Supporting information for

Polysulfide-Driven Low Charge Overpotential for Aprotic Lithium-Oxygen Batteries

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Figure S1. SEM images showing the morphology of CNT cathode (a) before charge and (b) after the 1\textsuperscript{st} discharge. Scale bars, 200 nm (a), 500 nm (b).

Noted: The toroid-type products are observed after the 1\textsuperscript{st} discharge process for CNT cathode.
Figure S2. XRD patterns of CNT(1000 mAh g⁻¹) and CNT/Li₂S₆ (1000 mAh g⁻¹ and 7500 mAh g⁻¹) after the 1ˢᵗ discharge.
Figure S3. EDX result of the CNT/Li$_2$S$_6$ after the 1$^{st}$ discharge.
Figure S4. HR-TEM image for the 1\textsuperscript{st} discharge products of CNT/Li\textsubscript{2}S\textsubscript{6} cathode.
Figure S5. S 2p core-level XPS peak of the CNT cathode with Li$_2$S$_6$ additives before charge.

CNT was impregnated in the TEGDME solvent with Li$_2$S$_6$ additives, and then CNT was washed by acetonitrile and dried to do the XPS characterizations. We didn’t observe any obvious S 2p in XPS, demonstrating that the Li$_2$S$_6$ additives can be fully washed away by acetonitrile. Therefore, after the 1st discharge, the S signal observed on the CNT/Li$_2$S$_6$ cathode mainly originates from the discharge product, not from the remained Li$_2$S$_6$ additives.
Figure S6. DEMS of CNT/Li$_2$S$_6$ for (a) the 1$^{\text{st}}$ and (b) the 50$^{\text{th}}$ discharge process at a current of 0.7 mA at a limited capacity of 500 mAh g$^{-1}$.

The consumed ratio of electron and O$_2$ was confirmed by DEMS. O$_2$ is the only consumed gas and no evidence for the consumption of other gases (CO$_2$, H$_2$ etc.) during discharge process. The number of electrons per O$_2$ molecule for CNT/Li$_2$S$_6$ cathode is 1.23 (Figure S7a, Table S1). In addition, after the 50$^{\text{th}}$ discharge process, no O$_2$ consumption can be observed for the first platform.
Figure S7. Cyclic voltammograms of CNT/Li$_2$S$_6$ under O$_2$, where CNT/Li$_2$S$_6$ is first discharged to 2.0 V, then charged to 4.3 V, and finally the CNT/Li$_2$S$_6$ cathode conducts the second discharge process to 2.0 V.
Figure S8. (a) Cyclic voltammograms and (b) the corresponding 1st charge-discharge curves (b) of Li$_2$S$_6$ (Li-S batteries under O$_2$), where Li$_2$S$_6$ is first charged to 4.3 V, and then is discharged to 2.7 V; (c) cyclic voltammograms and (d) the corresponding 1st charge-discharge curve of Na$_2$S$_2$O$_3$ (Li-Na$_2$S$_2$O$_3$ batteries under O$_2$), where Na$_2$S$_2$O$_3$ is first charged to 4.3 V, and then is discharged to 2.7 V, (e) discharge-charge curves of
the \( \text{Li}_2\text{S}_6 \) under Ar (Li-S batteries under Ar), where \( \text{Li}_2\text{S}_6 \) is first discharged to 1.5 V, and then is charged to 3.0 V.

Since \( \text{Li}_2\text{S}_4\text{O}_6 \) is inactive in TEGDME solvent,[1] polysulfide (\( \text{Li}_2\text{S}_2 \) and soluble \( \text{Li}_2\text{S}_6 \)) and thiosulfate (\( \text{Li}_2\text{S}_2\text{O}_3 \)) are main active materials for charge process. Therefore, the charge processes of polysulfide (\( \text{Li}_2\text{S}_2 \) and \( \text{Li}_2\text{S}_6 \)) and \( \text{Li}_2\text{S}_2\text{O}_3 \) are separately studied by assembling two kinds of batteries: Li-S batteries (active materials: \( \text{Li}_2\text{S}_6 \) and \( \text{Li}_2\text{S}_2 \)) and Li/Na\( \text{S}_2\text{O}_3 \) batteries (active materials: \( \text{Na}_2\text{S}_2\text{O}_3 \)). Because the ORR occurred at 2.7 V, we should limit the discharge voltage of Li-S batteries and Li/Na\( \text{S}_2\text{O}_3 \) batteries above 2.7 V to separately study the discharge behavior. Therefore, we first charge the Li/Na\( \text{S}_2\text{O}_3 \) batteries and Li-S batteries to 4.0 V followed by discharging to 2.7 V under O\(_2\) atmosphere.

