Metal-organic framework-based separator for lithium–sulfur batteries

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Supplementary Figures:

Supplementary Figure 1 | (a) MOF thin film. (b) The Precursor MOF@GO separator. (c) The prepared MOF@GO separator. (d) GO separator. (e) The peered-off filter.
Supplementary Figure 2 | By SEM images, the GO laminates in lithium sulfur batteries were detached themselves gradually over time. (After 200th charge/discharge cycles with GO separator) (Scale bar, 1μm)
Supplementary Figure 3 | Characterization of MOF@GO separator. (a) SEM images depicted show that the detachment of GO laminates has been greatly relieved in the side of GO layers. (After 200th charge/discharge cycles with MOF@GO separator) (Scale bar, 1 μm) (b) The morphology of MOF particles remains intact in the side of MOF layers. (After 200th charge/discharge cycles with MOF@GO separator) (Scale bar, 100 nm)
Supplementary Figure 4 | Thermogravimetric analysis. The wt% of sulfur in the CMK-3/S composite was determined to ~70%, respectively.
Supplementary Figure 5 | The schematic images of permeating measurements. (a) There exits the polysulfide ions in the left side (Red solutions). (b) The MOF@GO separator lies between these two tubes. (c) The blank electrolyte is in the right side.
Supplementary Figure 6 | Characterization of GO laminates. SEM images depicted show the morphology of the pre-synthesized GO laminates. (Scale bar, 1μm)
Supplementary Figure 7 | (a) Tapping-mode AFM image and (b) the corresponding height profile of GO laminates.
Supplementary Figure 8 | The analyses based on the IR spectra. (a) The IR spectra of the dehydrated MOF particles before the electrochemical process. (b) The IR spectra of the MOF particles after the process over 100 charge/discharge cycles.
Supplementary Figure 9 | The illustration of solid UV-Vis spectra. The MOF particles illustrate no obvious changes before/after the charge/discharge process over 100 cycles.
Supplementary Figure 10 | The CVs in lithium sulfur batteries. (a) CV profiles with a pristine separator (Celgard 2400) at a scan rate of 0.1 mV s\(^{-1}\). (b) CV profiles with a MOF@GO separator at a scan rate of 0.1 mV s\(^{-1}\).
**Supplementary Figure 11** | CVs at different scan rates of lithium sulfur batteries with (a) pristine separator (Celgard 2400) and (b) MOF@GO separators in lithium sulfur batteries. (c) The linear fits of the CV peak currents for the lithium sulfur batteries with pristine separator ($\alpha_1, \beta_1, \gamma_1$) and with MOF@GO separators ($\alpha_2, \beta_2, \gamma_2$).

**Supplementary Figure 12** | Electrical impedance of (a) pristine separator (Celgard) and (b) MOF@GO separator. Ion conductivity of (c) pristine separator (Celgard) and (d) MOF@GO separator.
**Supplementary Figure 13** | Nitrogen sorption data for MOF@GO separators. N$_2$ sorption isotherm at 77 K and its analytical pore size distribution.
Supplementary Figure 14 | The grown crystal facets at different growth rates on the basis of crystalline growth mechanism. (a) Cubic, along the (001) direction. (b) Octahedron, along the (111) direction. (c) Cuboctahedron, along the (001) direction and (111) direction simultaneously.
Supplementary Figure 15 | The structural properties of binuclear Cu(II) paddlewheel subunits.

After dehydration (removing the water in cavities), it provides the only affordable vacancy for the formation of Cu-S bond.
Supplementary Figure 16 | The IR spectra of the MOF samples after the charge or discharge over 50th cycles. (Under the adequate dehydration)
Supplementary Table

**Supplementary Table 1** | Comparisons of the linear fitting values with/without MOF@GO separator

<table>
<thead>
<tr>
<th></th>
<th>$D(\alpha)$ (cm$^2$/s)</th>
<th>$D(\beta)$ (cm$^2$/s)</th>
<th>$D(\gamma)$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine Separator</td>
<td>1.45×10$^{-9}$</td>
<td>2.0×10$^{-8}$</td>
<td>2.0×10$^{-9}$</td>
</tr>
<tr>
<td>MOF@GO Separator</td>
<td>1.5×10$^{-9}$</td>
<td>1.5×10$^{-8}$</td>
<td>2.1×10$^{-9}$</td>
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</table>

**Supplementary Table 2** | Comparisons of the electrochemical performance with serial separators in lithium-sulfur batteries

