Mechanical properties of lithiated silicon: A candidate electrode for lithium ion batteries

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Mechanical properties of lithiated Si – a candidate electrode for Li-ion batteries

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Albufeira, Portugal

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Mobile energy storage: Li ion batteries

- Longer
- Lighter
- Smaller
- Stronger
- Cheaper
- Safer

http://www.samsung.com
http://hacknmod.com

Silicon is a potentially attractive anode for Li ion batteries
Lithium-ion battery: discharging

1. **LiCoO$_2$** (140 Ah/kg)

   - Positive electrode
   - Non-aqueous liquid electrolyte

2. **Silicon** (4200 Ah/kg)

   - Negative electrode

   **Specific energy**:

   

   \[
   135 \text{ Ah/kg} \times 3.2 \text{ V} = 433 \text{ Wh/kg}
   \]

   **DOE goal for materials**: 400 Wh/kg


ECI 2015 – W.D. Nix
In-situ TEM of crystalline Si nanoparticles during lithiation

M.T. McDowell, I. Ryu, S. W. Lee et al., Advanced Materials, 2012

Fracture at surface

ECI 2015 – W.D. Nix
Lithiation of an amorphous Si nanoparticle

M.T. McDowell et al, Nano Letters (2013)
Lithiation of amorphous silicon on Ni

Unlithiated  Lithiated  Cross-Sectioned

Modeling requires mechanical properties of Li-Si

ECI 2015 – W.D. Nix
Nanoindentation of unlithiated and lithiated amorphous Si films on Mo substrates

- Molybdenum is notably stronger than nickel
- Amorphous silicon films may blister upon lithiation
- Material between blisters is suitable for nanoindentation

Precise positioning of indents is required

ECI 2015 – W.D. Nix
Nanoindentation in mineral oil reservoir

New Approach for Indentation of Li-Si

- Designed holder for precise lateral \((x,y)\) positioning.

![Diagram with labels](image)

I. Fluid cell diamond tip
2. 100x oil immersion objective
3. Mineral oil immersion bath
4. Lithiated silicon pillar sample
5. Removable sample mounting puck
6. Modified fluid reservoir holder

Agilent Technologies Nanoindenter XP

L.A. Berla, 2014

ECI 2015 – W.D. Nix
Nanoindentation of lithiated amorphous silicon

![Graph showing hardness and modulus of lithiated silicon](image)

- **Load (mN)**: 0 to 16
- **Displacement (nm)**: 0 to 800

- **Hardness & Modulus**
- **Creep**

*ECI 2015 – W.D. Nix*
Mo substrate affects modulus – extrapolation to find modulus of Li-Si
Composition dependence of Young’s modulus

![Graph showing composition dependence of Young's modulus](image)
Hardness affected by surface topology and substrate yielding – plateaus observed in between
Hardness (and yield strength) strongly affected by Li concentration

Composition dependence of mechanical properties should be included in modeling of Li-Si
Power law creep with a high exponent is observed

\[ \varepsilon = \frac{1}{h} \frac{dh}{dt} \]

Compute strain rate at each point with spline fit (six neighboring points – polynomials of order 3)

\[ p \sim P / h^2 \]

\[ (\sim \text{mean contact pressure}) \]

Assume power law form:

\[ \varepsilon = B p^n \]
What is the correct $h$ vs. $\Delta t$ law for power law creep?

\[ \varepsilon = \frac{1}{h} \frac{dh}{dt} = B p^n = B \left( \frac{P}{\alpha h^2} \right)^n \]

\[ \int_{h_o}^{h} h^{2n-1} dh = \int_{t_0}^{t} B \frac{p^n}{\alpha^n} dt \]

\[ h = \left( h_o^{2n} + 2nB \frac{p^n}{\alpha^n} \Delta t \right)^{1/2n} \]

Belehradek function

\[ h = C_1 (\Delta t - C_2)^{C_3} \]

\[ C_1 \equiv \left( 2nB \frac{p^n}{\alpha^n} \right)^{1/2n} \quad -C_2 \equiv \frac{h_o^{2n}}{2nB \frac{p^n}{\alpha^n}} \quad C_3 \equiv \frac{1}{2n} \]
Comparison with indentation creep method of Su et al. 

\[ \varepsilon = \frac{1}{h} \frac{dh}{dt} = Bp^n = B\left(\frac{P}{\alpha h^2}\right)^n \]

\[ \int_0^h h^{2n-1} dh = \int_0^t B \frac{P^n}{\alpha^n} dt \]

\[ h = \left(2nB \frac{P^n}{\alpha^n}\right)^{1/2n} t^{1/2n} \]

\[ h = C_1 t^{C_3} \]

\[ \log(h) = \log(C_1) + C_3 \log(t) \]

\[ C_1 \equiv \left(2nB \frac{P^n}{\alpha^n}\right)^{1/2n} \]

\[ C_3 \equiv \frac{1}{2n} \]
Su et al. results for amorphous selenium
Su, .. Oliver, Pharr, et al., JMPS 2013

Uniaxial creep

Indentation creep

Non-constant exponent from power law fitting

\[ h = \left( \frac{2nB}{\alpha^n} \right)^{1/2n} t^{1/2n} \]
Comparison of Power Law and Belehradek

**Power Law function**

\[ h = C_1 t^C_3 \]

- \[ C_1 = 7.02794 \]
- \[ C_3 = 0.53296 \]

**Belehradek function**

\[ h = C_1 (\Delta t - C_2)^C_3 \]

- \[ C_1 = 687.13241 \]
- \[ C_2 = -2.15914 \]
- \[ C_3 = 0.020374 \]

