electrochemical station, and the S-SEs were processed by the same pre-operation. 7200 test points in total were measured within 2 h. The average value of the last 1000 points was considered as the steady-state current, and the electronic conductivities of S-SEs were calculated by the equation $\gamma=I_s \cdot L/S \cdot U$. In which the I_s represented the steady-state current; the U meant the applied voltage (5 V); the L (1.53 cm) and the S (0.785 cm²) was the thickness and the area of the S-SEs wafers.

Purity measurements by filtration:

Considering the impurities in the sintered Li₂S samples are insoluble in alcohol, a simple filtration method was used for purity detection based on the filtration test for impurities. 0.5 g of obtained Li₂S was dissolved into 50 mL alcohol and was fully stirred in the glove box. Then, the suspension was filtered in the filtration device, and the weight of the residue was measured (the weight difference of fully dried filter paper before and after the filtration), indicating the weight of impurities. The above-mentioned process would be repeated five times to minimize the errors, and finally obtain the purity of Li₂S by calculation.

Figures and Tables

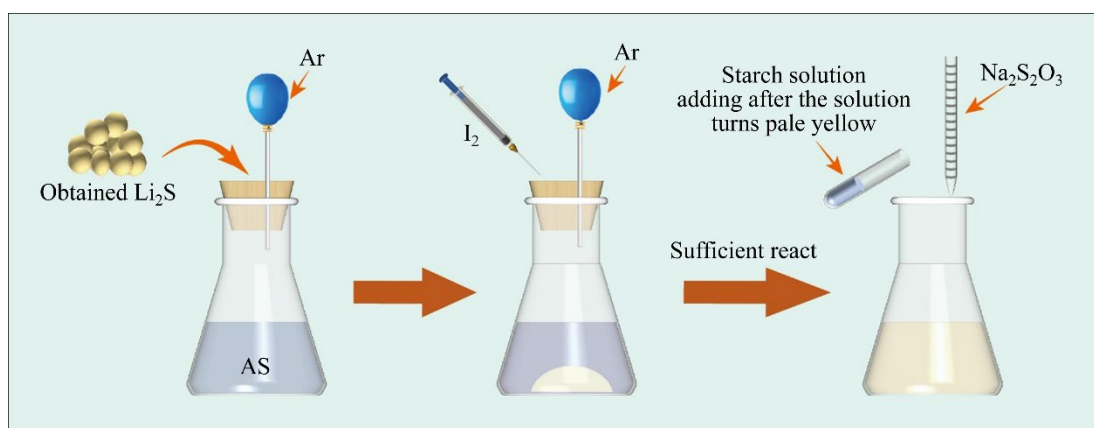


Figure S1 Schematic of iodometric titration process for purity test of Li₂S

Titration details:

During the titration process, the main occurring reactions are exhibited as below:



When Li₂S is added to the absorption solution, the S²⁻ is fixed as ZnS precipitation in case its volatilization into the air. After adding enough standard iodine solution, the S²⁻ in the system is oxidized to S by iodine. Then, the remaining iodine solution is titrated by Na₂S₂O₃, and the molar amount of I₂ consumed by S²⁻ oxidation in the reaction (S2) is calculated by the amount of Na₂S₂O₃, which is equal to the content of Li₂S. Finally, the purity of Li₂S is calculated [1].