<table>
<thead>
<tr>
<th>Separator</th>
<th>Sulfur Cathode</th>
<th>Sulfur wt%</th>
<th>mass area ratio / mg/cm$^2$</th>
<th>Cycles</th>
<th>Initial Capacity mAh g$^{-1}$</th>
<th>Capacity Retention mAh g$^{-1}$</th>
<th>Fading rate (per cycle)</th>
<th>Current density</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super P / Celgard</td>
<td>Sulfur/ Super P</td>
<td>60%</td>
<td>0.5</td>
<td>500</td>
<td>1350</td>
<td>740</td>
<td>0.09%</td>
<td>0.5C</td>
<td>3</td>
</tr>
<tr>
<td>graphene / PP</td>
<td>Sulfur/ Carbon Black</td>
<td>70%</td>
<td>1.3</td>
<td>500</td>
<td>933</td>
<td>663</td>
<td>0.064%</td>
<td>1C</td>
<td>4</td>
</tr>
<tr>
<td>Graphene Oxide</td>
<td>Sulfur/ Carbon nanotubes</td>
<td>63%</td>
<td>0.12</td>
<td>100</td>
<td>920</td>
<td>708</td>
<td>0.23%</td>
<td>0.1 C</td>
<td>1</td>
</tr>
<tr>
<td>single-wall carbon nanotube</td>
<td>Sulfur/ Super P</td>
<td>70%</td>
<td>0.13</td>
<td>300</td>
<td>1132</td>
<td>501</td>
<td>0.18%</td>
<td>0.2 C</td>
<td>5</td>
</tr>
<tr>
<td>Carbon coating</td>
<td>Sulfur/ Super P</td>
<td>60%</td>
<td>0.2</td>
<td>200</td>
<td>1389</td>
<td>828</td>
<td>0.2%</td>
<td>0.2 C</td>
<td>6</td>
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<tr>
<td>MCNT@PEG</td>
<td>Sulfur/</td>
<td>60%</td>
<td>0.15</td>
<td>500</td>
<td>1250</td>
<td>490</td>
<td>0.12%</td>
<td>1 C</td>
<td>7</td>
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</table>
### Supplementary Note

**Supplementary Note 1. Calculation of Li\(^+\) diffusion coefficients**

The ion conductivity of our MOF@GO separator has been calculated, which indicates the highly transport capability to lithium ions against polysulfide anions. Generally, the MOF@GO separator can introduce no notable influence on the transfer of lithium ions across the separator, and play an important role in blocking the dissolved polysulfide ions simultaneously. Therefore, we have studied impedance properties to gain a better understanding the electrochemical performance due to the diffusion effect on sulfur cathode in cells. Compared with the lithium batteries with/without MOF@GO separators, a series of CVs with different scan rates are used to investigate Li\(^+\) diffusion coefficients according to the equation, to confirm whether the diffusion from sulfur cathode side to the anode side has to be subjected to great suppression or impediment:

<table>
<thead>
<tr>
<th></th>
<th>Carbon Paper</th>
<th>Sulfur/Carbon Paper</th>
<th>Sulfur/Super P</th>
<th>PEG/Microporous Carbon Sulfur/Super P</th>
<th>MOF@GO Sulfur/CMK3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>50%</td>
<td>0.7</td>
<td>500</td>
<td>781</td>
<td>468</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.08%</td>
<td>1 C</td>
</tr>
<tr>
<td>Mesoporous carbon</td>
<td>60%</td>
<td>0.5</td>
<td>500</td>
<td>1059</td>
<td>683</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.071%</td>
<td>1 C</td>
</tr>
<tr>
<td>PEG/Microporous Carbon</td>
<td>70%</td>
<td>0.15</td>
<td>500</td>
<td>1300</td>
<td>780</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.08%</td>
<td>1 C</td>
</tr>
<tr>
<td>MOF@GO</td>
<td>70%</td>
<td>0.3</td>
<td>1,500</td>
<td>1207</td>
<td>855</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.019%</td>
<td>1 C</td>
</tr>
</tbody>
</table>

This work
The equation\(^1\):

\[ I_p = 2.69 \times 10^5 n^{3/2} S D^{1/2} v^{1/2} C \]  
(Equation S1)

where \( n \) is the number of electrons per specific reaction, for \( Li^+ \) it is 1; \( S \) is the surface area of the electrode which is 1.53 cm\(^2\) in this work; \( C \) is the concentration of \( Li^+ \) ions in the material, \( I_p \) is the current intensity and \( v \) is the scan rate. And the diffusion coefficients could be calculated using the slope of fitting line \( I_p \) and \( v^{1/2} \). Under the conditions with pristine separators (Celgard 2400 separators), the anodic peak was assigned at around 2.5 V and the cathodic peaks at around 2.0 and 2.3 V as peak \( \alpha_1, \beta_1, \gamma_1 \), respectively.

