Perovskite-type La_{0.56}Li_{0.33}TiO₃ as an effective polysulfide promoter for stable lithium-sulfur batteries in lean electrolyte condition

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Experimental. All the chemicals were analytical grade without further purification. La_{0.56}Li_{0.33}TiO₃ was prepared via a sol-gel route as follows. Stoichiometric amount of citric acid (A.R.), Ti(OBu)₄ (A.R.), La(NO₃)₃•6H₂O (A.R.) and LiNO₃ (A.R.) was successively dissolved in ethanol (A.R.) under stirring at room temperature. In order to get gel, the above solution was placed into an oil bath at 80 °C with continued stirring. Then synthesized gel was dried at oven under 80 °C to form xerogel. After grind, the xerogel was sintered at 350 °C for 4 h. The obtained precursor was ground again and then calcined at 900 °C for 2 h. Finally, the La_{0.56}Li_{0.33}TiO₃ (LLTO) was obtained.

Synthesis of the LLTO/CNT/S composite. Sulfur was infused into the composite hosts by a melting-diffusion method. Typically, LLTO, CNT (original from Cnano Technology, Beijing, China) and sulfur powders mixed in a weight ratio of 7:23:70

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were strongly grinded for 10 min, and then were sealed in a vial and heated at 155 °C for 12 h, affording LLTO-7/CNT/S. The areal amount of LLTO was 0.38 mg cm⁻². LLTO-10/CNT/S, LLTO-15/CNT/S, TiO₂-7/CNT/S (TiO₂ original from aladdin) and CNT/S were prepared in similar ways except for using different weight ratios for the mixture. The areal loadings of sulfur for the LLTO-15/CNT/S, TiO₂-7/CNT/S and CNT/S were about 3.8 mg cm⁻².

Materials Characterization. The structures and morphologies of the as-synthesized composites were performed via scanning electron microscopy (SEM, Hitachi S-4800). To investigate the phase ingredient of the samples, X-ray diffraction (XRD, Model LabX-6000, Shimadzu, Japan) was recorded under the 2θ range of 10° - 80° . To investigate the sulfur loading in the as-prepared samples, thermogravimetric analyses (TGA) was conducted on a Series Q500 instrument (TA Instruments, USA) in an N₂ atmosphere at 10 °C min⁻¹ from room temperature to 600 °C. To research the surface chemical component and functional groups of the as-prepared samples, X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific) were examined.

Electrochemical Measurements. The cathode electrodes were synthesized by active material and polyvinylidene fluoride (PVDF) binder and the mixed slurry of the weight ratio was 90:10. The mixed slurry was casted on a carbon-coated aluminum foil. Various sulfur areal loadings were obtained via the doctor blade-coating technology. Then, the foil was dried at 60 °C for 12 h in the vacuum and cut into disks of 10 mm diameter. The electrolyte is 1 mol L⁻¹ lithium bis(trifluoromethane)

sulfonimide (LiTFSI) in a mixture of equal volumes of 1,3 dioxolane (DOL) and 1,2dimethoxyethane (DME) with the 1 wt% LiNO₃ additive. The anode was metal lithium and the separator was the Celgard 2400 membranes. The coin cells were fabricated in the glove box under argon atmosphere. The galvanostatic charge/discharge data were carried out on a battery testing system (CT-3008, Neware Co., Ltd.) between 1.7 and 2.8 V (vs Li⁺/Li). The cyclic voltammetry (CV) was tested on an electrochemical workstation (Princeton Applied Research VersaSTAT3, AMETEK, Inc.) with a low scan rate of 0.1 mV s⁻¹ and a wide voltage range of 1.7-2.8 V. The electrochemical impedance spectroscopy (EIS) was researched by the same instruments over a frequency range from 100 kHz to 1 Hz with an alternating current voltage of 5 mV.

Lithium polysulfides adsorption tests. Lithium polysulfide (Li₂S₆) solution was prepared by dissolving the stoichiometric amounts of sulfur and lithium sulfide (Li₂S) with a molar ratio of 5:1 in a mixed solvent of DME/DOL (1:1 by volume). The concentration of Li₂S₆ solution was set as 5 mmol L⁻¹.

Assembly of Li_2S_6 symmetric cells. The mixtures of mass ratio of LLTO to PVDF binder was 90:10. The mixed slurry was casted on a carbon-coated aluminum foil. Then, the foil was dried at 60 °C for 12 h in the vacuum and cut into disks of 10 mm diameter. Two identical electrodes were assembled into a standard 2025-coin cell with a PP membrane as the separator, and Li_2S_6 -based electrolyte was added. The electrolyte also contained 1 mol L⁻¹ LiTFSI and 1% LiNO₃. The CV of symmetric cell was performed at a scan rate of 10 mV s⁻¹ between -0.8 V and 0.8 V.



Fig. S1 (a) Transmission electron microscopy and (b) High-resolution transmission electron microscopy images of LLTO.



Fig. S2 Contact angle images of water on the (a) CNT@PP and (b) LLTO@PP membranes.



Fig. S3 TGA traces for (a) CNT/S in N_2 , (b) LLTO-7/CNT/S in Air, CV curves of (c) CNT/S, (d) LLTO-7/CNT/S.



