In situ Stress-Measurements on Li-ion Battery Electrode Materials

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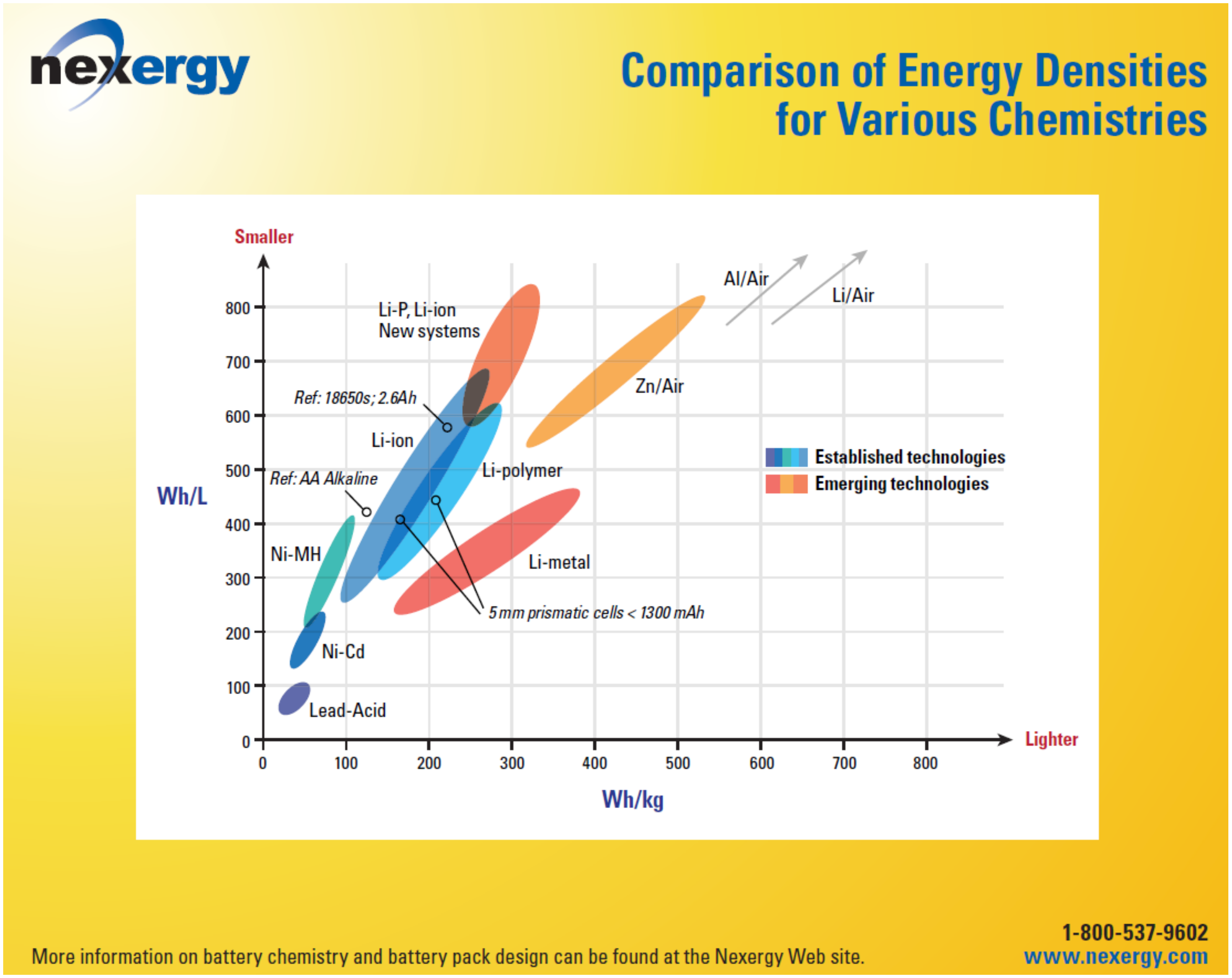
NASA (EPSCoR)

