Perovskite-type La$_{0.56}$Li$_{0.33}$TiO$_3$ as an effective polysulfide promoter for stable lithium-sulfur batteries in lean electrolyte condition

Manfang Chen, a Cheng Huang, a Yongfang Li, a Shouxin Jiang, a Peng Zeng, a Gairong Chen, b Hongbo Shu, a Hong Liu, a Zhihao Li, a Xianyou Wang a

(a: National Base for International Science & Technology Cooperation, National Local Joint Engineering Laboratory for Key Materials of New Energy Storage Battery, Hunan Province Key Laboratory of Electrochemical Energy Storage & Conversion, School of Chemistry, Xiangtan University, Xiangtan 411105, China

b: Chemistry & Chemical Engineering School, Xin Xiang Xue Yuan, Henan453003, China)

Experimental. All the chemicals were analytical grade without further purification. La$_{0.56}$Li$_{0.33}$TiO$_3$ was prepared via a sol-gel route as follows. Stoichiometric amount of citric acid (A.R.), Ti(OBu)$_4$ (A.R.), La(NO$_3$)$_3$•6H$_2$O (A.R.) and LiNO$_3$ (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$_{0.33}$TiO$_3$ (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.

* Corresponding author: Xianyou Wang Tel: +86 731 58293377; fax: +86 731 58292052. E-mail address: wxianyou@yahoo.com.
were strongly grind 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, TiO$_2$-7/CNT/S (TiO$_2$ 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, TiO$_2$-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 2$\theta$ 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 N$_2$ 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 1,2-dimethoxyethane (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 Li₂S₆ 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 Li₂S₆-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) 1\textsuperscript{st} and (c, d) 50\textsuperscript{th} cycle of the LLTO-7/CNT/S and CNT/S electrodes; the fitted impedance value of the as-prepared composites at (e) 1\textsuperscript{st} and (f) 50\textsuperscript{th}.
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 1<sup>st</sup> and (e) 50<sup>th</sup> cycles and CNT/S electrode (d) at 1<sup>st</sup> and (f) 50<sup>th</sup> 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.
Table S1 Electrochemical performances of the as-prepared composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>E/S (µL E mg⁻¹)</th>
<th>Current (mA cm⁻²)</th>
<th>Initial Capacity (mAh g⁻¹)</th>
<th>Capacity retention after 50 cycles (%)</th>
<th>Capacity retention after 100 cycles (%)</th>
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<tbody>
<tr>
<td>LLTO-7/CNT/S</td>
<td>7</td>
<td>0.4</td>
<td>988</td>
<td>96.2</td>
<td>94.9</td>
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<tr>
<td></td>
<td>6</td>
<td>0.8</td>
<td>910</td>
<td>97.7</td>
<td>95.3</td>
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<td>LLTO-10/CNT/S</td>
<td>6</td>
<td>1.0</td>
<td>837</td>
<td>87.3</td>
<td>83.9</td>
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<tr>
<td></td>
<td>5</td>
<td>2.0</td>
<td>702</td>
<td>75.5</td>
<td>64.4</td>
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<tr>
<td>LLTO-15/CNT/S</td>
<td>6</td>
<td>0.8</td>
<td>852</td>
<td>90.9</td>
<td>89.9</td>
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Table S2 Electrochemical performances of the LLTO-10/CNT/S composite

<table>
<thead>
<tr>
<th>Sulfur areal loading (mg cm⁻²)</th>
<th>E/S (µL E mg⁻¹)</th>
<th>Initial areal Capacity (mAh cm⁻²)</th>
<th>Reversible areal Capacity (mAh cm⁻²)</th>
<th>Capacity retention after 30 cycles (%)</th>
</tr>
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<tbody>
<tr>
<td>3.8</td>
<td>6</td>
<td>3.7</td>
<td>3.5</td>
<td>94.6</td>
</tr>
<tr>
<td>5.2</td>
<td>5</td>
<td>4.5</td>
<td>4.0</td>
<td>88.9</td>
</tr>
<tr>
<td>6.4</td>
<td>6</td>
<td>4.9</td>
<td>4.3</td>
<td>87.8</td>
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Table S3 Electrochemical performances comparison with the reported polar cathodes

<table>
<thead>
<tr>
<th>Sulfur &amp; Areal sulfur loading (mg cm⁻²)</th>
<th>Sulfur content (%)</th>
<th>E/S (µL E mg⁻¹)</th>
<th>Reversible areal capacity (mAh cm⁻²)</th>
<th>Capacity decay (cycle⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/CC@Co₄N-PCNA</td>
<td>10%&amp;1.25</td>
<td>45</td>
<td>1.40</td>
<td>0.23%(100 cycles, 0.5C)</td>
<td>[1]</td>
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<tr>
<td>S/Nb₂O₅</td>
<td>60%&amp;1.5</td>
<td>33</td>
<td>1.39</td>
<td>0.14%(200 cycles, 0.5C)</td>
<td>[2]</td>
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<tr>
<td>S/CNTs/Co₃S</td>
<td>56%&amp;1.2</td>
<td>15</td>
<td>1.50</td>
<td>0.18%(100 cycles, 0.2C)</td>
<td>[3]</td>
</tr>
<tr>
<td>S/NiS@C-HS</td>
<td>50% &amp; 2.3</td>
<td>20</td>
<td>1.65</td>
<td>0.14%(200 cycles, 0.2C)</td>
<td>[4]</td>
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<tr>
<td>ZnS-CB/S</td>
<td>70%&amp;1.4</td>
<td>12</td>
<td>1.23</td>
<td>0.10%(200 cycles, 0.2C)</td>
<td>[5]</td>
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<tr>
<td>FeP/rGO/CN</td>
<td>75% &amp; 1.0</td>
<td>10</td>
<td>1.04</td>
<td>0.20%(100 cycles, 0.1C)</td>
<td>[6]</td>
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<tr>
<td>LLTO-10/CNT/S</td>
<td>70%&amp;3.8</td>
<td>6</td>
<td>2.80</td>
<td>0.10%(150 cycles, 1.0 mA cm⁻²)</td>
<td>This work</td>
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</table>

CC@Co₄N-PCNA: vertical zeolite imidazole frameworks (ZIFs) derived porous carbon nanosheet arrays embedded by Co₄N nanoparticles.
CNTs/Co$_3$S$_4$-NBs: interconnected carbon nanotubes inserted/wired hollow Co$_3$S$_4$ nanoboxes;

C-HS: 3D carbon hollow spheres;

CB: carbon black.

References