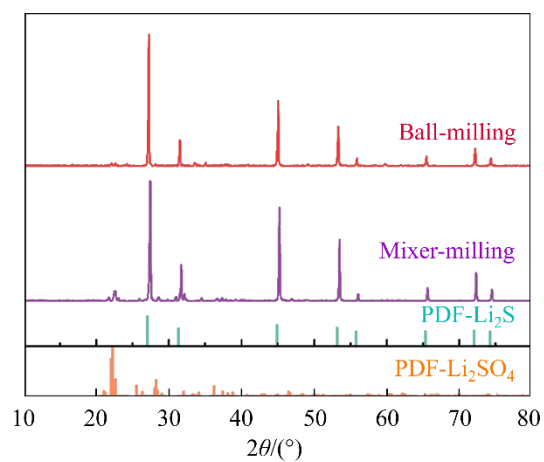


Figure S2 XRD patterns of Li_2S prepared by different mixing methods

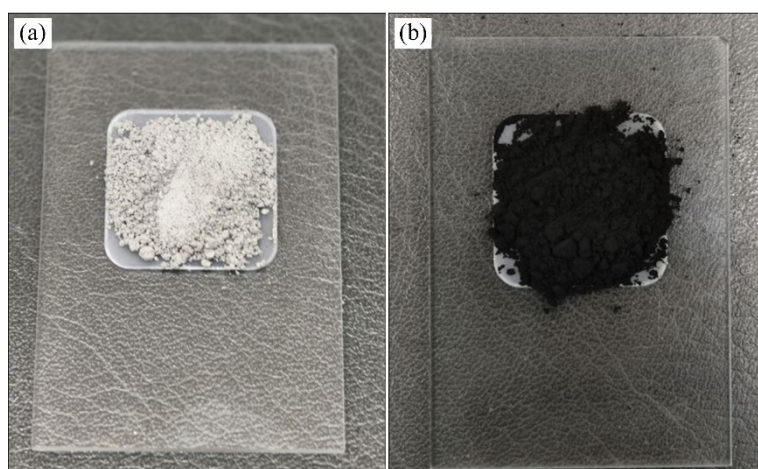


Figure S3 Photographs of Li_2S prepared by different mixing methods: (a) Ball-milling; (b) Mixer-milling

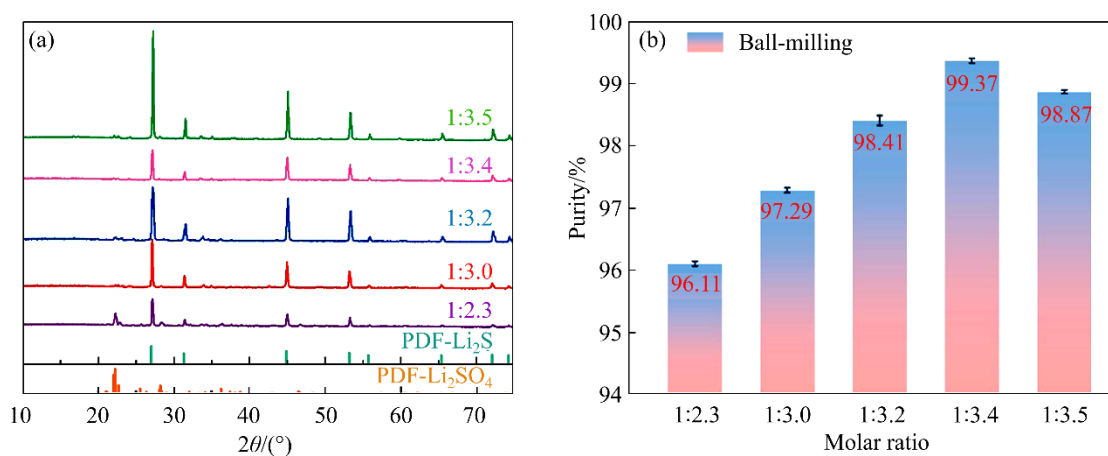


Figure S4 (a) XRD patterns and (b) purity of Li_2S mixed by ball-milling and sintered with various raw materials molar ratios from 1:2.3 to 1:3.5

