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Performance enhancing LbL coatings on separator for lithium-sulfur batteries

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Outline:

- Lithium-Sulfur batteries
- Layer-by-layer method
- Characteristics of LbL coating
- Electrochemical performance of Li-S battery with LbL coated separator
- Conclusion
Challenges of Li/S battery

So far limited progress due to a series of practical issues:

**Major Issues:**

① Low electronic conductivity of sulfur
(low rate capability, isolated active material)

② Low mass-loading of sulfur (≤ 2 mg/cm²)
(low volumetric capacity of the battery)

③ Solubility of the lithium polysulfides (LiₓSᵧ) in the electrolyte
(low utilization of the sulfur cathode and in severe capacity decay upon cycling)

④ Lithium dendrite formation (safety issue)

\[
\begin{align*}
S_8 + 2Li & \rightarrow Li_2S_8 \quad (1) \\
Li_2S_8 + 2Li & \rightarrow 2Li_2S_4 \quad (2) \\
Li_2S_4 + 2Li & \rightarrow 2 Li_2S_2 \quad (3) \\
Li_2S_2 + 2Li & \rightarrow 2 Li_2S \quad (4)
\end{align*}
\]
Thin and light clay-containing tri-layer coating on PP separator

\[(\text{PEI/Clay/PAA})_n\]

Halloysite  Montmorillonite

tri-layer system deposited by layer-by-layer technique
Structure of clay mineral

Montmorillonite (MMT)

\[ \text{Si}_8^{\text{IV}}(\text{Al}_{3.33}\text{Mg}_{0.33}\text{Fe}_{0.33})^{\text{VI}}\text{O}_{20}(\text{OH})_4 \ 0.67\text{Na}^+ \ \text{nH}_2\text{O} \]

Poly(acrylic acid) (PAA)

Branched poly(ethyleneimine) (PEI)

\[ x, y \sim 180 \ \text{nm} \]
\[ z \sim 1 \ \text{nm} \]

Mechanism

PP separator → PEI solution → Clay solution → PAA solution

$n$ times

Sulfur cathode → Polysulfide ion diffusion retention → Li anode

$S_{n}^{2+}$

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Growth of multilayers

(PEI/MMT/PAA)ₙ at pH 5

Capacity at 10th cycle, mAhg⁻¹

Number of tri-layers

Coulombic efficiency, %

Thickness, nm

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SEM micrographs of pristine and coated separators

(PEI/MMT/PAA)$_2$ at pH 2

(PEI/Hal/PAA)$_5$ at pH 2

conventional

cross-sectional view

(PEI/MMT/PAA)$_2$ at pH 5

(PEI/Hal/PAA)$_5$ at pH 2

100nm

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Cross-sectional view

(BPEI/MMT/PAA)$_{10}$

pH 2

700 nm

Celgard 25 um

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Thermal Shrinkage

Images of pristine and coated separators after heat treatment at 90 °C, 120 °C, and 150 °C for 20 minutes.

Thermal shrinkage of routine and coated separators at 90 °C, 120 °C, and 150 °C for 20 minutes.
Electrolyte uptake of pristine and coated separators: (PEI/MMT/PAA)$_5$ at pH 2 and pH 5; (PEI/Hal/PAA)$_5$ at pH 2 and pH 5.
Polysulfide diffusion and conductivity

Diffusion of LiS₆ in tetrahydrofuran through pristine and (PEI/Clay/PAA)₅ coated separators within 24 hours

<table>
<thead>
<tr>
<th></th>
<th>Thickness (µm)</th>
<th>Bulk resistance (ohm)</th>
<th>Ionic conductivity (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP separator</td>
<td>25</td>
<td>5.16</td>
<td>0.1703</td>
</tr>
<tr>
<td>MMT pH2</td>
<td>25.45</td>
<td>5.22</td>
<td>0.1720</td>
</tr>
<tr>
<td>MMT pH5</td>
<td>25.35</td>
<td>5.19</td>
<td>0.1724</td>
</tr>
<tr>
<td>Hal pH2</td>
<td>25.25</td>
<td>5.25</td>
<td>0.1697</td>
</tr>
<tr>
<td>Hal pH5</td>
<td>25.25</td>
<td>5.23</td>
<td>0.1704</td>
</tr>
</tbody>
</table>
Cyclic voltammetry

CV curves for conventional and coated PP separators.
Li-sulfur cell, S/KB cathode with 70 wt.% sulfur
Cycle performance

- Cathode: S/KB  Sulfur content = 70%
- Sulfur mass loading = 1.5 mg/cm²
- The rate capability - 0.1C

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Polysulfide ion diffusion retention

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Conclusion

- MMT and Hal containing thin film polyelectrolyte multilayers were prepared and investigated as coating on PP membrane separator for Li/S batteries.

- \((\text{PEI/MMT/PAA})_5\) at pH 5 and \((\text{PEI/Hal/PAA})_5\) at pH 2 tri-layer systems have substantially improved essential membrane properties such as electrolyte uptake and thermal shrinkage compared to routine separator.

- Abovementioned LbL assemblies served as exceptionally good polysulfide diffusion barriers and thereby restrained pronounced capacity diminution and raised the coulombic efficiency of lithium sulfur electrochemical cells.

- Coulombic efficiency of the cell was improved by increase of number of tri-layers and 6 tri-layers was found as sufficient
Thank you for your attention!