Dendrite Prevention in Li metal and Li Ion Batteries

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1. Introduction

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5. Summary
Comparison of Specific Energy of Various Batteries

1. Introduction

- Practical specific energy based on state of the art cells
- Theoretical specific energy based on active components

<table>
<thead>
<tr>
<th>Battery Type</th>
<th>Specific Energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-acid</td>
<td>0</td>
</tr>
<tr>
<td>Ni-cadmium</td>
<td>0</td>
</tr>
<tr>
<td>Ni-zinc</td>
<td>0</td>
</tr>
<tr>
<td>NiH2</td>
<td>0</td>
</tr>
<tr>
<td>NiMH</td>
<td>0</td>
</tr>
<tr>
<td>Zebra</td>
<td>0</td>
</tr>
<tr>
<td>Silver zinc</td>
<td>0</td>
</tr>
<tr>
<td>NaS</td>
<td>0</td>
</tr>
<tr>
<td>LiCoO2/graphite</td>
<td>0</td>
</tr>
<tr>
<td>LiCoO2/Li</td>
<td>0</td>
</tr>
<tr>
<td>Li-S</td>
<td>0</td>
</tr>
<tr>
<td>Li-O2, Best estimate</td>
<td>0</td>
</tr>
</tbody>
</table>
Challenges on Li Metal Batteries

Two main barriers:
1. Dendrite growth; 2. Low Coulombic efficiency

(a) Li metal batteries
(b) The typical morphology of Li dendrite (Chianelli, 1976)
(c) Main problems related with dendrite and low Coulombic efficiency.
2. Self-Healing Electrostatic Shield (SHES) Mechanism

Foundation: Nernst Equation

\[ E_{\text{Red}} = E_{\text{Red}}^\phi - \frac{RT}{ZF} \ln \frac{\alpha_{\text{Red}}}{\alpha_{\text{Ox}}} \]

The effective reduction potentials of selected cations

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Cs⁺</th>
<th>Rb⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stand reduction potential (1M)</strong></td>
<td>-3.040 V</td>
<td>-3.026 V</td>
<td>-2.980 V</td>
</tr>
<tr>
<td><strong>Effective reduction potential at 0.05M</strong></td>
<td>-</td>
<td>-3.103 V</td>
<td>-3.06 V</td>
</tr>
<tr>
<td><strong>Effective reduction potential at 0.01M</strong></td>
<td>-</td>
<td>-3.144 V</td>
<td>-3.098 V</td>
</tr>
</tbody>
</table>

*Assume the activity coefficient of additive species equals 1 at dilute condition.

An cation may have an \( E_{\text{Red}} \) lower than those of Li⁺.
Self-Healing Electrostatic Shield (SHES) Mechanism

- SEI layer will form once Li metal contact liquid electrolyte.
- Li ions can diffuse through SEI layer and deposit on Li surface.
- SHES additives (such as Cs ions) will stay outside of SEI layer.
- Formation and stability of SEI layer are the main factors affecting the Coulombic efficiency of Li deposition/stripping processes.
3. Effect of CsPF$_6$ Additive on The Morphology of Li Deposition

- Control electrolyte: 1 M LiPF$_6$ in PC.
- CsPF$_6$ concentration in the electrolyte: (a) 0 M, (b) 0.001 M, (c) 0.005 M, (d) 0.01 M, and (e) 0.05 M.

 Cs$^+$ additive can effectively suppress Li dendrite growth.
In-Situ Observation of Li Deposition

**Li deposition without additive**  
(1M LiPF$_6$ in PC)  
- Needle-like dendritic growth perpendicular to the surface

**Li deposition with additive**  
(1M LiPF$_6$ in PC with 0.05M CsPF$_6$)  
- Dense film growth
Simulation of Li Growth in Different Electrolyte Solutions

- **1M LiPF$_6$ solution in PC**: Needle-like dendritic growth
- **1M LiPF$_6$ + 0.05M CsPF$_6$ solution in PC**: Dense film growth

[Images showing the growth patterns and associated videos]

*Li_deposition_no_add.avi*  
*Li_deposition_Cs.avi*
Effects of Other Additives: Rb\textsuperscript{+}, P1 and P2

- SHES mechanism is effective for Cs, Rb, and P2.

1M LiPF\textsubscript{6} in PC without or with 0.05 M additive
Are Additives Deposited on Li films?

The SHES additives can be used for long term cycling.

### ICP Analysis on the Deposited Lithium Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposited Li film from 1 M LiPF$_6$/PC</td>
<td>0.035 M</td>
</tr>
<tr>
<td>Deposited Li film from 0.05 M CsPF$_6$ in 1 M LiPF$_6$/PC</td>
<td>0.014 M Cs: 0</td>
</tr>
<tr>
<td>Deposited Li film from 0.05 M RbPF$_6$ in 1 M LiPF$_6$/PC</td>
<td>0.056 M Rb: &lt; detection limit (~10 µM)</td>
</tr>
</tbody>
</table>

The SHES additives can be used for long term cycling.
XPS and EDX Analysis on the Deposited Lithium Films

No Cs can be identified (within the detectable limit) in the film deposited in an electrolyte containing Cs.
Main components and structure of SEI films from electrolytes with and without Cs⁺-additive are very close.

Cs⁺-additive does not participate in the SEI film-forming process.
Morphology Evolution during Repeated Li-Deposition/striping

Self-amplification of chaotic/dendritic growth ➔ Self-healing of ordered/smooth growth

(a) 1 hr deposition in the control electrolyte.
Significant Li dendrite was formed.

(b) Additional 14 hr in the electrolyte with Cs$^+$ additive.
All Li dendrite was soothed.

