Understanding crucial roles of natural clinochlore in reinforcing Li-S batteries

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Fabrication of Cli-C@PP Separator: Briefly, 0.2 g of clinochlore powders, 0.2 g of carbon black (Super-P, Nanjing Modges Energy Technology Co., LTD), and 0.1 g of PVDF binder (Nanjing Modges Energy Technology Co., LTD) were added into 8 mL of N, N-Dimethylformamide (DMF) and stirred for 12 h to form an even slurry. The even slurry was then coated onto the surface of the commercial Celgard 2500 separator (PP) and then dried at 60 °C for 12 h.

Carbon/sulfur (C/S) Cathode Synthesis: Carbon (Super C45, MTI, HF-Kejing) and sublimed sulfur (Canrd New Energy Technology Co., Ltd) with a ratio of 3:7 were ground uniformly in a mortar to obtain a C/S mixture. The C/S mixture was then heated at 160 °C for 12 h to obtain a C/S composite. A slurry was prepared through mixing 80% of C/S composite, 10% of Super C45, and 10% of PVDF in NMP and stirred for 8 h. The obtained slurry was doctor-bladed onto carbon-coated Al foil and dried at 60 °C for 12 h. For high sulfur loading, the cathode slurry was coated onto the surface of carbon paper.

Physical Characterization: The lattice feature of clinochlore powders were studied by X-ray diffraction (Bruker D8). Scanning electron microscopy (FEI Inspect F50), high-resolution transmission electron microscopy (Talos, F200S) was used for imaging the morphology and structure. X-ray photoelectron spectroscopy (ESCALAB Xi₊, Thermo Fisher Scientific, USA) was applied to explore valence state change of clinochlore. ThetaLite (Biolin instrument, Finland) was used for checking the static contact angle of PP, C@PP and Cli-C@PP separators.

Electrochemical Characterization: CR2032 coin cells were assembled with the C/S cathode, lithium metal anode, PP, C@PP or Cli-C@PP separators in the Ar-filled glove box, respectively. 1.0 M LiTFSI in a DME-DOL solution (1:1 v/v) with 2wt% LiNO₃ was used as the Li-S batteries electrolyte. The rate and cyclic performances of cells were measured with a galvanostatic mode at a voltage window of 1.7 V~ 2.8 V using Neware battery testing system (Neware, China). Cyclic voltammetry of Li-S cells was performed on a CHI660 electrochemical station with a voltage window of 1.7 V~ 2.8 V at 0.2 mV s⁻¹. Electrochemical impedance spectroscopy of cells were also measured with CHI660 electrochemical station with an AC amplitude of 0.05 V in the frequency range of 0.1 Hz ~ 100000 Hz. For high sulfur loading cathode, the E/S ratio was 8.0 μ L mg⁻¹. Symmetrical Cells Assembling and Testing: Symmetrical cells were assembled to investigate the conversion kinetics of Li_2S_6 on the surfaces of carbon and clinochlore, respectively. The working electrode and counter electrode were prepared by coating identical active material and PVDF on carbon paper at a ratio of 4:1. 60 µL of 0.1 M Li₂S₆ solution was used as the electrolyte. Cyclic voltammetry measurements were performed on a CHI660 electrochemical station with a voltage window of -1.5~1.5 V at 5 mV s⁻¹.

Li₂S Dissolution Tests: First, 0.25 M Li₂S₈ electrolyte was prepared by mixing Li₂S (Aladdin, China) and sulfur powders at a molar ratio of 1:7 and dissolved into ethylene glycol dimethyl ether with 1.0 M LiTFSI by stirring at 50 °C for 24 h. Clinochlore, carbon and PVDF were uniformly dispersed in NMP and then dropped onto carbon paper to obtain the cathode. For the Li₂S dissolution, coin-type cells were assembled with the commercial Celgard 2400 as separator, and the lithium foil as anode. 20 μ L of Li₂S₈ electrolyte was added to the cathode side, and 20 μ L of 1M LITFSI electrolyte was dropped onto the lithium anode side. The batteries were galvanostatically discharged to 1.70 V at 0.10 mA. Then, the cells were potentiostatically charged at 2.35 V until 25000 s for the sufficient dissolution of Li₂S.

In-situ Raman Spectroscopy: Li-S coin cells with a quartz window on positive shell were used for *in-situ* Raman spectroscopy measurements with Renishaw InVia Raman microscopy. For the investigation the shuttling effect of lithium polysulfides, a hole with 3 mm is firstly made on the lithium metal to collect Raman signals on the separator/Li metal interface. The cells were run at a galvanostatic mode with a charge/discharge rate of 0.1 C. Raman signals were simultaneously recorded using a 785 nm laser with a 1 μ m laser spot on the separators near the lithium ring.