Energy Density of Battery Chemistries



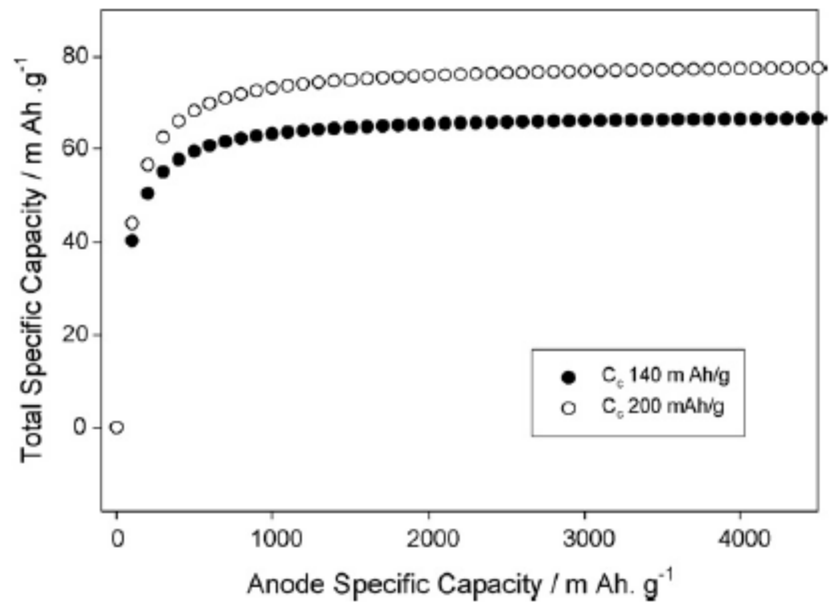
Why Silicon Anodes?

$$\text{Total cell (mAh g}^{-1}) = \frac{1}{(1/C_A) + (1/C_c) + (1/Q_M)} = \frac{C_A C_C Q_M}{C_A Q_M + C_C Q_M + C_A C_C}$$

- C_A and C_C are theoretical specific capacities of anode and cathode.
- $1/Q_M$ is the specific mass of all other components; depends on battery design