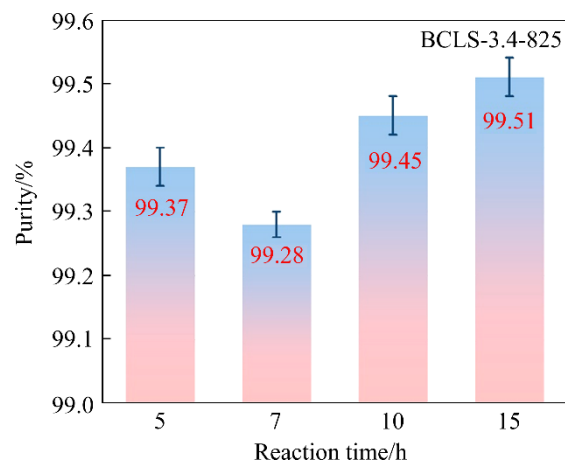


Figure S5 Purity of BCLS-3.4-825 by sintering for different time from 5 to 15 h

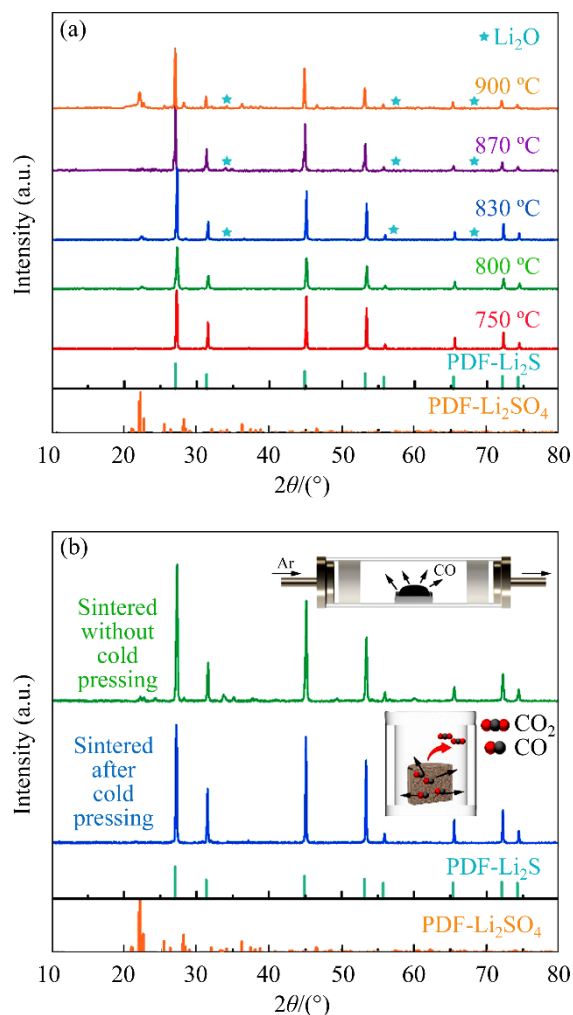


Figure S6 (a) XRD patterns of BPLS sintered at different temperature; (b) XRD patterns of Li_2S sintered with or without cold pressing

During the reaction process, Li_2S can be synthesized according to the following equation:

$$\text{Li}_2\text{SO}_4 + 2\text{C} \rightarrow \text{Li}_2\text{S} + 2\text{CO}_2(\text{g}) \quad (\text{S4})$$

$$\text{Li}_2\text{SO}_4 + 4\text{C} \rightarrow \text{Li}_2\text{S} + 4\text{CO}(\text{g}) \quad (\text{S5})$$

According to Gibbs' free energy, when the temperature reaches 680 °C, both reactions (S4) and (S5) can be spontaneous. And when the temperature reaches 725 °C, reaction (S5) is more favorable to occur [2]. Besides, the molar ratio of Li_2SO_4 and carbon is close to 1:4 in the precursor, which further promotes the reaction (S5) to generate CO. Moreover, the produced CO is also a reducing gas, which could promote Li_2SO_4 for the further reduction to obtain high purity Li_2S [3]. Figure S6(a) shows the XRD patterns of the samples obtained by compression sintering and un-compression sintering. During the sintering process, the low internal porosity of the compacted precursor leads to fewer channels and longer paths for the diffusion of generated CO. This provides a local high concentration of reducing atmosphere for the Li_2SO_4 reduction inside of the precursor wafer, and promotes the secondary purification of the obtained Li_2S [4].

