In-Situ, \textit{in-Operando} PeakForce Imaging of Li-Ion Batteries in Glovebox

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Regulatory requirements
OUTLOOK FOR GLOBAL FUEL ECONOMY AND GREENHOUSE GAS regulations

**CHINA**
- 6.9L/100km in 2015 (37 mpg)
- 5.0L/100km by 2020 (56 mpg)
- Local taxation

**U.S. FEDERAL**
- 35.5 mpg in 2016
- 54.5 mpg by 2025
- Gasoline $3-4/gallon

**EUROPEAN UNION**
- 130gCO₂/km in 2015 (43 mpg)
- 95gCO₂/km in 2020 (58 mpg)
- Local CO₂ taxation

**CANADA**
- Green Levy
- 6.6L/100km (35.5 mpg) in 2016

**KOREA**
- 140g/km (39.5 mpg)

**JAPAN**
- 29% CO₂ 2010 → 2015

**INDIA**
- 150gCO₂/km by 2015 (43 mpg)

**MEXICO**
- 10.8 km/l by 2015

**AUSTRALIA**
- 190 gCO₂/km in 2015 (43 mpg)
- 155 gCO₂/km by 2024

**CALIFORNIA**
- 80% CO₂ reduction by 2050
- ZEV, PZEV rules

**REGULATORY REQUIREMENTS**

- **CALIFORNIA**: 80% CO₂ reduction by 2050, ZEV, PZEV rules.
- **U.S. FEDERAL**: 35.5 mpg in 2016, 54.5 mpg by 2025, Gasoline $3-4/gallon.
- **EUROPEAN UNION**: 130gCO₂/km in 2015 (43 mpg), 95gCO₂/km in 2020 (58 mpg), Local CO₂ taxation.
- **CANADA**: Green Levy, 6.6L/100km (35.5 mpg) in 2016.
- **CHINA**: 6.9L/100km in 2015 (37 mpg), 5.0L/100km by 2020 (56 mpg), Local taxation.
- **KOREA**: 140g/km (39.5 mpg).
- **JAPAN**: 29% CO₂ 2010 → 2015.
- **INDIA**: 150gCO₂/km by 2015 (43 mpg).
- **MEXICO**: 10.8 km/l by 2015.
- **AUSTRALIA**: 190 gCO₂/km in 2015 (43 mpg), 155 gCO₂/km by 2024.
## Regulatory requirements

### Outlook for Global Fuel Economy and Greenhouse Gas Regulations

<table>
<thead>
<tr>
<th>Country</th>
<th>Green Levy</th>
<th>2015 (MPG)</th>
<th>2020 (MPG)</th>
<th>Year</th>
</tr>
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<tbody>
<tr>
<td>U.S.</td>
<td>35.5</td>
<td>54.5</td>
<td>2025</td>
<td></td>
</tr>
<tr>
<td>Europe</td>
<td>58</td>
<td>2020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>6.9</td>
<td>5.0</td>
<td>2020</td>
<td></td>
</tr>
<tr>
<td>Korea</td>
<td>140</td>
<td>39.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japan</td>
<td>29%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>European Union</td>
<td>130</td>
<td>95</td>
<td>2020</td>
<td>2025</td>
</tr>
<tr>
<td>Australia</td>
<td>190</td>
<td>155</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **U.S.**: 35.5 mpg in 2016, 54.5 mpg by 2025, Gasoline $3-$4/gallon
- **Europe**: 58 mpg by 2020
- **China**: 6.9L/100km in 2015, 5.0L/100km by 2020
- **Korea**: 140 gCO2/km in 2015, 39.5 mpg
- **Japan**: 29% CO2 reduction from 2010 to 2015
- **Europe**: 130 gCO2/km in 2015, 95 gCO2/km by 2020
- **Australia**: 190 gCO2/km in 2015, 155 gCO2/km by 2024
ELECTRIFICATION

All-new 2016 Chevrolet Volt

2015 Chevrolet Spark EV

2015 Cadillac ELR

Chevrolet Bolt Concept
High capacity electrodes: *lithiated Si*

Dominique Larcher, Shane Beattie, Mathieu Morcrette, Kristina Edström, Jean-Claude Jumas and Jean-Marie Tarascon, “Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries,” *J. Mater. Chem.*, 2007, 17, 3759 – 3772
Challenges for Si Based Negative Electrodes

