Nano-spatially confined and interface-controlled lithiation-delithiation combined in in-situ formed (SnS-SnS$_2$-S)/FLG composite: A route to ultrafast and cycle-stable anode for lithium-ion batteries

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Fig. S1. TG profile of (SnS-SnS$_2$-S)/FLG.

Fig. S2. DSC curves of EG and (SnS-SnS$_2$-S)/FLG.
Calculation of contents of SnS, SnS\(_2\), S, FLG in the (SnS-SnS\(_2\)-S)/FLG composite.

1. Based on the deconvoluted peak areas, the ratio of Sn\(^{4+}\)/Sn\(^{2+}\) is 0.4, the ratio of S\(^2-\)/S\(^0\) is 1.48. Set the content of SnS is \(x\), so the content of SnS\(_2\) is \(183\times0.4x/151\), the content of S is \(32\times(0.4x+0.4x^2)/1.5/151\), respectively.

2. Based on the TG curve of the (SnS-SnS\(_2\)-S)/FLG composite, 50 wt% of the weight is lost during 200–800 °C, which originates from the combustion of S, FLG and oxidation of SnS\(_x\).

\[
\begin{array}{cccccc}
\text{SnS} + O_2 & \rightarrow & \text{SnO}_2 + \text{SO}_2 & \Delta m & \text{SnS}_2 + 3O_2 & \rightarrow \text{SnO}_2 + 2\text{SO}_2 & \Delta m \\
151 & 151 & 0 & 183 & 151 & 32 \\
x & x & 0 & 183\times0.4x/151 & 0.4x & 32\times0.4x/151 \\
\end{array}
\]

Set the content of FLG is \(y\), and then equations can be:

\[
\begin{cases}
x + 183\times0.4x/151 + 32\times1.2x/151 + y = 1. \\
32\times0.4x/151 + 32\times1.2x/151 + y = 0.50.
\end{cases}
\]

So \(x = 0.357\), \(y = 0.379\).

Finally, the contents of SnS, SnS\(_2\), S, FLG in the (SnS-SnS\(_2\)-S)/FLG composite can be determined to be 35.7, 17.3, 9.1, 37.9 wt%.
Fig. S3. SEM images of (a) EG powder, (b) Sn powder, (c) S powder.
Fig. S4. HRTEM image of the SnS-SnS\(_2\)-S.

Fig. S5. HRTEM image of the SnS/FLG.
Fig. S6. HRTEM image of the SnS$_2$/FLG.

Fig. S7. HRTEM image of the (SnS-SnS$_2$)/FLG.
Fig. S8. Ex-situ XRD patterns of the (SnS-SnS$_2$-S)/FLG anode taken at different discharge/charge states (vs. Li/Li$^+$): (a) discharged to 1.6 V, (b) discharged to 0.85 V, (c) discharged to 0.01 V, (d) charged to 0.80 V, (e) charged to 2.0 V, (f) charged to 3.0 V. (Discharged/charged galvanostatically at 0.05 A g$^{-1}$).
Fig. S9. XRD patterns of the (SnS-S)/FLG and (SnS_2-S)/FLG.

Fig. S10. Cycling performance of the (SnS-S)/FLG and (SnS_2-S)/FLG tested at 0.2 A g\(^{-1}\).
Fig. S11. Elemental mapping of (SnS-SnS$_2$-S)/FLG after 500 charge/discharge cycles.
Fig. S12. Rate performance of SnS/FLG, SnS\textsubscript{2}/FLG and (SnS-SnS\textsubscript{2})/FLG tested at various current densities (vs. Li/Li\textsuperscript{+}).
Fig. S13. CV curves of (a) SnS/FLG, (b) SnS$_2$/FLG and (c) (SnS-SnS$_2$)/FLG at various scan rates, from 0.2 to 1.5 mV s$^{-1}$. 
Fig. S14. Capacitive contribution at different scan rates of (a) SnS/FLG, (b) SnS$_2$/FLG and (c) (Sn-SnS$_2$)/FLG.
Fig. S15. Corresponding relationship between peak currents and sweep rates of the SnS/FLG, SnS$_2$/FLG, (SnS-SnS$_2$)/FLG and (SnS-SnS$_2$-S)/FLG.

The anodic peak currents $I_p$ at different scan rates are adopted to calculate the Li$^+$ diffusion coefficients ($D$) of these electrodes according to the following Randles Sevcik equation: $I_p = 2.69 \times 10^5 ACD^{1/2}n^{3/2}\nu^{1/2}$, where $A$ stands for the anode area (cm$^2$), $C$ is for the shuttle concentration (mol cm$^{-3}$), $n$ is for the involved electron numbers in the redox action, and $\nu$ is for the scan rate (V s$^{-1}$). With this data, a fitting straight-line can be obtained with $\nu^{1/2}$ as the x-axis and $I_p$ as the y-axis. Therefore, the line slope and Li$^+$ diffusion coefficient can be calculated and listed in Table S1.

Table S1. Line slopes and Li$^+$ diffusion coefficients of the SnS/FLG, SnS$_2$/FLG, (SnS-SnS$_2$)/FLG and (SnS-SnS$_2$-S)/FLG.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Line slop</th>
<th>Diffusion coefficient (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS/FLG</td>
<td>0.06115</td>
<td>3.96×10$^{-7}$</td>
</tr>
<tr>
<td>SnS$_2$/FLG</td>
<td>0.06791</td>
<td>4.96×10$^{-7}$</td>
</tr>
<tr>
<td>(SnS-SnS$_2$)/FLG</td>
<td>0.08027</td>
<td>6.83×10$^{-7}$</td>
</tr>
<tr>
<td>(SnS-SnS$_2$-S)/FLG</td>
<td>0.08695</td>
<td>8.01×10$^{-7}$</td>
</tr>
</tbody>
</table>
Fig. S16. (a) Nyquist plots, (b) the corresponding linear fits in the low-frequency region of the SnS/FLG, SnS$_2$/FLG, (SnS-SnS$_2$)/FLG and (SnS-SnS$_2$-S)/FLG.
Fig. S17. CV profiles of (SnS-SnS$_2$-S)/FLG scanned at 0.1 mV s$^{-1}$ (vs. Na/Na$^+$).

In the first cathodic sweep, the peaks located at 0.75~1.95 V associate with the conversion reaction of S and SnS$_x$ with Na$^+$ as well as the formation of SEI. And the peaks at 0.01~0.5 V are ascribed to the alloying reaction between Sn and Na$^+$ to form Na$_x$Sn alloy. In the anodic sweep, the peaks at 0.09, 0.24 and 1.2 V correspond to the dealloying of Na$_x$Sn alloy and conversion of Sn with Na$_2$S. And the peaks at 2.0 and 2.35 V are ascribed to the conversion of Na$_2$S to polysulfides.