For Li-S batteries, charge processes of \( \text{Li}_2\text{S}_2 \) and \( \text{Li}_2\text{S}_6 \) were separately conducted. In terms of charge process of \( \text{Li}_2\text{S}_6 \) (Li-S batteries under O\(_2\)), two typical peaks at 3.14 V and 3.94 V (Figure S8a) as well as corresponding charge curve (Figure S8b) are observed. The peak at 3.14 V corresponds to the oxidation of \( \text{Li}_2\text{S}_6 \) to high-order polysulfide (\( \text{Li}_2\text{S}_x, 6 \leq x \leq 8 \)), while the peak at 3.94 V is ascribed to the oxidation of high-order polysulfide to sulfur (Figure S8a).[2] These two oxidation peaks are also be identified from CNT/\( \text{Li}_2\text{S}_6 \) cathode, implying that the peaks at 3.22 V and 3.86 V of CNT/\( \text{Li}_2\text{S}_6 \) are due to oxidation of low-order polysulfide (\( \text{Li}_2\text{S}_2 \) and \( \text{Li}_2\text{S}_6 \)) to high-order polysulfide (equation 3, \( \text{Li}_2\text{S}_x, 6 \leq x \leq 8 \)), and high-order polysulfide to sulfur, respectively.
For the oxidation process of Na$_2$S$_2$O$_3$ (Li-Na$_2$S$_2$O$_3$ batteries), the peak at 3.51 V (Figure S8c and S8d) is due to the oxidation of Li$_2$S$_2$O$_3$ to Li$_2$S$_4$O$_6$ and the capacity of 258 mAh g$^{-1}$ is near the theoretical capacity of Na$_2$S$_2$O$_3$ (339 mAh g$^{-1}$). Meanwhile, similar peak (3.55 V) is detected by charge process of CNT/Li$_2$S$_6$ cathode (Figure 3a), indicating that the middle peak of CNT/Li$_2$S$_6$ is due to the oxidation of Li$_2$S$_2$O$_3$ to Li$_2$S$_4$O$_6$.

For discharge process of Li-S batteries (active materials: Li$_2$S$_6$) under O$_2$, the peak at 2.84 V is due to the reduction of sulfur to high-order polysulfide (Li$_2$S$_x$, 6$\leq x \leq$8). In addition, inactive Li$_2$S$_4$O$_6$ is inactive and cannot be reduced from 4.0 V o 2.7 V. Therefore, the new reduction peak at 2.84 V of CNT/Li$_2$S$_6$ belongs to the conversion of sulfur to high-order polysulfide (Li$_2$S$_x$, 6$\leq x \leq$8).

It should be noted that the voltage of oxidation and reduction plateaus of Li$_2$S$_6$ (Li-S batteries under O$_2$) under O$_2$ are different from the typical oxidation and reduction potential of lithium-sulfur (Li-S) batteries under Ar (Figure S8e). This is due to the fact that Li$_2$S$_6$ (Li-S batteries under O$_2$) is charged under O$_2$ atmosphere, resulting in the obviously positive voltage shift of both oxidation and reduction plateau.
Figure S9. (a) Discharge curves of Li$_2$S$_6$ (Li-S batteries under Ar) when discharging to 1.85 V; (b) S 2p core level XPS spectrum of the discharge product when Li$_2$S$_6$ (Li-S batteries under Ar) is discharged to 1.85 V; (c) charge-discharge curves of Li$_2$S$_2$ (Li-S batteries under O$_2$). Li$_2$S$_2$ is first charged to 4.0 V, and then is discharged to 2.7 V.

Note: The mass of active materials in Figure S9a and Figure S9c is calculated by the mass of Li$_2$S$_6$, and CNT respectively.

For the oxidation process of Li$_2$S$_2$ under O$_2$, we obtained the Li$_2$S$_2$ when Li$_2$S$_6$ is discharged to 1.85 V under Ar. The main discharge product is Li$_2$S$_2$ despite the existence of Li$_2$S (Li-S batteries under Ar, Figure S9b). The Li$_2$S$_2$ is charged to 4.0 V, and then is discharged to 2.7 V under O$_2$ (Li-S batteries under O$_2$). During charge process, the platform at 3.14 V is due to the oxidation of Li$_2$S$_2$ to high-order polysulfide (Figure 9c, Li$_2$S$_x$, $6 \leq x \leq 8$), while the platform at 3.89 V is due to the oxidation of high-order polysulfide (Figure 9c, Li$_2$S$_x$, $6 \leq x \leq 8$) to sulfur. For discharge process, the discharge process from 3.2 V to 2.7 V is due to the reduction of sulfur to high-order polysulfide (Figure 9c, Li$_2$S$_x$, $6 \leq x \leq 8$)
Figure S10. The Li$_2$S$_6$ additives were charged to 3.6 V and 4.0 V under O$_2$, respectively. (a) S 2p core level XPS spectrum of the discharge product when Li$_2$S$_6$ (under O$_2$) is charged to 3.6 V; (b) S 2p core level XPS spectrum of the discharge products when Li$_2$S$_6$ (under O$_2$) is charged to 4.0 V.