**Coupled mechanical and chemical degradation at multi-scale leading to low cycle efficiency and short life**

1. Mechanical Fracture: Si particle crack, fracture, pulverization, loss of active materials.
   - Si-Si Bonds
   - 3600 mAh/g
   - 10 X graphite
   - Up to 300% expansion

2. Low current efficiency: unstable solid electrolyte interphase (SEI) caused by huge volume expansion and contraction in Si particles.
   - SEI
   - Electrode
   - Cell Pack

3. Electrode integrity: loss of electrical contact between particles.

Y. Cui. et.al Stanford, 2012,

G. Liu et.al LBNL, 2012
Efficiency and Cycle life

USABC battery performance goal

<table>
<thead>
<tr>
<th></th>
<th>USABC mid-term goal</th>
<th>USABC long-term goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific energy (Wh/kg)</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Energy density (Wh/l)</td>
<td>230</td>
<td>300</td>
</tr>
<tr>
<td>Specific discharge power (W/kg)</td>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>Discharge power density (W/l)</td>
<td>460</td>
<td>600</td>
</tr>
<tr>
<td>Specific regenerative power (W/kg)</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Regenerative power (W/l)</td>
<td>230</td>
<td>300</td>
</tr>
<tr>
<td>Life (years)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Life cycles</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Operation temperature (°C)</td>
<td>-40 to +50</td>
<td>-40 to 85</td>
</tr>
<tr>
<td>Selling price ($/kWh)</td>
<td>150</td>
<td>100</td>
</tr>
</tbody>
</table>

Desirable lifetime for LIBs used in EVs: 15 years or (1 charge/day) x (365 days/year) x 15 years = 5475 charge/discharge cycles

Solid-electrolyte interphases (SEIs)

- SEI: the passivation layer formed between (solid) electrode and (liquid) electrolyte

Key Questions to Address

- How does SEI evolve during cycling?
- Which SEI compounds are desirable/undesirable?
- How can we modify or control the SEI layer?
- How does mechanical deformation influence SEI?
**Initial Mechanics Analysis**

The size limit to mitigate each failure mechanism resulting in SEI instability is derived from solid mechanics.

- Fracture of Si particles
- SEI peel-off from Si particles during lithiation
- Buckling delamination during delithiation

\[
I_{\text{frac}} \propto \left( \frac{\Gamma(1-\nu)F^2D^2}{E(1+\nu)\Omega^2I^2} \right)^{1/3}
\]

\[
I_{\text{delam}} / \sqrt{h} \propto \sqrt{E\Gamma_{\text{int}} / \tau_{\text{int}}^2}
\]

\[
I_{\text{buckle}} = \frac{(\alpha_1\Gamma_{\text{int}} + \alpha_2\Gamma)(1+\nu)(1-2\nu)}{2\pi E \varepsilon_0^2}
\]

- \(\Omega\): partial molar volume of Li in Si,
- \(E\): Young’s modulus,
- \(\Gamma\): fracture energy of lithiated Si,
- \(\tau_{\text{int}}\): interfacial sliding strength,
- \(I\): surface current density,
- \(D\): Li diffusivity,
- \(\nu\): Poisson ratio,
- \(\Gamma_{\text{int}}\): interfacial delamination toughness,
- \(H\): SEI film thickness,
- \(F\): Faraday’s constant.

Experimental validation and material properties are required in order to DESIGN SEI and Si nanostructures.
Bruker AFMs for Multidisciplinary Research

1. **Bruker AFMs provide multidimensional information:**
   - Topography, mechanics, electricity, magnetics, electrochemistry, spectroscopy…

2. **In situ for in operando studies under controlled ambience**
   - Liquid, temperature, ambient, illumination…
PeakForce Tapping (2009, Bruker)

- Probe is modulated at 1~2 kHz, allowing for imaging at high scan rate and high pixel resolution.
- Feedback setpoint: maximum force or peak force of the tapping cycle.
- Sinusoidal ramping: direct force control of imaging forces with ultra-low setpoints (< 50 pN).
- Linear force control: automatic image optimization, ScanAsyst.
- A triggered force curve at every tapping cycle: PeakForce QNM (Quantitative Nano Mechanics).