➢ Cs$^+$ additive can effectively smooth the existing dendrite.
Effect of Cs\(^+\) on Morphologies of Deposited Li Films After Cycling

Li films deposited on Cu foils after repeated deposition/stripping cycles in beaker cells (no pressure effect).

- **No additive**
  - 2th deposition
  - 3th deposition
  - 10th deposition

- **With Cs\(^+\) additive**
  - 2th deposition
  - 3th deposition
  - 10th deposition

➢ SHES mechanism is effective for cycling.
SEM Images on the Cross Section of Li Films

1 M LiPF$_6$ in PC

- Dendritic surface
- Random growth

1 M LiPF$_6$ in PC + 0.05 M CsPF$_6$

- Smooth surface
- Highly ordered growth
Dendrite-Free Li Deposition with High CE

- Smooth surface with small bumps
- Cross section
- Uniform growth of dense Li films. The growth pattern can be controlled by electrolyte

CE=96.42%
4. Dendrite-Free Li Deposition with High Coulombic Efficiency

Main Challenges:

1. Li Dendrite Growth
   - Cs or Rb additives based on the SHES mechanism can effectively prevent dendrite growth when PC is used as the solvent.

2. Low Coulombic Efficiency
   - Li will react with PC during cycling and lead to lower efficiency (~76%).

   - Electrolyte solvents and salts need to be optimized to obtain both dendrite-free Li deposition and high Coulombic efficiency.
Self-Healing Electrostatic Shield (SHES) Mechanism

- SEI layer will form once Li metal contact liquid electrolyte.
- Li ions can diffuse through SEI layer and deposit on Li surface.
- SHES additives (such as Cs ions) will stay outside of SEI layer.
- Formation and stability of SEI layer are the main factors affecting the Coulombic efficiency of Li deposition/stripping processes.
The morphology and failure mechanism of Li electrodes during Li deposition and dissolution

• Coin cell configuration: Li | 1M LiPF$_6$ in EC-PC | Cu

✓ The average Coulombic efficiency of Li anode is significantly improved by using EC-PC with high EC contents.
Effect of Cs-Additive on Li Cycling Efficiency & Morphology in EC-PC

- Coin cell configuration: Li | Cu with 1M LiPF$_6$ w. or w/o 0.05M CsPF$_6$ in EC-PC

- Without Cs-additive: Li films are not shining when deposited in either PC or EC-PC (8:2) electrolytes.

- With Cs-additive: Both Li films show metallic shining.

✓ New electrolyte with Cs-additive demonstrates both high Coulombic efficiency and dendrite free morphology.
Effect of Carbonate Solvents on Li Coulombic Efficiency

<table>
<thead>
<tr>
<th>Carbonate solvent</th>
<th>Average lithium Coulombic efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without CsPF&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>PC</td>
<td>76.5%</td>
</tr>
<tr>
<td>EC</td>
<td>94.8%</td>
</tr>
<tr>
<td>EC-PC (8:2 wt)</td>
<td>93.1% with dendrite</td>
</tr>
<tr>
<td>DMC</td>
<td>23.6%</td>
</tr>
<tr>
<td>EMC</td>
<td>7.3%</td>
</tr>
<tr>
<td>VC</td>
<td>97.1%</td>
</tr>
<tr>
<td>VEC</td>
<td>97.6%</td>
</tr>
<tr>
<td>FEC</td>
<td>98.2%</td>
</tr>
<tr>
<td>EL1</td>
<td>98.0%</td>
</tr>
</tbody>
</table>

- Tested in Li | Cu cells.
- Li Coulombic efficiency is greatly affected by carbonate solvent. Cyclic carbonates give high efficiency while linear carbonates result in very poor efficiency.
- Dendrite-free Li deposition with >98% CE obtained.
Morphology Changes During Long Term Cycling of Li Electrode in Li/LTO Cells

![Surface morphologies of Li electrodes after 100 cycles in coin cells of Li|Li₄Ti₅O₁₂ system containing electrolytes without (a) and with (b) Cs⁺-additive.](image)

- **SHES mechanism is effective during long term cycling.**
Columbic efficiency of the full cell: 99.97% (with excess Li)
Cycling stability of the full cell: Only 3.3% capacity fade in 660 cycles

Cell: Li/Li$_4$Ti$_5$O$_{12}$
1 M LiPF$_6$ in PC with 0.05 M CsPF$_6$
ShES Additive Prevents Li Dendrites on Overcharged Carbon Electrodes

100% overcharge (i.e. overcharged to 200% of the nominal capacity)

Optical images

- White dots are Li
- Pristine HC electrode
- Without additive
- With Cs-

200% overcharge (i.e. overcharged to 300% of the nominal capacity)

Optical images

- Without additive
- With Cs-

SEM images

- Dendritic Li was deposited on the surface
- Spherical Li was deposited on the surface

Cs Additive can prevent Li dendrite growth on overcharged carbon electrodes
Optical and SEM images of the surface morphologies of the hard carbon electrodes after charged to 300% of the regular capacity in the control electrolyte (a, b, c) and in an electrolyte with 0.05 M CsPF$_6$ additive added in the control electrolyte (d, e, f).

New Additive can prevent Li dendrite growth on overcharged carbon electrodes
5. Summary

- The Self-Healing Electrostatic Shield (SHES) mechanism has been proposed to suppress Li dendrite growth.
- Novel additives (Cs, Rb, etc.) based on the SHES mechanism can effectively suppress Li dendrite growth on Li metal batteries.
- High Coulombic efficiency (>98%) can be obtained if the appropriate solvent is used.
- The SHES mechanism may also be used to prevent dendrite growth during other metal depositions.
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