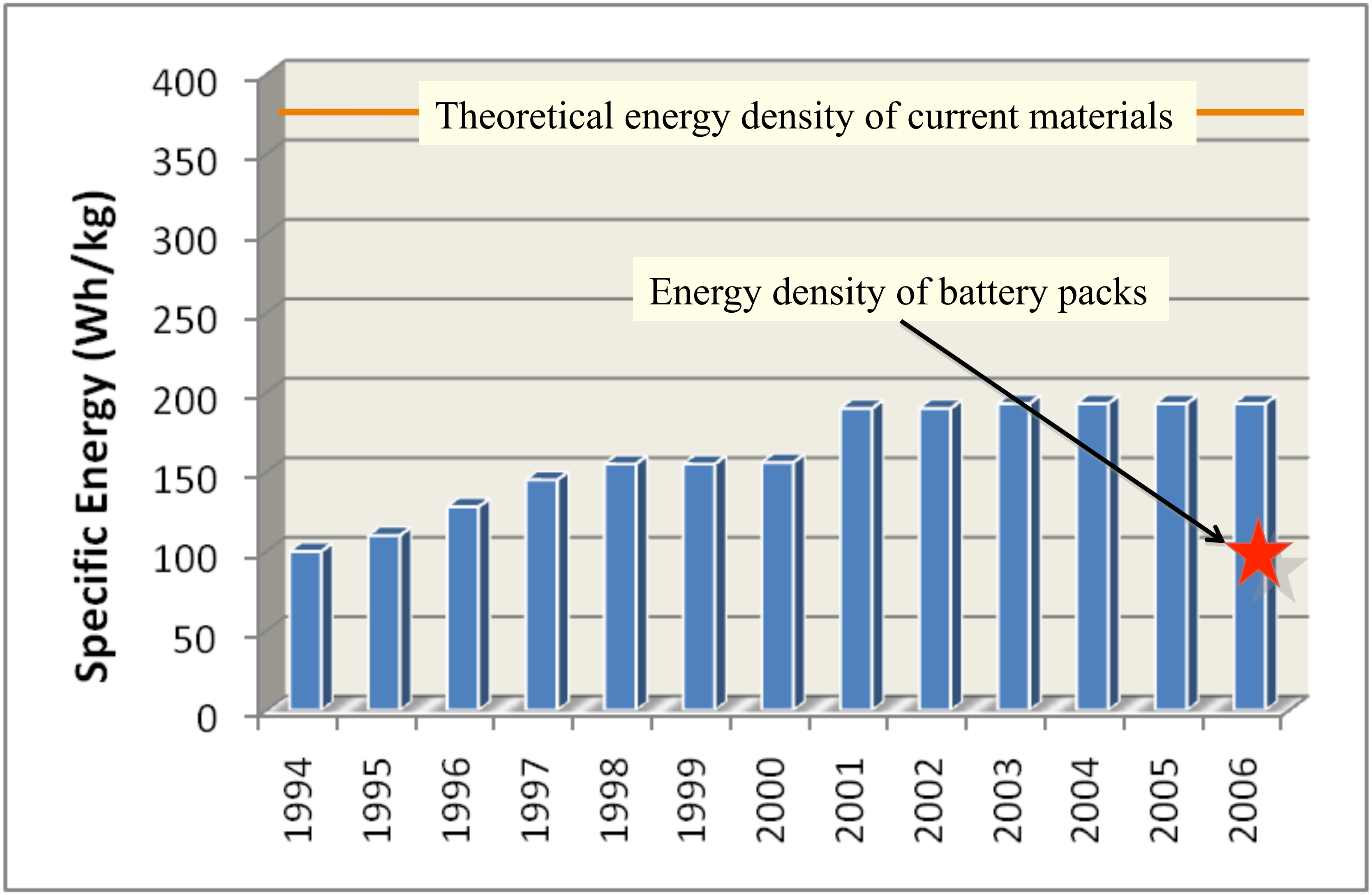
C_A (graphite) = 372 mAh/g
C_A (silicon) = 3750 mAh/g
C_C ($LiCoO_2$) = 135 mAh/g
C_C (LiMnO2, LiFePO4, etc) ~ 160 – 200 mAh/g
C_C (V and Cr oxides) ~ 300 – 500 mAh/g
Q_M (Sony 18650G8) = 130 mAh/g

(Appleby et al. JPS 2007)



- Opportunity to develop higher charge capacity anodes based on Si to realize substantial reduction in battery weight.

Energy Density Increase of Consumer Electronic Li-ion Batteries



Source: V. Srinivasan, LBNL

Source: TIAX, LLC

Challenges in Employing Silicon Anodes

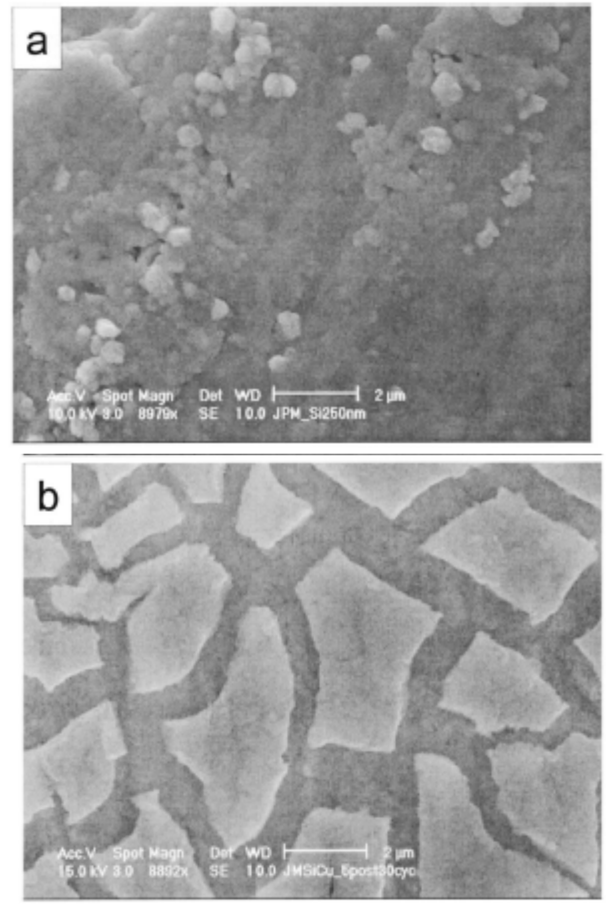
Journal of Electrochemical Society, 1981

