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Nissan Leaf battery: mass = 600 lb, range
~ 100 miles, battery cost ~ $18,000
## Basic Economics of Car Batteries – An elementary argument

<table>
<thead>
<tr>
<th>Fuel cost to drive a mile</th>
<th>~ $0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of gas tank</td>
<td>~ $0.00</td>
</tr>
<tr>
<td>Fuel cost drive a mile</td>
<td>~ $0.02</td>
</tr>
<tr>
<td>Cost of battery</td>
<td>~ $500/kWh (Volt has a 16 kWh battery ~ $8000)</td>
</tr>
</tbody>
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- Need to drive 100,000 miles in Volt to recover the up-front battery cost.
- Must reduce cost/kWh and must make them last for 3000 – 4000 cycles.
- To reduce cost, must make them more compact, i.e., increase the energy density.
- To increase energy density, develop new electrode materials, better materials design, better electrolytes, newer battery chemistries, ...
Basic Anatomy of a Li-ion Battery

Lithium-ion battery

Electrolyte LiPF$_6$ in Ethylene carbonate/diethyl carbonate

Conductive additives

Binder

Li$^+$$e^-$$C_6$$\rightarrow$$LiC_6$

LiCoO$_2$$\rightarrow$$Li^+$$e^-$$CoO_2$

Image source: V. Srinivasan, LBNL
Electrode Potentials During Charging-Discharging

\[ LiCoO_2 \rightarrow Li^+ + e^- + Li_{1-y}CoO_2 \]

**Electrolyte oxidation**

**Solvent reduction- Passive film formation**

**Lithium deposition**

**Cobalt oxide**

140 mAh/g

**Graphite**

372 mAh/g

**Voltage (V) vs. Li**

\[ xLi^+ + xe^- + C_6 \rightarrow Li_xC_6 \]

\[ x \text{ in } Li_xC_6 \text{ or } y \text{ in } Li_{1-0.51y}CoO_2 \]
How to Increase the Energy Density of Li-ion Batteries?

- Promising materials: Si, Al, Sn, their alloys and composites (theoretical charge capacity of graphite ~ 370 mAh/g, Si ~ 3750 mAh/g).
- Silicon-based anodes can result in ~ 30% increase in energy density.
- The challenge is not just energy density, but also cycle life and calendar life.
Volume Expansion Induced Mechanical Damage in Silicon-based Anodes

• Managing the volume expansion-induced stress field and the associated “mechanical degradation” is a primary challenge in developing a new generation of higher energy density rechargeable batteries.
• Chemical degradation in a battery is closely coupled to mechanical damage.
• Mechanical damage and electrochemical performance are extremely sensitive to micro-structural parameters, materials choice and processing parameters.
Basic understanding of the mechanics of the constituent materials, structures and interfaces.
Quantitative description of mechanical damage modes.
Understanding of how mechanics and electrochemistry interact with each other.
Predictive modeling tools for cycle-life and capacity fading.
Real-time Measurement of Stress in Si Films During Electrochemical Cycling

Sample geometry

Elastic substrate

- Cu film (250 nm)
- Si film: sputter deposited (50 - 200 nm)

Stoney equation

\[
\sigma_f = \frac{1}{6} \left( \frac{1}{R} - \frac{1}{R_0} \right) \frac{E_s t_s^2}{(1 - V_s) t_f}
\]

MOSS – Multi-beam Optical Stress Sensor;
Measurement sensitivity: \( R \sim 10,000 \) m
Potential and Stress Evolution under Constant Current Lithiation and Delithiation

- Lithiated silicon undergoes extensive plastic deformation.
- The ability to undergo extensive plastic deformation underpins the mechanisms of damage evolution in all Si-based anode architectures (films, composites, nano/micro wires, core-shell, ...).
Potential and stress hysteresis in silicon anodes during electrochemical cycling

Hysteresis area: Total energy loss in a cycle

Hysteresis area: mechanical energy loss in a cycle due to plasticity

- Mechanical energy loss due to plasticity is 38% - 44% of the total energy loss.

- Low cycle fatigue due to large plastic strains.