In the reduction step, the primary side reaction occurring in an Ar atmosphere is represented by the following equation:



According to Gibbs' free energy theory, this reaction can only occur spontaneously when the temperature reaches 800 °C [5]. Figure S6(b) shows the XRD pattern of the cold-pressed sample after sintering at 750–900 °C. Only when the temperature reaches 830 °C, a small Li_2O peak can be seen in the XRD patterns, which indicates that the side reaction in the carbothermal reduction process is mainly affected by temperature.

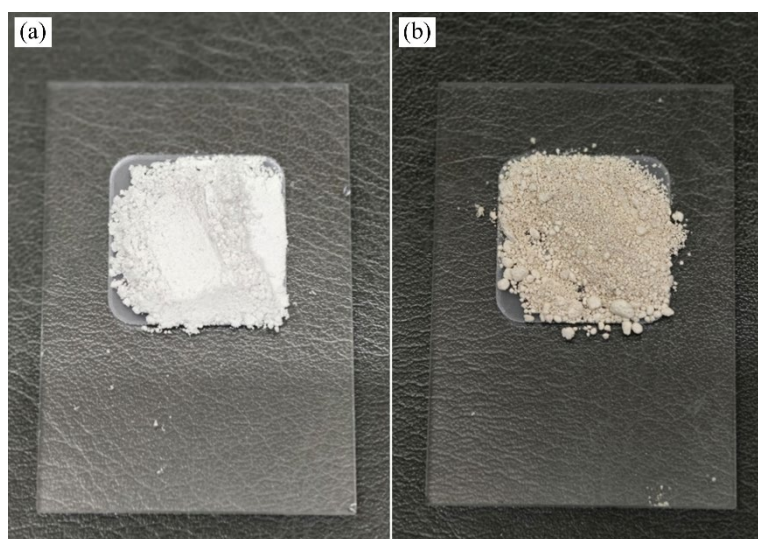