We separately charged the Li$_2$S$_6$ (Li-S batteries under O$_2$) to 3.6 V and 4.0 V. No S signal can be identified in XPS results when Li$_2$S$_6$ is charged to 3.6 V, indicating the charge process of Li$_2$S$_6$ from 3.0 V to 3.6 V is due to oxidation of Li$_2$S$_6$ to soluble high-order polysulfide (Li$_2$S$_x$, $6 \leq x \leq 8$). Due to high solubility of high-order polysulfide, high-order polysulfide is totally washed by acetonitrile and cannot be detected by XPS (Figure S10a). When Li$_2$S$_6$ is charged to 4.0 V (Li-S batteries under O$_2$), the typical S$_{2p}$ peaks of charged products are in consistence with S$_8$ molecules. This result indicated that charge process of Li$_2$S$_6$ from 3.6 V to 4.0 V was due to oxidation of high-order polysulfide (Li$_2$S$_x$, $6 \leq x \leq 8$) to sulfur.
Figure S11. Charge profile of the CNT/S cathode under O$_2$.

The CNT/S cathode was charged from 3.0 V to 4.0 V under O$_2$. The voltage increases sharply and no obvious platform can be observed, indicating that sulfur is stable and cannot be oxidized from 3.0 V-4.0 V under O$_2$ atmosphere.
Figure S12. Cycle performance of Li$_2$S$_6$ (Li-S batteries under Ar). The higher charge capacity compared to the discharge capacity is due to the shuttle effect.
Figure S13. (a) Raman spectra of CNT/Li$_2$S$_6$ cathode after 50 cycles; (b) SEM images of CNT/Li$_2$S$_6$ cathode after 50$^{th}$ recharge; (c)-(d) EDX mapping of O and S for selected area in panel (b).
Table S1. O$_2$ electrochemistry quantified by DEMS: ratios of the number of electrons to oxygen molecules upon reduction (discharge process).

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>discharge(e/O$_2$)</th>
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<tbody>
<tr>
<td>CNT(Li$_2$S$_6$)</td>
<td>1 1.23</td>
</tr>
<tr>
<td></td>
<td>50 1.13</td>
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### Table S2. Summary of carbon-based catalysts and their related performance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Charge overpotential</th>
<th>Cycle performance</th>
<th>Ref</th>
</tr>
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<tr>
<td>Au@cracked carbon submicron tube</td>
<td>1.3 V at 400 mA g⁻¹</td>
<td>112 cycles at 400 mA g⁻¹ with 1000 mAh g⁻¹</td>
<td>[4]</td>
</tr>
<tr>
<td>Reduced graphene oxide (LiI)</td>
<td>around 0 V at 100 mA g⁻¹</td>
<td>2000 cycles at 1000 mA g⁻¹ with 1000 mAh g⁻¹</td>
<td>[5]</td>
</tr>
<tr>
<td>Carbonized and activated wood/Ru</td>
<td>0.72 V at 0.1 mA cm⁻¹</td>
<td>100 cycles at 0.1 mA cm⁻¹ with 0.6 mAh cm⁻¹</td>
<td>[6]</td>
</tr>
<tr>
<td>Mesoporous Carbon Nanocube/Ru (LiNO₃)</td>
<td>0.14 V at 200 mA g⁻¹</td>
<td>120 cycles at 400 mA g⁻¹ with 1000 mAh g⁻¹</td>
<td>[7]</td>
</tr>
<tr>
<td>Polyethylene film@CNT</td>
<td>0.4 V at 2000 mA g⁻¹</td>
<td>610 cycles at 400 mA g⁻¹ with 1000 mAh g⁻¹</td>
<td>[8]</td>
</tr>
<tr>
<td>Ketjen Black (UH₂O₂)</td>
<td>0.26 V at 100 mAg⁻¹</td>
<td>50 cycles at 500 mAg⁻¹ with 1000 mAh g⁻¹</td>
<td>[9]</td>
</tr>
<tr>
<td>Textile</td>
<td>0.75 V at 0.1 mA cm⁻¹</td>
<td>50 cycles at 0.1 mA cm⁻¹ with 1.0 mAh cm⁻¹</td>
<td>[10]</td>
</tr>
<tr>
<td>ZnO/VACNTs</td>
<td>0.63 V at 0.1 mA cm⁻¹</td>
<td>112 cycles at 0.1 mA cm⁻¹ with 1000 mAh g⁻¹</td>
<td>[11]</td>
</tr>
<tr>
<td>CNT/Li₂S₆</td>
<td>0.19 V at 0.5 A g⁻¹</td>
<td>147 cycles at 0.5 A g⁻¹ with 500 mAh g⁻¹</td>
<td>This work</td>
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References