- The significant contribution from plastic dissipation immediately suggests a strong coupling between stress and potential.
Stress-potential coupling in electrode materials

Larche-Cahn (1978) theory for chemical potential for a solid solution

\[ \mu = \mu_0 + kT \log\left( \frac{c}{c_0} \right) - \frac{\Omega \eta}{3} \sigma_{kk} - \Omega \beta_{ijkl} \sigma_{ij} \sigma_{kl} \]

- \( \sigma_{ij} \): stress tensor
- \( \eta = \frac{\partial \varepsilon_v}{\partial c} \), \( \varepsilon_v \): volumetric strain
- \( \beta_{ijkl} = \frac{\partial S_{ijkl}}{\partial c} \), \( S_{ijkl} \): Elastic Compliance Tensor
- \( \Omega \): Reference atomic volume

\[ eE = \mu_{ref} + kT \log\left( \gamma \frac{c}{c_0} \right) - \frac{\Omega \eta}{3} \sigma_{kk} - \Omega \beta_{ijkl} \sigma_{ij} \sigma_{kl} \]

- Mechanics and electrochemistry are coupled naturally through solution thermodynamics
Measurement of Elastic Modulus of Lithiated Silicon as a Function of Li Concentration

- Elastic modulus decreases by ~ 50%.
- Useful data for modeling mechanical response of electrode microstructures, especially when combined with the ability to deform plastically.
How strong is the stress-potential coupling?

Equilibrium potential

\[ eE = \mu_{ref} + kT \log \left( \frac{c}{c_0} \right) - \frac{\Omega \eta}{3} \sigma_{kk} - \Omega \beta_{ijkl} \sigma_{ij} \sigma_{kl} \]

\[ \Delta E = \frac{\Omega \eta}{3e} \Delta \sigma_{kk} \]

\[ \Omega \approx 2 \times 10^{-27} \text{ m}^3/\text{atom}; \quad \eta \approx 0.75; \]
\[ e = 1.6 \times 10^{-19} \text{ C}; \quad \sigma_{kk} \approx 2 \text{ GPa} \]

\[ \Delta E \approx 63 \text{ mV/GPa} \]

- The effect of stress is non-trivial in all materials that can sustain high stresses.
Experimental Measurement of Stress-Potential Coupling

- Measured stress – potential coupling $\Delta E$ 98-105 mV/GPa
- Agrees “reasonably well” with the back of the envelope calculation of 63 mV/GPa
- Important consequences for silicon anode performance, especially in relation to Li plating and safety.
Effect of Stress on Equilibrium Cell Potential

Equilibrium potential in stress-free state and no current

Equilibrium potential under tensile stress

Equilibrium potential under compressive stress

State of charge/Li concentration (C)
Effect of Stress on Charge/Discharge Capacity

Equilibrium potential in stress-free state and no current

Equilibrium potential under tensile stress

Equilibrium potential under compressive stress

Upper cut-off potential

Lower cut-off potential

State of charge/Li concentration (C)
Local Effects Due to Inhomogeneous Stress Field – Possible Li Plating

Severe compressive stress at particle-particle contact

- Local high compressive stresses in a complex microstructure can lead to enhanced conditions for Li plating.
What happens to crystalline Si particles during first cycle lithiation?

- Formation of well-defined phases as determined by the Si-Li phase diagram

Boucamp, Lesh, Huggins, 1981

415°C
Room temperature lithiation of crystalline silicon

- Crystalline – amorphous phase transformation during first cycle lithiation is traumatic to the material; the resulting damage stays with the material for the rest of its life.
- Since stresses can be large (~ 1 GPa), they can alter the thermodynamic driving force for phase transformation.