Fig. S4 (a) Cycle performance and (b) charging-discharging curves of LLTO/CNT.



Fig. S5 (a) Cycle performance for the TiO_2 -7/CNT/S electrode at 0.8 mA cm⁻² under lean electrolyte condition (E/S=6), Capacity analysis of (b) upper-discharge plateau (Q_H) and (c) lower-discharge plateau (Q_L) of the LSB for the as-prepared electrodes.



Fig. S6 Electrochemical impedance spectra (inset is the equivalent circuit) and relationship between Z' and $\omega^{-1/2}$ of the (a, b) 1st and (c, d) 50th cycle of the LLTO-7/CNT/S and CNT/S electrodes; the fitted impedance value of the as-prepared composites at (e) 1st and (f) 50th.



Fig. S7 Optical photographs of (a) LLTO-7/CNT/S and (b) CNT/S after cycles. SEM images of LLTO-7/CNT/S electrode (c) at 1st and (e) 50th cycles and CNT/S electrode (d) at 1st and (f) 50th cycles;



Fig. S8 SEM images of (a) LLTO-7/CNT/S, (b) LLTO-10/CNT/S, (c) LLTO-15/CNT/S, (d) CNT/S.



Fig. S9 CV curves of (a) LLTO-10/CNT/S, (b) LLTO-15/CNT/S.



Fig. S10 (a) Cycle performances for the as-prepared electrodes at 1.0 mA cm⁻² under lean electrolyte condition, the typical charge-discharge curves at different cycles for (b) LLTO-7/CNT/S, (c) LLTO-10/CNT/S and (d) LLTO-15/CNT/S.



Fig. S11 Cycle performance for the LLTO-15/CNT/S electrode at 0.8 mA cm⁻² under lean electrolyte condition (E/S=6).



Fig. S12 Charging/discharging voltage profiles for (a) LLTO-10/CNT/S, (b) CNT/S at various current densities.



Fig. S13 The cross sections for various sulfur areal loading (a) 3.8 mg cm^{-2} , (b) 5.2 mg cm^{-2} , (c) 6.4 mg cm^{-2} .



Fig. S14 Cycle performances of LLTO-10/CNT/S at 0.2 mA cm⁻² under lean electrolyte condition and different sulfur areal loading.

Samples	E/S (µL _E mg ⁻¹ s)	Current (mA cm ⁻²)	Initial Capacity (mAh g ⁻¹)	Capacity retention after 50 cycles (%)	Capacity retention after 100 cycles (%)
LLTO-7/CNT/S	7	0.4	988	96.2	94.9
		0.8	910	97.7	95.3
	6	1.0	837	87.3	83.9
LLTO-	6	2.0	702	75.5	64.4
10/CNT/S		1.0	852	90.9	89.9
	5	0.8	800	90.1	/
LLTO-	6	0.8	855	84.2	75.1
15/CNT/S		1.0	786	95.9	85.7

Table S1 Electrochemical performances of the as-prepared composites

Table S2 Electrochemical performances of the LLTO-10/CNT/S composite

Sulfur loading cm ⁻²)	areal (mg	$\begin{array}{c} E/S\\ (\mu L_E mg^{-1}s) \end{array}$	Initial areal Capacity (mAh cm ⁻²)	Reversible Capacity cm ⁻²)	areal (mAh	Capacity retention after 30 cycles (%)
3.8		6	3.7	3.5		94.6
5.2		5	4.5	4.0		88.9
6.4		6	4.9	4.3		87.8

Table S3 Electrochemical performances comparison with the reported polar cathodes

	Sulfur content (%) &Areal sulfur loading (mg cm ⁻²)	E/S (μL _E mg ⁻¹ s)	Reversible areal capacity (mAh cm ⁻²)	Capacity decay (cycle ⁻ ¹)	Refere nces
S/CC@Co ₄ N-	10%&1.25	45	1.40	0.23%(100 cycles, 0.5C)	[1]
PCNA					
S/Nb ₂ O ₅	60%&1.5	33	1.39	0.14%(200 cycles, 0.5C)	[2]
S/CNTs/Co ₃ S	56%&1.2	15	1.50	0.18%(100 cycles, 0.2C)	[3]
₄ -NBs					
S/NiS@C-HS	50%& 2.3	20	1.65	0.14%(200 cycles, 0.2C)	[4]
ZnS-CB/S	70%&1.4	12	1.23	0.10%(200 cycles, 0.2C)	[5]
FeP/rGO/CN	75%&1.0	10	1.04	0.20%(100 cycles, 0.1C)	[6]
Ts-S					
LLTO-	70%&3.8	6	2.80	0.10%(150 cycles, 1.0 mA	This
10/CNT/S				cm ⁻²)	work

CC@Co4N-PCNA: vertical zeolite imidazole frameworks (ZIFs) derived porous

carbon nanosheet arrays embedded by Co₄N nanoparticles;

CNTs/Co₃S₄-NBs: interconnected carbon nanotubes inserted/wired hollow Co₃S₄ nanoboxes;

C-HS: 3D carbon hollow spheres;

CB: carbon black.

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