The values are evaluated to be \( D(\alpha_1) = 1.45 \times 10^{-9} \) cm\(^2\)/s; \( D(\beta_1) = 2.0 \times 10^{-9} \) cm\(^2\)/s; \( D(\gamma_1) = 2.68 \times 10^{-9} \) cm\(^2\)/s. In contrast, for the MOF-based separators, the corresponding redox peak was assigned as peak \( \alpha_2, \beta_2, \gamma_2 \), respectively. The diffusion coefficients were calculated to be \( D(\alpha_2) = 1.5 \times 10^{-9} \) cm\(^2\)/s, \( D(\beta_2) = 1.9 \times 10^{-9} \) cm\(^2\)/s; \( D(\gamma_2) = 2.1 \times 10^{-9} \) cm\(^2\)/s (Supplementary Table 1).

Therefore, these similar values of \( D_{Li^+} \) indicated that the introduced MOF@GO separator would not significantly degrade the diffusion of the lithium ion. The average values of \( D_{Li^+} \) indicated that the introduced MOF@GO separator did not obviously decrease the diffusion of the lithium ion in lithium batteries. In comparison with pristine separator, the MOF-based separators illustrate negligible effects on the transfer of lithium ions across the separator in cells. Meanwhile, it is still able to provide excellent selectivity to lithium ions against unfavorable polysulfide anions, simultaneously. Despite the introduced MOF@GO separator may cause the subtle increase of lithium-ion transfer resistance, it can still indicate the comparable capability of lithium-ion transport, highly efficient lithium-ion diffusion coefficient and ion conductivity, and the excellent rate performance in lithium sulfur batteries.

As mentioned in the manuscript, due to the MOF@GO separator, its effective blocking towards dissolved polysulfide has resulted in great improvement in the cycling performance in lithium sulfur batteries. Moreover, the diffusion-related experiment, as EIS, for the separator alone are our preferred pathway for \( Li^+ \) ion diffusion. What counts is whether the ion diffusion would suffer from increasing hindrance by the MOF-based separator.

\[ \text{Supplementary Note 2. Calculation of ion conductivity} \]
To better understand the ion transition in the membranes, the ion conductivity is also calculated. Actually, the permeating capability of MOF@GO separators for lithium ions is also beneficial to know its performance of enhanced rate capability. As usual, the introduced MOF@GO separators would cause the slight increase of lithium-ion transfer resistance. In experimental, cells were prepared by inserting pristine Celgard 2400 separators or the MOF@GO separators between two blocking stainless steel electrodes with the electrolyte. The working temperature was raised from ambient temperature (30 °C) to 65 °C and all cells were recorded at constant temperatures. Ionic conductivity measurements were performed by electrical impedance spectroscopy (EIS).

According the equation²:
\[ \sigma = \frac{L \times S}{R - 1} \]  
(Equation S2)

where \( \sigma \) is the ion conductivity, \( L \) is the distance between the two stainless steel electrode, the \( S \) is the geometric area of electrode/electrolyte interface and the \( R \) is the intercept at the real axis in the impedance Nyquist plot.

**Supplementary Note 3.** The Nitrogen adsorption behavior of MOF@GO separators

The permanent porosity of our self-assembled MOF@GO separators was studied using gas permeation experiments. On the basis of its microporous properties, it is supposed to function as the effective ionic sieve with its highly narrowed pore sizes.

For the sake of the gas adsorption, the nitrogen adsorption isotherm has been measured at 77 K and 1 atm. It is noteworthy that its pore size distributions can be precisely measured and calculated due to its adsorption behavior of our MOF based separator. In experimental, Nitrogen adsorption with a typical reversible type I isotherm was performed and analyzed the pore size distribution. The Brunauer–Emmett–Teller (BET surface area) with a saturated adsorption amount of 368.2 cm\(^3\) (STP) g\(^{-1}\) is consistent with theoretical calculation. Accordingly, it can be regarded that by the non-local density functional theory (NLDFT) model, pore size distribution in our separators can be confirmed as a narrow arrangement below 9 Å.
Supplementary References