*Indentation of amorphous Li\(_{3.75}\)Si*
Short time creep to avoid possible drift effects (using the Belehradek fitting function)

\[ h = C_1 (\Delta t - C_2)^{C_3} \]

- \( C_1 = 687.13241 \)
- \( C_2 = -2.15914 \)
- \( C_3 = 0.02037 \)

\( h \equiv \) contact pressure

\( p \equiv \text{contact pressure} \)
Longer time creep using CSM and method of Maier et al. (with the Belehradek function)

Maier, Merle, Göken, Durst, J. Mater. Res. 28, 1177 (2013)

nine indentations

Power law creep confirmed

$\Delta t$ (s)

$10^{-2}$

$10^{-3}$

Pressure (GPa)

$n_{avg} = 24.8$

$C_1 = 640.40246$

$C_2 = -27.32007$

$C_3 = 0.02294$
Drift is small in this case. Power law creep again confirmed. Determining drift term in displacement data (using the Belehradek function).
Possible physical interpretation of power law creep with high stress exponent

Stress-driven thermally activated flow

\[ \dot{\varepsilon} = \varepsilon_0 \exp \left( -\frac{\Delta G(\tau)}{k_B T} \right) = Bp^n \quad n \approx 24 \]

Activation volume

\[ \Delta V^* = -\left( \frac{\partial \Delta G(\tau)}{\partial \tau} \right)_T = k_B T \left( \frac{\partial \ln \dot{\varepsilon}}{\partial \tau} \right)_T = \frac{nk_B T}{\tau} \]

\[ \Delta V^* \approx \frac{n3\sqrt{3}k_B T}{p} \approx 0.38 \text{nm}^3 \quad V(Li_{15}Si_4) = 0.3\text{nm}^3 \]
Conclusions

• Silicon is an attractive candidate material for anodes in Li ion batteries.

• Huge volume changes and deformation are associated with lithiation and delithiation.

• Nanoindentation is useful in determining the composition dependence of hardness and modulus of amorphous Li-Si alloys.

• Nanoindentation can be used to study observed creep effects in Li-Si alloys.

• Stiffness measurements allow drift effects to be removed from indentation creep.
Thank you for your interest and attention
Oil-immersion nanoindentation

Fused silica standard

Presence of protective oil does not influence indentation results

--- Verified on a wide range of materials ---
Storage of Li-Si in mineral oil

- Mineral oil is used to protect metallic Li from reacting with air.
- Similarly, mineral oil can be used to slow the oxidation of Li-Si.

Indentation in mineral oil!
Protection of Li-Si in mineral oil is required

- Mineral oil is used to protect metallic Li from reacting with air.
- Similarly, mineral oil can be used to slow the oxidation of Li-Si.

Indentation in mineral oil!

Li-Si in air

Li-Si in oil

4 hr 0 min
Creep recovery makes drift measurements problematic for Li-Si alloys

(a) Creep

(b) Start of creep, Start of recovery
Similar power law creep at reduced stress (using the Belehradek function)

Maier, Merle, Göken, Durst, J. Mater. Res. 28, 1177 (2013)

After unloading from 15 mN to 5.8 mN – to 520 MPa

power law creep again confirmed
Delithiation

Unlithiated  
Delithiated  
Cross-Sectioned

$d=2600 \text{ nm}$

Modeling requires mechanical properties of Li-Si
Ngan’s function fits this small time data well (five fitting coefficients)

Thus, Ngan’s function gives similar stress exponent as Belehradek function
Good fit to $h$-versus-$\Delta t$ data gives stress exponent similar to what we get with Belehradek function.

$h = C_1 + C_2 \exp(-\Delta t/C_3) + C_4 \exp(-\Delta t/C_5)$. 

Linear Fit:
\[ y = 24.91x - 6.04 \]
Sensitivity of results (strain rate versus pressure) to quality of fit to $h$ versus $\Delta t$ data.
Young’s modulus of all Li-Si alloys

![Graph showing Young's modulus vs. contact depth for various Li concentrations. The x-axis represents contact depth in nanometers (nm), and the y-axis represents Young's modulus in GPa. Different markers and line styles are used to represent different Li concentrations: $x_{Li} = 0$, $x_{Li} = 0.52$, $x_{Li} = 0.64$, $x_{Li} = 0.71$, $x_{Li} = 0.79$, and $x_{Li} = 1$. The graph illustrates how the modulus changes with contact depth and Li concentration.]
Nanoindentation overview

Oliver & Pharr Method

\[ h_c = h - \varepsilon \frac{P}{S} \]

\[ A_c = \pi a_c^2 = f(h_c) \]

\[ H = \frac{P}{A_c} \quad E_r = \frac{S}{2\beta} \sqrt{\frac{\pi}{A_c}} \]

From tip shape calibration
Creep effects are observed

L.A. Berla, 2014

Peak Load = 15 mN
Hardness $\text{Li}_{15}\text{Si}_4$ ~ 1.5 GPa
Hardness a-Si ~ 10 GPa

Fully lithiated silicon
1) Ramp to peak load ($p$ ~1.5 GPa)
2) Hold (600 s)
3) Unload

Unlithiated a-silicon
1) Ramp to peak load
2) Unload to pressure $p$~1.5 GPa
3) Hold (600 s)
4) Unload

Creep measurement

Creep in lithiated phase!
(minimal recovery)
Conclusions

• The Nanoindenter of Pethica and Oliver came along at the perfect time to help in the development of thin film technologies.

• It caused me to completely change directions in research.

• The method of Oliver and Pharr helped to establish nanoindentation as the most widely applicable technique for the study of small scale materials.

• The study of lithiated silicon thin films on Mo substrates described here is just another application of this well established technique.