Electrified Vehicles for Personal Transportation, the Role of Surface Coatings, and the Use of Thin Films for Electrode Characterization

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Rutooj Deshpande, Juchuan Li, Yang-Tse Cheng
Outline

- Automotive context
- Why do LiIon cells fail?
- The use of thin-film surface coatings to
  1. enhance lithium ion electrode performance (particularly life)
     - positives and negatives
  2. characterize and understand active material behavior
     - stress evolution and solute (Li) diffusion
- Summary
EMERGING VS. MATURE MARKETS – GLOBAL COMPARISON: 2010

Source: GM Economics & Trade; IMF; U.S. Census Bureau/Haver Analytics
TOP 10 MARKETS BY NEW VEHICLE SALES IN 2011

- **2011 Sales (M)**
  - Emerging Markets: 39.5
  - Mature Markets: 36.5
  - World Total: 76.0

- **China Growth (%)**
  - vs. 2010: 2%
  - vs. 2005: 325%
  - vs. 2000: 854%

**Vehicle Sales (M)**

- China
- EU
- U.S.
- Japan
- Brazil
- India
- Russia
- Canada
- S. Korea
- Australia

- **2000**
- **2005**
- **2009**
- **2010**
- **2011**
PERSONAL MOBILITY MUST BE REINVENTED FOR THE 21st CENTURY

Data from U.S. Census Bureau and GM Global Market & Industry Analysis

PERSONAL MOBILITY MUST BE REINVENTED FOR THE 21st CENTURY

Data from U.S. Census Bureau and GM Global Market & Industry Analysis
Future vehicles will use alternative energy sources like bio-fuel, grid electricity, and hydrogen.

Main challenges:
- Higher kWh/kg & kWh/m³
- Lower cost
STOP-START SYSTEMS

Starter Motor

Electric Auxiliary Pump

~ 0.5 kWh battery
eAssist™ ROLLOUT

2012 BUICK REGAL

2013 CHEVROLET MALIBU

~ 1 kWh battery
2-MODE RWD HYBRIDS

~ 2 kWh battery
The Volt proves electric driving can be spirited

- Top Speed – 100 mph
- 0-60 mph in less than 9 seconds
- Torque – 273 lb.-ft.
- Quarter mile in less than 17 seconds

Main challenges
- Higher kWh/kg & kWh/m³
- Lower cost

16 kWh battery
Why do LiIon cells fail?

What do surface coatings have to do with cell life?
By changing an electrode voltage, new electrolytes can be employed with improved stability.

For traction applications, conventional lithium ion cells still dominate...lower utilization for improved durability & abuse tolerance.
Summary: role of surface layers on + and –

<table>
<thead>
<tr>
<th>Newer lithium ion</th>
<th>V</th>
<th>Electrochemical reaction</th>
<th>Conventional lithium ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.35</td>
<td>NiOOH + H₂O + e⁻ = Ni(OH)₂ + OH⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>LiₓMO₂ + xLi⁺ + xe⁻ = LiMO₂ (M: Ni, Co, Mn)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>FePO₄ + Li⁺ + e⁻ = LiFePO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>H⁺ + e⁻ = 0.5H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~ 2.5 V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>~ 3.3 V</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Solvent oxidation on Pt ~ 2.1 V vs Li

O₂ + 2H⁺ + 2e⁻ = 2H₂O
-1.5 Li₄Ti₅O₁₂ + 3Li⁺ + 3e⁻ = Li₇Ti₅O₁₂

Solvent reduction on negative ~ 0.8 V vs Li

-2.9 C₆ + Li⁺ + e⁻ = LiC₆
-3 Li⁺ + e⁻ = Li

~ 1.2 V

~ 1.3 V

~ 4 V

Underscores the importance of protective surface coatings, be they formed in situ or ex situ

- Disruption of the protective surface coating (e.g., due to dilation, crack propagation, etc.) is deleterious to cell life
Negative electrode
Mathematical modeling of high-power-density insertion electrodes for lithium ion batteries

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\textsuperscript{c}General Motors Advanced Technology Vehicles, 1996 Technology Drive, Troy, MI 48007-7083, USA

- Solvent reduction at \(~0.8\)V vs Li on first cycle
- Then \(~100\)% Coulombic efficiency
- Next slide for more detail
Formation of the SEI…solvent reduction (ethylene carbonate)