Obrovan and Krause, ECS 2007
Experimental Measurement of Stress Jump Associated with Phase Transformation in Si

Moving phase boundary

(a-\text{Si}) \rightarrow (100) \text{Si wafer} \rightarrow (x-\text{Si})

Phase Boundary Depth (nm)

\[ \sigma \cdot h \left(10^3 \text{ Pa} \right) \]

Compressive stress in amorphous layer $\sim 0.5 \text{ GPa}$
• Sharp phase boundary ~ 1 nm
• Dependence of phase transformation kinetics on crystal orientation?
Cyclic Voltammetry of Si on different crystal planes

Phase boundary initiation potential changes with crystal orientation (100 – 120 mV)

Crystalline to amorphous phase transformation is sluggish on (100) planes compared to (110) and (111) planes. At a given potential, the phase boundary appears to move ~ 2 times as fast on (110) plane compared to (100) plane.
Lithiation-delithiation of Si (100) Wafer

- Lithiation process:
  - a-Si (amorphous silicon) deposition
  - Li insertion at constant flux; stress is compressive.
  - Product of stress and film thickness
  - ~ constant potential during lithiation

- Delithiation process:
  - Li removal at constant flux; stress becomes tensile
  - Phase transformed film fractures under tensile stress

Graph:
- Tensile stress (σ) vs. Compressive stress (c) vs. Time (hr)
- Potential (V) vs. Time (hr)

Graph highlights:
- Compressive stress during lithiation:
  - Movement from negative to positive values
- Tensile stress during delithiation:
  - Movement from positive to negative values
- Potential (V) curve:
  - Cell potential increases with time
  - Potential plateau during certain stages of lithiation and delithiation
Lithiation-delithiation of Si (100) Wafer and fracture

- Can the crack network be stabilized so that additional cycling does not induce further damage?
Cycling a Si wafer – coulombic efficiency

Wafer Cell 201: 0.18V – 0.6V
Core-collapse in wound electrodes

Source: Presentation Prof. T. Takamura “Carbon Material in Power Sources”. June 2005, ZSW Ulm

Li-ion batteries Hazard and use assessment, Exponent, 2011
Buckling of Constrained Rings

Omara et al, 1997; Chan and McMinn, 1966; El-Bayoumy, 1972
Stress and Damage Evolution in Composite Electrodes

- Complex microstructure (active particles, binder, conductive additive, porosity)
- Stress measurement can serve the following purposes:
  1. Serve as a quantitative measure of how materials and process parameters influence damage evolution through the stress field
  2. Serve as a diagnostic tool to predict long term performance and cycle life
  3. Enable development of detailed mechanics models that can predict failure modes and hopefully inform the materials design process to mitigate damage evolution

Gen2 PHEV Anode – Argonne National Laboratory
SEM image of the composite anode cross section, the vertical length-bar is corrected for the 52-degree glancing angle.
The composite electrode is epoxy bonded to a Si (111) wafer resulting in a 4-layer structure:

\[
\sigma^* = \frac{h_1^2 M_1 \kappa}{6h_4 f \left( h_i, M_i \right)}
\]

where \( \sigma^* \) is the average stress, \( h_1 \) is the thickness of the active material, \( M_1 \) is the modulus of the active material, \( \kappa \) is the curvature, \( f \) is the function of thicknesses and moduli of the four layers, and \( h_i \) and \( M_i \) are the thickness and modulus of the \( i \)-th layer (Elastic wafer, Copper CC, Epoxy, Active material).
SEM image, cross-section of the wafer-composite structure
From left, the layers are Si $<111>$ wafer, Epoxy layer, Cu substrate and the graphite anode
ANL Gen 2 Negative Electrodes: Electrochemical and Mechanical Data
Cycled galvanostatically at 50 μA/cm² (ca. C/36 rate)
Correlation between “staging” and rate of stress evolution

- Influence of elastic modulus evolution with lithiation in graphite?
- Rate of volume expansion during staging?
- Needs further investigation.
Buckling of Constrained Rings

Compressive stress necessary to initiate buckling in a single layer = 5 – 20 MPa
Relevance of Mechanics Phenomena in the Design and Performance of Energy Storage Materials?

• A comprehensive understanding of the mechanics phenomena is important to place battery electrode design on a quantitative foundation.
• Demonstrated the importance of mechanical properties of lithiated silicon.
• Stress-potential coupling in Si and its implications
• Stress field associated with phase transitions in Si and the damage it causes
• Can cracked wafer geometry be a viable anode architecture?
• Stress evolution in composite electrodes