- SEI scratching at Peak Force of 10 nN
- Imaging at Peak Force <1 nN
PeakForce Enabled Modes

- PeakForce tapping for mechanics, electricity, electrochemistry, and spectroscopy.
  
  PeakForce QNM  PeakForce TUNA  PeakForce KPFM

  PeakForce SSRM  PeakForce SECM

- PeakForce EC-AFM: PeakForce imaging during electrochemical reactions.

Potential Ramp Profile: 1.5 --> 0.36
Bruker FastScan/ICON Platform

- Contact Mode
- Tapping Mode
- Phase Imaging
- Lift Mode
- Dark Lift
- Nano-Indentation
- Nanolithography
- Force Volume
- Piezo Response
- Force Modulation
- Lateral Force Microscopy (LFM)
- Magnetic Force Microscopy (MFM)
- Surface Potential (KPFM)
- Scanning Capacitance Microscopy (SCM)
- Scanning Spreading Resistance Microscopy (SSRM)
- Scanning Microwave Impedance Microscopy (sMIM)
- Tunneling AFM (TUNA)
- Conductive AFM (CAFM)
- Electrochemical AFM (EC-AFM)
- Scanning Electrochemical Microscopy
- Scanning Tunneling Microscopy (STM)
- EC-STM
- Torsional Resonance Mode (TRmode)
- TR-TUNA
- Thermal Analysis (VITA)

ScanAsyst
PeakForce QNM
PeakForce TUNA
PeakForce KPFM
PeakForce SSRM
PeakForce SECM
PeakForce IR
Ambient Control: Glovebox
ICON EC Setup

- Scanner Head
- Fluid Probe Holder
- EC Cell
- ICON EC Chuck w/Heater RT~65°
EC Cell & AFM Probe Holder

Chemically Compatible --- Easy Assembly --- Closed Cell

AFM Probe Holder
EC Cell
Closed Cell
When Engaged

Glass cover plate
Kalrez O-ring
Teflon / Kel-F cell bodies
Sample
In-Situ AFM Study of Failure Mechanisms of Solid Electrolyte Interphase (SEI) in Lithium-Ion Batteries

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Questions that we want to address

• What are the mechanical properties of SEI layer?
  • Elastic Modulus
  • Fracture Toughness etc.

• How does SEI layer fail?
  • Does it crack?
  • Does it delaminate?
  • Does it spall off?

• How can we tailor SEI properties so that it can withstand volume expansion and contraction of high capacity materials like Si
Experimental Approach

Utilize “lateral sliding” of patterned Si island structure to apply strain in the SEI layer and look for failure using in-situ AFM.

- **Sample Configuration**
  (prepared using photolithography)

  ```
  a-Si
  (15um X 15um X 225nm)
  Cu (200nm)
  Ti (20nm)
  Quartz Wafer
  40mm X 40mm X 500um
  ```
AFM Setup

Lithium Foil as CE/RE

Patterned Island Si Anode

Ni wire connecting lithium foil

Assembled EC Cell
Effect of Deformation of Island on SEI layer
• ~330nm thick SEI after 1\textsuperscript{st} cycle

• After delithiation, edge of the island is thicker compared to center of island which suggests more SEI formation at edge
SEI Crack Evolution During 2nd Cycle

1.5 V

5 μm
• Apart from cracks at corners, new cracks in the shear lag region (edge region) were generated.

• During 2\textsuperscript{nd} cycle, center of island comes back to original height suggesting very minimal “new SEI” formation but edge of the island continues to form new SEI.
Quantification of Island Sliding

Average (overall) strain of ~10% at full lithiation
Roughness Evolution

Edge of the island much rougher compared to center of island
A Close look at SEI Crack

- Most of the cracking occurs in shear lag region.
- Corners of the island has 3D deformation compared to the edge with 2D deformation. This leads to severe cracking in corner compared to edge of island.
- There seems to be partial delamination at the interface of SEI/Si during delithiation (at crack sites).
Tracking Evolution of SEI Crack

- 1.5V_Delithiation
- 0.4V_Delithiation
- 0.05V_Scan2
- 0.05V_Scan1
- 0.2V_Scan3
- 0.2V_Scan2
- 0.2V_Scan1
- 1.5V

