Effects of Binders and Cycling on Cell's Impedance Parameters and Fading

E. Peled
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Acknowledgment

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Challenges and Goals

• Understanding the charge-discharge processes and the modes of capacity fading
• Increasing cycle life, sulfur utilization, battery power and reducing polysulfides (PSs) shuttle
• Safety, mainly avoiding lithium dendrite formation during high rate charging

Lithium side reactions

• A competition between the electrolyte reduction reactions and the PSs reduction reactions, which one is worse?
• At high state of charge (SOC) and at low state of discharge (SOD) lithium reduces the PSs
• At low SOC and high SOD lithium reacts with the electrolyte
• Both processes are leading to the formation of a secondary porous SEI, to the precipitation of solids inside the separator and the cathode voids and to a sluggish transport of lithium ions in the electrolyte (an increase of the labyrinth factor)
Effects of PSs shuttle

- Reducing the Coulombic efficiency
- Passivating the lithium anode with insoluble products (Li$_2$S and Li$_2$S$_2$)
- Degrading the lithium anode due to the formation of unstable solid-electrolyte interphase (SEI)

Means suggested to minimize the PS shuttle problem

- A carbon barrier layer between the cathode and the separator (our focus)
- Sulfur–carbon and sulfur–polymer nanocomposites
- Sulfur and Li$_2$S nano cages
- Porous curent collectors
- Surface-coated separators
- Addition of nitrate and other SEI precursors
The battery was assembled at the discharge state

Why?

1. Minimize the effect of cathode volume expansion on discharge (78%)
2. Best when using silicon anode, avoiding pre-lithiation of the anode
3. Similar to the manufacturing of all lithium ion batteries
Effect of Cathode Binders, 2M LiTFSI + 0.15M LiNO₃

<table>
<thead>
<tr>
<th>Binder</th>
<th>Q_loss (%/cycle)</th>
<th>Q₁disc. (mAh/gS)</th>
<th>Current Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>0.14</td>
<td>623</td>
<td>95</td>
</tr>
<tr>
<td>PVDF</td>
<td>0.2</td>
<td>778</td>
<td>96</td>
</tr>
<tr>
<td>PVP</td>
<td>0.25</td>
<td>889</td>
<td>98</td>
</tr>
<tr>
<td>LiPAA</td>
<td>0.26</td>
<td>1184</td>
<td>97</td>
</tr>
</tbody>
</table>

PVDF

PANI

PVP

LiPAA

This project receives funding from the European Union’s Horizon 2020 research and innovation programme under Grant Agreement No 666221.
Effect of cycling and binders on $Q_{\text{loss}}$, $Q_T$ and $Q_H$

<table>
<thead>
<tr>
<th>Binder</th>
<th>Cycle10</th>
<th>Cycle 200</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_T$ (mAh/gS)</td>
<td>$Q_H/Q_T$ (%)</td>
</tr>
<tr>
<td>PANI</td>
<td>529</td>
<td>50</td>
</tr>
<tr>
<td>PVDF</td>
<td>653</td>
<td>39</td>
</tr>
<tr>
<td>PVP</td>
<td>717</td>
<td>32</td>
</tr>
<tr>
<td>LiPAA</td>
<td>907</td>
<td>31</td>
</tr>
</tbody>
</table>

$Q_H/Q_T$ is constant $\rightarrow$ an equal loss of all sulfur species
**Effect of a Barrier Layer (placed on the cathode), PVDF Binder**

2M LiTFSI + 0.15M LiNO₃

<table>
<thead>
<tr>
<th>Layer</th>
<th>CE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unprotected</td>
<td>96.3</td>
</tr>
<tr>
<td>TORY</td>
<td>99.9</td>
</tr>
<tr>
<td>GDL&amp;SGL</td>
<td>99.5</td>
</tr>
</tbody>
</table>

- The barriers increase CE, \( Q_{in} \), and mostly \( Q_L \) and the fading rate
- More \( \text{Li}_2\text{S} \) and \( \text{Li}_2\text{S}_2 \) are formed
Effect of Cycling and Barrier Layer, PVDF binder
2M LiTFSI + 0.15M LiNO3.