Figure S7 Photographs of (a) BPLS-3.7-750 and (b) CLS

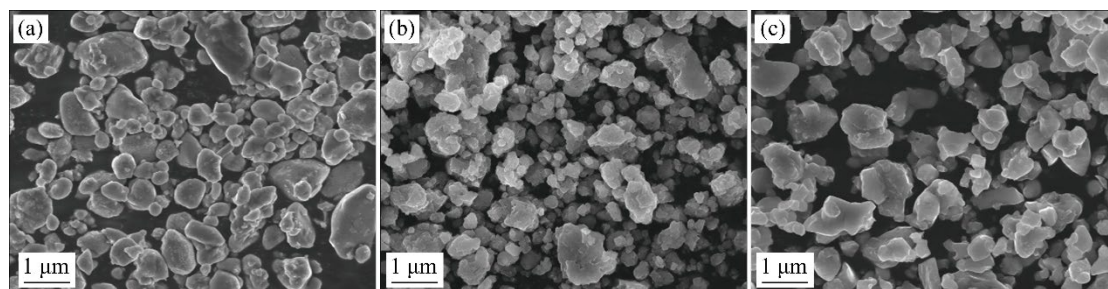


Figure S8 SEM images of (a) BC-LPSC, (b) BP-LPSC and (c) C-LPSC

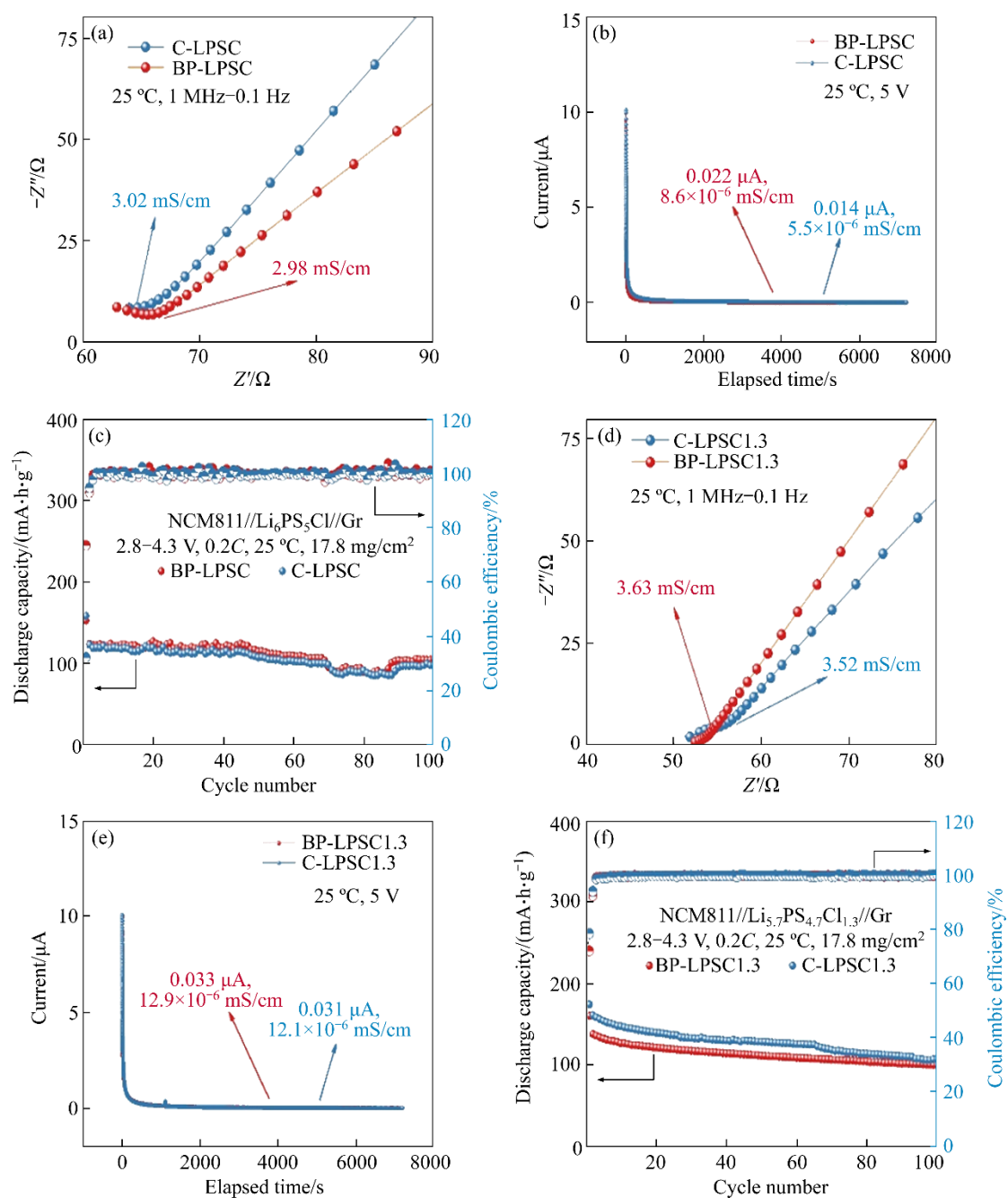


Figure S9 (a, d) Nyquist plots of BP-LPSC and C-LPSC (a), BP-LPSC1.3 and C-LPSC1.3 (d); (b, e) Time-dependent DC of SS//BP-LPSC//SS and SS//C-LPSC//SS (b), SS//BP-LPSC1.3//SS and SS//C-LPSC1.3//SS (e) under a constant voltage of 5 V and 25 °C; (c, f) Cycle performance curves of NCM811//Li₆PS₅Cl//Gr ASSLBs using BP-LPSC and C-LPSC (c) and NCM811//Li_{5.7}PS_{4.7}Cl_{1.3}//Gr ASSLBs using BP-LPSC1.3 and C-LPSC1.3 (f) at 25 °C