Height (a.u.):

- 6.2 um from top
- 6.7 um from top
Tracking Displacement to Calculate Local Strain

\[ \varepsilon = \frac{du}{dx} \]

<table>
<thead>
<tr>
<th>V</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>15</td>
</tr>
<tr>
<td>0.05</td>
<td>32</td>
</tr>
</tbody>
</table>
Fracture Toughness Calculation

The energy release rate $G$ can be written as:

$$G = \frac{\sigma^2 h}{E_f} \omega(\alpha, \beta, a/h)$$

This results in values of $\omega$:

$$0.85 \leq \omega \leq 1.38$$

Ye et al., Int. J. of Solids Structures, 29 (21), 2639-48, 1992
First Cycle Lithiation: Two Phase Lithiation Phase Front

1st Cycle (0.3 V Hold)

The lithiation front velocity was estimated to be 2.2nm/s.
SEI layer: After 7 cycles

1.5V
Conclusions

- Li-Ion battery is a complex material and engineering system.
- In situ, in operando characterization at the nano scale is required to reveal the dominant factors governing battery lifetime and performance.
- Bruker AFMs with PeakForce tapping and glovebox integration provide a versatile solution for Li-Ion battery research.
- With high resolution AFM scanning we were able to observe for the first time the failure of the SEI layer and how it evolved during cycling.
- With this observation, we were able to calculate the critical strain at which this failure starts and also estimate fracture toughness which will be very useful in understanding mechanics of SEI layer.
DOE-BMR

If you need Bruker AFM help:
Atomic Force Microscope Technical Support Group
Phone: +1 800-873-9750
E-mail: AFM.Support@bruker.com
Website: www.bruker.com
Bruker Support: http://brukersupport.cony
Resources: www.nanoscaleworld.bruker-axs.com
Bruker Probes: www.brukerafmprobes.com
# PeakForce Tapping vs Other Modes

<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Contact Mode</strong></td>
<td>• Simple and direct force control.</td>
<td>• Relatively high contact force and shear force cause tip wearing</td>
</tr>
<tr>
<td></td>
<td>• Provides lateral force signal.</td>
<td>and possible sample damage, even with soft cantilever.</td>
</tr>
<tr>
<td></td>
<td>• Tip has solid contact with sample, good for electrical measurement.</td>
<td>• Sensitive to optical interference and laser signal drift.</td>
</tr>
<tr>
<td></td>
<td>• Extensions of this technique: Conductive AFM, SCM, Piezoresponse.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Relatively high contact force and shear force cause tip wearing</td>
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<tr>
<td></td>
<td>• Sensitive to optical interference and laser signal drift.</td>
<td></td>
</tr>
<tr>
<td><strong>Tapping Mode</strong></td>
<td>• Less tip and sample wear compared to contact mode.</td>
<td>• More complicated than contact mode.</td>
</tr>
<tr>
<td></td>
<td>• Usually less normal tip-sample force than in contact mode, no shear force.</td>
<td>• No direct force control.</td>
</tr>
<tr>
<td></td>
<td>• Phase signal relates to sample properties.</td>
<td>• Tip only intermittently or never contacts surface, so technique is</td>
</tr>
<tr>
<td></td>
<td>• Less sensitive to optical interference and laser signal drift compared to</td>
<td>not compatible with some electrical measurements.</td>
</tr>
<tr>
<td></td>
<td>contact mode</td>
<td>• Requires cantilever tuning to find resonance frequency.</td>
</tr>
<tr>
<td></td>
<td>• More complicated than contact mode.</td>
<td>• Difficulty for imaging in vacuum and liquid</td>
</tr>
<tr>
<td><strong>PeakForce Tapping Mode</strong></td>
<td>• Direct force control, typically requires only pN peak force, and minimized shear force.</td>
<td>• Scan speed is limited by the peak force tapping frequency, but similar to regular Tapping Mode.</td>
</tr>
<tr>
<td></td>
<td>• Force-distance curve at every pixel allows for quantitative mechanical</td>
<td></td>
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<tr>
<td></td>
<td>measurement.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Does not rely on cantilever resonance frequency, so no need to tune the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cantilever.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Auto optimization of feedback parameters for topographic measurements.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Good for electrical measurement.</td>
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