Cycle 10

- The fading rate is higher for $Q_L$
- A preferential loss of Li$_2$S and Li$_2$S$_2$ species
- Thus Li$_2$S and Li$_2$S$_2$ species may become inactive or lost contact to the carbon

Cycle 200
The barriers increase CE, $Q_{in}$ and mostly $Q_L$ and the fading rate.

More $Li_2S$ and $Li_2S_2$ are formed.
Effect of Barrier Layer, PANI Binder
2M LiTFSI + 0.15M LiNO3.

Cycle 10

- The fading rate is similar for both $Q_L$ and $Q_H$
Effect of Reducing the Current After 400 Cycles (from 100 to 20 micro-Amps)

**LiPAA binder**. Electrolyte: 2M LiTFSI + 0.15M LiNO₃

A support for an irreversible loss of sulfur capacity, starting at cycle 1
EIS Studies, Nyquist Impedance –
Which Equivalent Circuit to Choose?

(Measurements were taken at the end of discharge)

- $\text{Re}(Z)/\text{ohm}$
  - $1.00020 \text{ Hz}$
  - $215.344 \text{ Hz}$
  - $0.46387 \text{ Hz}$

- $\text{Im}(Z)/\text{ohm}$
  - $0.0100058 \text{ Hz}$

- $R_1 = R_b$
- $R_2 = R_{ct}$ for the redox of S species at the cathode
- $R_3 = R_{SEI}$
- $C_3 = C_{SEI}$ (a typical value $= 10E-6 \text{ F/cm}^2$)
- $L_{SEI} \sim 1\text{nm}$
- Electrode area $= 1 \text{ cm}^2$

$$L_{sei} = \frac{A \cdot \varepsilon \cdot \varepsilon_0}{C_{sei}}$$
Effect of Binders Without a Barrier Layer

![Graph showing the capacity of different binders over cycles](image)

### Table: Cell Performance

<table>
<thead>
<tr>
<th>Cell</th>
<th>Cycles</th>
<th>$R_b$ (ohm)</th>
<th>$R_{SEI}$ (ohm)</th>
<th>$R_{CT}$ (ohm)</th>
<th>$\sigma$ (ohm·s$^{-1/2}$)</th>
<th>$Q_{loss}$ (%/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>35</td>
<td>10.6</td>
<td>87.8</td>
<td>256.8</td>
<td>44.3</td>
<td>0.2</td>
</tr>
<tr>
<td>PANI</td>
<td>46</td>
<td>11.0</td>
<td>98.6</td>
<td>323.7</td>
<td>9.2</td>
<td>0.14</td>
</tr>
<tr>
<td>PVP</td>
<td>88</td>
<td>7.3</td>
<td>207.6</td>
<td>1416.0</td>
<td>83.0</td>
<td>0.25</td>
</tr>
<tr>
<td>LiPAA</td>
<td>11</td>
<td>8.4</td>
<td>158.6</td>
<td>15.3</td>
<td>137.2</td>
<td>0.26</td>
</tr>
</tbody>
</table>

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Effect of Binders Without a Barrier Layer

- **D** $\propto$ $\sigma^{-2}$
- $\sigma$ - Warburg factor
Effect of Cycling Without a Barrier layer, PVDF Binder