Example reactions only…many others contribute to the formation of the solid electrolyte layer

- For computed IR spectra of surface species in an EC electrolyte, see S. Matsuta, T. Asada, and K. Kitaura. *J. Electrochem. Soc.* 147(2000)1695-1702…dimers found to be lowest energy

- Experimental FTIR data indicates predominance of [Li(OCOO)CH₂]₂ for EC and EC+DEC systems with 1M LiPF₆, see C. R. Yang, Y. Y. Wang, C. C. Wan, *J. Power Sources*, 72(1998)66.
Positive electrode
The use of surface coatings to enhance lithium ion electrode performance
- first, negative electrodes
Ultrathin Multifunctional Oxide Coatings for Lithium Ion Batteries

Xingcheng Xiao, Peng Lu, and Dongjoon Ahn

Synthetic SEI approach, $\text{Al}_2\text{O}_3$ over $\text{Li}_x\text{Si}$
The use of surface coatings to enhance lithium ion electrode performance
- positive electrodes
Commercial electrodes, primary vs secondary particles, composition analyses. FIBS analysis of NCM + LiMn$_2$O$_4$
FIBS & imaging: cathode 3D.avi
NCM + LiMn$_2$O$_4$ and carbon conductive additive

NCM:
Li(Ni$_x$Co$_y$Mn$_z$)O$_2$
The effect of Al₂O₃-coating coverage on the electrochemical properties in LiCoO₂ thin films

Yuhong Oh - Donggi Ahn - Seunghoon Nam - Byungwoo Park


Fig. 4 The charge-capacity retention after 100 cycles from Fig. 1a, and the Co dissolution and F⁻ concentration in the electrolyte from bare and Al₂O₃-coated LiCoO₂ films with different coverage, after an initial 4.6 V charge and being immersed for 12 days at 25 °C

Fig. 7 a The F⁻ concentration in the electrolyte from bare and Al₂O₃-coated LiCoO₂ films with 100% coverage, after an initial 4.6 V charge and being immersed for 12 days at 25 °C, 60 °C, and 25 °C with 200 ppm water, respectively. b The charge-capacity retention of Al₂O₃-coated LiCoO₂ films, after 100 cycles at 25 °C (Fig. 1), 60 °C (Fig. 5), and 25 °C with 200 ppm water (Fig. 6)

Fig. 9 Schematic figure of H₂O scavenging by Al₂O₃-coating layer
The utility of thin films for materials characterization and understanding

1. Mechanical behavior
2. Diffusion analyses
Improved cycling stability of silicon thin film electrodes through patterning for high energy density lithium batteries

X. Xiao\textsuperscript{a,\ast}, P. Liu\textsuperscript{b}, M.W. Verbrugge\textsuperscript{a}, H. Haftbaradaran\textsuperscript{c}, H. Gao\textsuperscript{c}

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\textsuperscript{c} School of Engineering, Brown University, Providence, RI 02912, USA

Morphology of Si film after cycling

• Typical “dry mud microcracks” formed under tension during the delithiation process
The crack spacing is around 5 to 10 microns, comparable to the pattern with 2000 mesh size.

- Can the gaps provide necessary stress relaxation?
- How large of a pad size can be accommodated?

Pattern size 40 x 40 µm²
Gap: 15 µm

Pattern size 17 x 17 µm²
Gap: 10 µm

Pattern size 7 x 7 µm²
Gap: 7 µm

Related Si island works


Cycling results and the influence of Si pad size

- Lithiation voltage lowered from 0.5 to 0.01 V

Representative voltage responses
In-situ Stress Measurement with MOSS system

(Multibeam Optical Stress Sensors)

\[ \frac{1}{R} = \left( \frac{d - d_0}{d_0} \right) \cos \alpha \frac{2L}{\cos \alpha} \]

Stoney Equation

\[ \sigma_f h_f = \frac{1}{6} M_s H_s^2 R \]

\[ \sigma_f \quad \text{in-plane film stress} \]

\[ h_f \quad \text{film thickness} \]

\[ M_s \quad \text{substrate biaxial modulus} \]

\[ H_s \quad \text{substrate thickness} \]

\[ R \quad \text{substrate radius of curvature} \]

Comparison of 50 nm thick Si samples: continuous film vs. 7x7 μm² pattern

Continuous Film

Patterned Sample
2\textsuperscript{nd} & 3\textsuperscript{rd} Cycle

Note stress ordinate scales differ

We seek the minimum crack spacing $L_{cr}$ that does not allow an extra crack to be formed in between the existing cracks.