Calculation Methods: Spin-polarized Density functional theory calculations were all conducted with the plane-wave code Vienna ab-initio simulation package (VASP) program within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation and the Van der Waals interactions are included with the DFT-D3 method of Grimme. The projected augmented wave (PAW) potentials were employed to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 500 eV. The valence electron configurations applied in this work are $3s^23p^2(Si)$, $3s^23p^1(Al)$, $2p^63s^2(Mg)$, $1s^22s^2$ (Li), $3s^23p^4$ (S), $2s^22p^4$ (O), $1s^1$ (H), respectively. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.02 eV. The electronic

energy was considered self-consistent when the energy change was smaller than 10^{-6} eV. The clinochlore (001) surfaces was applied to build up the calculation models. This slab was separated by a 15 Å vacuum layer in the Z direction between the slab and its periodic images. During structural optimizations of the surface models, a $3 \times 2 \times 1$ gamma-point centered k-point grid for Brillouin zone was used. And all the atomic layers were allowed to fully relax. The adsorption energy (E_{ads}) of an adsorbate A was defined as:

$E_{ads} = E_{ads/surf} - E_{surf} - E_{ads}$

where $E_{ads/surf}$, E_{surf} and E_{ads} are the energy of the adsorbates adsorbed on the surface slab, the energy of surface slab, and the energy of adsorbates respectively. To study the lithium ion migration barrier on the clinochlore surface, the energy barriers were determined by using the climbing image nudged elastic band (CI-NEB) method. The free energy was calculated using the equation:

$$G = E_{ads} + ZPE - TS$$

where G, E_{ads} , ZPE and TS are the free energy, total energy from DFT calculations, zero point energy, and entropic contributions, respectively.



Figure S1. a, SEM image of clinochlore powders. b, TEM image of clinochlore powders.



Figure S2. Characterization of the Cli-C@PP separator. **a**, SEM images of the Cli-C@PP separator, the inset is the digital picture of Cli-C@PP separator. **b**, Cross-section SEM images of the Cli-C@PP separator. **c-e**, Contact angle tests of the PP, C@PP and Cli-C@PP separators, respectively. **f**, EDS elemental mapping of the Cli-C@PP separator.



Figure S3. a, The whole diffusion pathway of Li ion on the clinochlore surface.



Figure S4. SEM and Cross-section SEM images of Li anodes based on PP (a, b), C@PP (c, d), and Cli-C@PP (e, f) cells after dendrite tests, the inset pictures are the digital photos of Li anodes retrieved from Li||Li symmetric cells.



Figure S5. **a-c**, CV curves of PP, C@PP and Cli-C@PP cells at various scan rates of 0.2, 0.4, 0.6 mV s⁻¹, respectively. Relationship between the peak current and the square root of scan rate ($v^{1/2}$) at **d**) I_{C1}, **e**) I_{C1}, and **f**) I_A.



Figure S6. Observation of polysulfide migration in homemade H-type cells.



Figure S7. a-f, The simulated adsorption structures of Li_2S , Li_2S_2 , Li_2S_4 , Li_2S_6 , Li_2S_8 and S_8 on the carbon surface. **g**, **h**, The simulated adsorption structures of S_8 and Li_2S on the clinochlore surface.



Figure S8. a, b, Potentiostatic charge curves of the 0.25 M Li_2S_8 electrolyte at 2.35 V on the carbon paper and carbon.

Separators	Capacity (mAh g ⁻¹)	Fading rate (%)	Cycles number	Loading sulfur	Refs
	Current density	Current density			
CBC-based SnO ₂ -SnS ₂	592.8 (3 C)	0.031% (1.5 C)	1000	-	1
MXene/MOF	504 (1 C)	-	100	mg cm ⁻²	2
CoS ₂ /Fe ₇ S ₈ @PP	521 (4 A g ⁻¹)	0.058% (1 A g ⁻¹)	500	mg cm ⁻²	3
FeOOH@PP	449 (2C)	0.05% (0.5 C)	500	3 mg cm ⁻²	4
MnO ₂ @PP	494 (2 C)	0.058% (0.5 Ć)	500	mg cm ⁻²	5
Ni-Co-P@C@PP	654.5 (5 Ć)	0.056% (0.5 C)	1000	1.8 mg cm ⁻²	6
CoS2/HPGC@PP	650 (2 C)	0.07% (1 C)	500	3.0 mg cm ⁻²	7
Asy-PP	769.5 (5 Ć)	0.03% (5 C)	1000	1.0-1.3 mg cm ⁻²	8
SB@PDA-PE	740.1 (5 C)	0.034% (3 Ć)	1200	2.0 mg cm ⁻²	9
L3DCO/3PS-PP	756 (5 C)	0.1% (1 C)	300	1.4 mg cm ⁻²	10
Al-CPP/PP	812 (4 C)	0.12% (1 Ć)	500	1.0 mg cm ⁻²	11
Mn/SNC-PP	302.9 (6 C)	0.037% (2 C)	1600	1.2 mg cm ⁻²	12
NiS ₂ -MnS-PP	456.2 (5 C)	0.0265% (3 Ć)	1000	2.52 mg cm ⁻²	13
CoFe@NC//PP	604 (4 C)	0.059% (1 C)	1000	1.4 mg cm ⁻²	14
TaVG-PP	853 (3 C)	0.03% (2 C)	1200	1.2 mg cm ⁻²	15
C-Fe-Phytate@PP	690 (5 C)	0.058% (1 Ć)	800	1.4 mg cm ⁻²	16
Cli-C@PP	770 (5 C)	0.072% (1 C)	500	1.4 mg cm ⁻²	This work

Table S1 Comparison with the reported lithium-S batteries separator.



Figure S9. The cyclic performances of Cli-C@PP separator at 1 C rate with different ratios of clinochlore powders, carbon black and 0.1 mg of PVDF binder. The results show that separator modified by 0.2 g of clinochlore powders, 0.2 g of carbon black, and 0.1 g of PVDF binder (namely: 4:4:2) show the best cyclic performances.



Figure S10. **a-c**, Cross-section SEM images of Li anode after cycling tests based on the PP, C@PP and Cli-C@PP cells, respectively. **d-f**, Sulfur elemental mapping on the Li anode surfaces after cycling tests based on the PP, C@PP and Cli-C@PP cells, respectively.

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