Stabilizing Electrodeposition of Metals in Batteries

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Acknowledgements: DMR1006323, KUS-C1-018-02 & DOE-BESC0001086

CFES Annual Conference, Troy NY
February 26, 2015
Why the fuss about Batteries?

Inherent intermittency of renewable energy generation technologies requires reliable storage!

Consumer demand for faster, lighter, smaller, more powerful, portable machines – frustrated by batteries!

The Lithium Metal Battery

The Lithium Ion Battery

Opportunities: Rechargeable Metal Anode Batteries (RMBs)

- Na, Al, Zn, Cu; Mg!
Stopping Dendrites: Proposed Solutions

σ = 10^{-4} – 10^{-2} \text{ S/cm}
η < 1 \text{ Pa-s}
EW: 3 V / 5 V

σ = 10^{-7} – 10^{-4} \text{ S/cm}
G' \leq \text{ MPa}
EW > 4 V

σ = 10^{-7} – 10^{-3} \text{ S/cm}
G' \sim \text{ GPa}
EW > 4 V

\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_{4} (\text{thio-LiSCON})
\text{Li phosphorus oxynitride (LiPON)}
An electrolyte modulus similar to lithium metal is required to stop dendrites.
Contradictory Evidence

Electrolyte modulus alone does not determine lifetime of lithium metal battery.
Modeling Dendrite Formation

\[ \frac{\partial C_c}{\partial t} = -\nabla \cdot \mathbf{W}_c , \]
\[ \frac{\partial C_a}{\partial t} = -\nabla \cdot \mathbf{W}_a , \]
\[ \mathbf{W}_c = -D_c \nabla C_c + \mu_c C_c \mathbf{E} , \]
\[ \mathbf{W}_a = -D_a \nabla C_a - \mu_a C_a \mathbf{E} , \]
\[ -\nabla \cdot \mathbf{E} = -\rho / \varepsilon \varepsilon_0 = - e (z_c C_c - z_a C_a) / \varepsilon \varepsilon_0 \]

Structured Electrolyte

\[
\begin{align*}
\frac{J}{F} &= -D_c \frac{dC_c}{dz} - m_c C_c \frac{df}{dz} \\
0 &= -D_a \frac{dC_a^m}{dz} + m_a C_a^m \frac{df}{dz} \\
\tilde{N}^2 f &= -\frac{r}{ee_0} = -e(z_c C_c - z_a C_a) / ee_0
\end{align*}
\]
Stability Analysis

- Perturb the cathode profile as
  \[ \tilde{H}_c = L + H'_c e^{\sigma t} e^{ikx} \]

- Expect all other variables to follow a similar variation
  \[ \tilde{C}_c = C_c + C'_c(z) e^{\sigma t} e^{ikx} \]
  \[ \tilde{\phi} = \phi + \phi'(z) e^{\sigma t} e^{ikx} \]
  \[ \tilde{J} = J + J'(z) e^{\sigma t} e^{ikx} \]

- Solve the transport problem for \( \sigma \)
  \[ \frac{\partial \tilde{H}_c}{\partial t} = -\frac{v_m}{F} \tilde{J} \cdot \tilde{n} \bigg|_{\tilde{H}_c} \quad \Rightarrow \quad H'_c \sigma = -\frac{v_m}{F} J' \bigg|_L \]

- \( \sigma \) determines the stability of deposition
  - \( \sigma > 0 \) means unstable deposition
  - \( \sigma < 0 \) means stable deposition
The perturbation becomes less stable with increasing wavenumber.

High wavenumber perturbations are stabilized by surface tension.

Tethering just 10% of anions produces a ten-fold reduction in both $\sigma_{mu}$ and $k_{cr}$; tethering 100% essentially eliminates instability.
Stop THE Unstable Modes!