- **Cycles**
  - 19 cycle
  - 35 cycle
  - 205 cycle

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$R_b$ (ohm)</th>
<th>$R_{SEI}$ (ohm)</th>
<th>$C_{SEI}$ (farads)</th>
<th>$L^*$ (nm)</th>
<th>$R_{CT}$ (ohm)</th>
<th>$C_{CT}$ (farads)</th>
<th>$\sigma$ (ohm·s$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>10</td>
<td>79</td>
<td>0.8E-6</td>
<td>8.4</td>
<td>56</td>
<td>0.8E-3</td>
<td>28</td>
</tr>
<tr>
<td>35</td>
<td>11</td>
<td>68</td>
<td>0.7E-6</td>
<td>9.5</td>
<td>172</td>
<td>0.6E-3</td>
<td>53</td>
</tr>
<tr>
<td>205</td>
<td>8</td>
<td>75</td>
<td>0.8E-6</td>
<td>9.1</td>
<td>668</td>
<td>0.15E-3</td>
<td>217</td>
</tr>
</tbody>
</table>

* Apparent SEI thickness (assuming roughness factor = 1)

**Equations**

- $L_{sei} = \frac{A \cdot \varepsilon \cdot \varepsilon_0}{C_{sei}}$
- $D \propto \sigma^{-2}$

$D$ – An Average diffusion coefficient

$\sigma$ - Warburg factor
Effect of **Barrier**, on: $R_b$, $R_{SEI}$, $L^{*}_{SEI}$, $\sigma$ and $R_{ct}$, PVDF binder

EIS of $Li_2S$(PVDF)-based cathode without barrier

<table>
<thead>
<tr>
<th>Cell</th>
<th>Cycles</th>
<th>$R_b$ (ohm)</th>
<th>$R_{SEI}$ (ohm)</th>
<th>$R_{CT}$ (ohm)</th>
<th>$\sigma$ (ohm·s$^{-\frac{1}{2}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>205</td>
<td>8</td>
<td>77</td>
<td>1228</td>
<td>181</td>
</tr>
<tr>
<td>Toray barrier</td>
<td>215</td>
<td>6</td>
<td>13</td>
<td>23</td>
<td>71</td>
</tr>
</tbody>
</table>

Toray BL increases $D$ and anode roughness! *(Safety issue?)* and reduces $R_{ct}$, $L_{SEI}$ and $R_{SEI}$

* Apparent SEI thickness (assuming roughness factor =1)
Conclusions

The major factors responsible for capacity fading are: The increase of $R_{CT}$, blocking of the cathode surface, formation of inactive sulfur species and the decrease of lithium diffusion coefficient ($D$) (increase of the labyrinth factor).

The increase of $R_{CT}$ results from blocking of the carbon surface by inactive Li$_2$S and Li$_2$S$_2$.

To our surprise $R_{SEI}$ and the apparent SEI thickness do not grow on cycling.

$Q_{in}$ and mostly $Q_L$, Coulombic efficiency, OCV stability (low self discharge), anode roughness (safety issue?) and durability are higher for cells with a PS barrier layer.

$R_{CT}$, $L_{SEI}$ and $R_{SEI}$ are much lower and the diffusion coefficient ($D$) is higher for cells with a barrier layer.

PANI, BL free cells, have the largest D and overvoltage values.

Cycle life is inversely proportional to sulfur utilization ($Q$).
Acknowledgment

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Thank you for your attention
**Experimental**

- Li$_2$S and carbon materials were ball milled (4 hours), mixed with a binder dissolved in N-methyl-2-pyrrolidone (NMP) to obtain cathodes composition: (Li$_2$S:carbon:binder) 45:45:10
- The cathode was casted on a Al/C foil.
- Electrolytes were dissolved (mostly) in dimethoxyethane (DME) and dioxolane (DOL) mixture(1:1 v:v).
- Celgard 2400 (X2) separator and lithium anode.
- 2032 coin-cell (1cm$^2$ electrode area).
- Typical cathode loading was ~1mg Li$_2$S/cm$^2$
- Several types of carbon matrices were tested as PS barrier layer. We placed the BL on the cathode (or on the separator)
Charge-Discharge of Li-S Rechargeable Battery

\[ S + 2Li^+ + 2e^- \leftrightarrow Li_2S \]