Table S1 Purity of Li₂S synthesized by different methods

Mixing method	Molar ratio	Sintering temperature/°C	Sintering time/h	Purity by filtration/%	Purity by titration/%
Mixer-milling	1:3	750	5	64.5	65.23
Mixer-milling	1:3	825	5	94.2	94.17
Mixer-milling	1:3	900	5	93.9	93.85
Mixer-milling	1:2	825	5	94.7	94.99
Mixer-milling	1:2.3	825	5	95.8	95.67
Mixer-milling	1:2.3	825	7	96.1	95.94
Ball-milling	1:2.3	825	5	96.3	96.11
Ball-milling	1:3	825	5	97.3	97.29
Ball-milling	1:3.2	825	5	98.4	98.41
Ball-milling	1:3.4	825	5	99.2	99.37
Ball-milling	1:3.5	825	5	98.7	98.87
Ball-milling	1:3.6	825	5	98.5	98.56
Ball-milling	1:3.4	750	5	96.7	96.78
Ball-milling	1:3.4	825	7	99.3	99.28
Ball-milling	1:3.4	825	10	99.3	99.45
Ball-milling	1:3.4	825	15	99.5	99.51
PVA-carbonizing	1:3	700	5	95.1	95.4
PVA-carbonizing	1:3.2	700	5	95.4	95.47
PVA-carbonizing	1:3.4	700	5	96.2	96.28
PVA-carbonizing	1:3.6	700	5	98.2	98.33
PVA-carbonizing	1:3.7	700	5	98.9	98.85
PVA-carbonizing	1:3.8	700	5	98.4	98.54
PVA-carbonizing	1:3.7	730	5	99.1	99.17
PVA-carbonizing	1:3.7	750	5	99.6	99.67
PVA-carbonizing	1:3.7	780	5	99.4	99.46
PVA-carbonizing	1:3.7	800	5	98.8	98.73
Commercial Li ₂ S				99.7	99.75

References

- [1] COLON M, TODOLÍ J L, HIDALGO M, et al. Development of novel and sensitive methods for the determination of sulfide in aqueous samples by hydrogen sulfide generation-inductively coupled plasma-atomic emission spectroscopy [J]. *Analytica Chimica Acta*, 2008, 609(2): 160–168. DOI: 10.1016/j.aca.2008.01.001.
- [2] KOHL M, BRÜCKNER J, BAUER I, et al. Synthesis of highly electrochemically active Li₂S nanoparticles for lithium–sulfur-batteries [J]. *J Mater. Chem. A*, 2015, 3(31): 16307–16312. DOI: 10.1039/C5TA04504E.
- [3] NAN Bing, FU Qiang, YU Jing, et al. Unique structure of active platinum-bismuth site for oxidation of carbon monoxide [J]. *Nature Communications*, 2021, 12(1): 3342. DOI: 10.1038/s41467-021-23696-7.
- [4] YU Rui-jiao, GUO Hang, YE Fang, et al. Multi-parameter optimization of stepwise distribution of parameters of gas diffusion layer and catalyst layer for PEMFC peak power density [J]. *Applied Energy*, 2022, 324: 119764. DOI: 10.1016/j.apenergy.2022.119764.
- [5] LI Zhe, ZHANG Shi-guo, ZHANG Ce, et al. One-pot pyrolysis of lithium sulfate and graphene nanoplatelet aggregates: In situ formed Li₂S/Graphene composite for lithium-sulfur batteries [J]. *Nanoscale*, 2015, 7(34): 14385–14392. DOI: 10.1039/C5NR03201F.