A nanoporous electrolyte with $a \ll \lambda_{cr}$, high modulus, and liquid-like conductivity may be sufficient to stop growth of unstable modes and dendrite proliferation.
Concentration of current on tips
Migration affected by matrix compression
Tugging of separator on the electrode

\[ C_a^f = 0.1 \]

\[ \sigma / J \sim k_L \]

\[ \sigma_{mv} / J \]

Unstable

Stable
As the electrolyte approaches a single-ion conductor, micron-sized dendrites are suppressed at electrolyte/separator moduli well below $G_{Li} \approx 3.4$ GPa.
Nanoporous Polymer Electrolytes

\[ t_{Li^+} = \frac{1}{2} \frac{\sigma^s}{\sigma^0} = \frac{1}{2} \frac{R^0_{\text{bulk}}}{R^s_{\text{bulk}}} = \frac{1}{2} \frac{I^s}{I^0} \frac{\Delta V - I^0 R^0_1}{\Delta V - I^s R^s_1} \approx 0.84 \]

<table>
<thead>
<tr>
<th>Single-ion conducting electrolytes</th>
<th>LIF salt-based electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>( t_{Li^+} )</td>
</tr>
<tr>
<td></td>
<td>Bruce-Vincent method</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.41±0.02</td>
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<tr>
<td>EC:DEC</td>
<td>1.68±0.10</td>
</tr>
<tr>
<td>PC</td>
<td>0.73±0.04</td>
</tr>
<tr>
<td>TEGDME</td>
<td>0.92±0.04</td>
</tr>
</tbody>
</table>

\( d_p = 3\text{nm} - 7\text{nm} \)
Nanoporous, almost single-ion conducting electrolytes stabilize electro-deposition of Li-metal in both cycling and polarization studies in symmetric cells.

Summary & Perspective

- Li batteries based on **metallic lithium anodes** offer good potential for energy storage at **comparable energy densities with fossil fuels**

- The **most unstable mode** for electrodeposition of metals is a strong function of the **mobile anion fraction** in an electrolyte

- Polymer-inorganic hybrids yield electrolytes with **tunable mechanical properties, reasonable ionic conductivity** and promising ability to prevent cell failure by dendrite short circuits

- **Single-ion conducting polymer electrolytes** provide promising solutions towards cost-effective and safe LMBs

- Researchers are now on the cusp of **multiple embodiments of Li metal battery technologies** capable of partially delivering on the theoretical promise of this chemistry
Model Nanoporous Membranes

FESEM – Vertically fractured PAA film

Chu et al., Adv. Mater., 2005
PVDF-Al₂O₃ Nanoporous Electrolytes

PVDF-Al$_2$O$_3$ Nanoporous Electrolytes


**Storage Modulus [MPa]**

- $G' (T=25^\circ C) \approx 0.5 \text{ GPa}$
- $G' (T=25^\circ C) \approx 0.33 \text{ GPa}$

**DC Ionic Conductivity [S/cm]**

- $\mu (T=25^\circ C) \approx 2 \text{ mS/cm}$
- $\mu (T=25^\circ C) \approx 1.25 \text{ mS/cm}$

+ PC & 1M LiTFSI

Tu, Z. Nanoporous Al$_2$O$_3$ Nanoporous Electrolytes

PVDF-HFP in DMF

Nanoporous PVDF-HFP

Nanoporous Al$_2$O$_3$
Nanoporous X-linked Polymer Electrolytes

\[ a_p(\phi) \approx \frac{8}{5} \sqrt{N_A \phi^b} \]

< 20 nm

\[ G_e(\phi, T) \approx \phi \frac{kT}{a_p(\phi)^2 b} < 1 \text{MPa} \]

Surface Energy Solutions for LMBs

- Limit Formation of Dendrites

High $\gamma$ $\implies$ Electrolyte additives (e.g. LiMX)

High $\mu_c$ $\implies$ Fast Li-ion conductor

$C^f_a > 0.05$ $\implies$ Partially tethered anion

$D << \lambda_{cr} < \lambda_{mu}$ $\implies$ Nanoporous electrolyte
Electrolyte modulus alone does not appear to determine lifetime of battery