Below this minimum crack spacing, the stress in the lithiated Si film cannot reach its plastic yield stress and therefore no strain localization in the film can take place to form an additional crack.

$$
\tau_{cr}^{int} = \min(\tau_{Y}^{Cu}, \tau_{f}^{int})
$$

$$
\tau_{Y}^{Cu} = 40 \text{ MPa}
$$

$$
\tau_{f}^{int} = 40 \text{ MPa}
$$


$$
\sigma_{Y}^{Si} = 1 - 1.75 \text{ GPa}
$$

$$
h = 0.1 \text{ \mu m}
$$

$$
L_{cr} = \frac{2\sigma_{Y}^{Si}}{\tau_{cr}^{int}} h \approx 5.1 - 8.9 \mu m
$$
Stress Mitigation during the Lithiation of Patterned Amorphous Si Islands

Sumit K. Soni,*, Brian W. Sheldon, Xingcheng Xiao, Mark W. Verbrugge, Dongjoon Ahn, H. Haftbaradaran, and Huajian Gao

\[
\langle \sigma \rangle h = \int_0^h \sigma(z) \, dz = (\sigma)^{\text{NOM}} h_o
\]

Figure 4. Comparison between experimentally measured and theoretically predicted values of nominal stress for 3D Si patterned islands (pattern size = 7 \mu m).

Figure 6. Comparison of maximum nominal compressive stresses measured during 2nd lithiation step for various Si thin film electrodes (50 nm thick) with the theoretical predicted values using Eqs. 9 and 10 for \( \tau_{fr} = 12.1 \) MPa.
We just discussed the utility of thin film to characterize and understand the mechanical behavior of active materials.

Next: utility of thin films to assess solute (Li) diffusion in host (Si) materials.
Thin-film (100 nm) electrode (lithiated Si)

- Small potential step excitation: linearize about the open-circuit potential and linearize about solute (Li) final concentration.
- Electrochemical Biot number $B$: lone dimensionless group...diffusion over kinetic resistance.

\[
Li^+ + e^- \leftrightarrow Li^0_{\text{host}}
\]

\[
i = i_0 \frac{F}{RT} (V - U)
\]

\[
B \equiv -l(i_o|_s) \partial U/\partial C|_s(DRT)
\]

\[
\frac{C(x, t) - C_0}{C_s - C_0} = 1 - 2B \sum_{n=1}^{\infty} \frac{\cos \left[ \lambda_n \left( 1 - \frac{x}{l} \right) \right]}{(\lambda_n^2 + B^2 + B) \cos \lambda_n} \exp \left( -\frac{\lambda_n^2 Dt}{l^2} \right)
\]

\[
\lambda \tan \lambda = B
\]

\[
I(t) = \frac{DQ}{l^2} B \exp \left( B^2 \frac{Dt}{l^2} \right) \text{erfc} \left( B \sqrt{\frac{Dt}{l^2}} \right)
\]

\[
I(t) = \frac{2QD}{l^2} \frac{B^2}{(\lambda_1^2 + B^2 + B)} \exp \left( -\frac{\lambda_1^2 Dt}{l^2} \right)
\]

Short time solution

Long time solution
Table 1. Diffusion Coefficient of Li in Si Calculated by Different Methods

<table>
<thead>
<tr>
<th>method</th>
<th>$D$ (cm$^2$ s$^{-1}$)</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>short time (eq 11)</td>
<td>$1.4 \times 10^{-13}$</td>
<td>49.4</td>
</tr>
<tr>
<td>short time linear fitting (eq 15 in ref 2)</td>
<td>$1.1 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>long time (eq 16)</td>
<td>$1.0 \times 10^{-13}$</td>
<td>45.7</td>
</tr>
<tr>
<td>long time (eq 16 in ref 2, slope)</td>
<td>$7.7 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>long time (eq 16 in ref 2, intercept)</td>
<td>$7.7 \times 10^{-14}$</td>
<td></td>
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Summary

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  - Importance of protective thin films for current and future electrode materials
- The use of thin-film surface coatings to
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     - positives and negatives
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