All-Solid Lithium Electrodes with Mixed-Conductor Matrix

B. A. Boukamp,* G. C. Lesh, and R. A. Huggins*
Department of Materials Science and Engineering, Stanford University, Stanford California 94305

Table II. Crystal structure, unit cell volume, formula units per unit cell, crystal volume per Si atom, and theoretical density for the Li-Si system

Compound and crystal structure	Unit cell volume (Å^3)	Formula units per unit cell	Volume per Si-atom (Å^3)	Theoretical density (g/cm^3)	Ref.
Si Cubic	160.2	8	20.0	2.33	
$Li_{12}Si_7$, ($Li_{1.71}Si$) Orthorhombic	2436	6	58.0	1.15	(15)
$Li_{14}Si_6$, ($Li_{2.33}Si$) Rhombohedral	308.9	1	51.5	1.43	(16)
$Li_{13}Si_4$, ($Li_{3.25}Si$) Orthorhombic	538.4	2	67.3	1.38	(17)
$Li_{22}Si_5$, ($Li_{4.4}Si$) Cubic	6592	16	82.4	1.18	(11, 18)

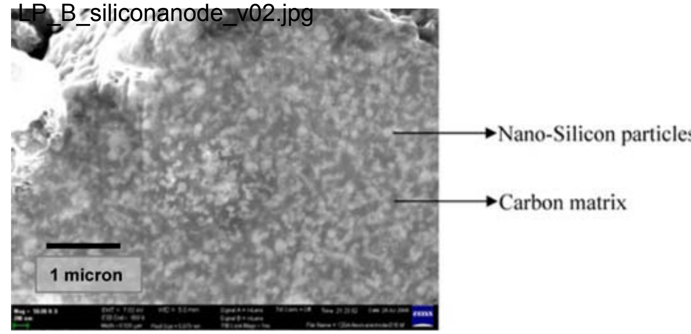


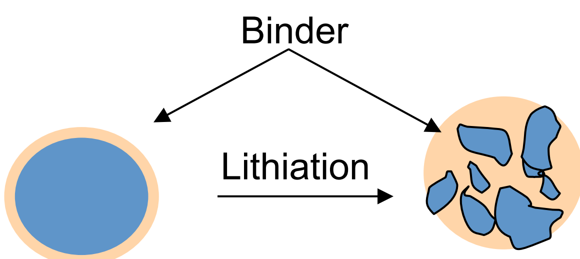
Maranchi et al. Electrochemical and solid state letters, 2003.

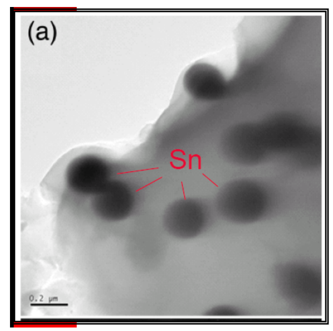
Some strategies to develop silicon based anodes

- Composites (eg. Silicon/graphite)
- Silicon particles in a binder (CMC)
- Reduce particle size to prevent cracking during expansion
  - Approach 1: Embed smaller particles in an inactive matrix (*e.g.,* Sony “Nexelion” battery)
  - Approach 2: Form micro/nano structures

http://www.tiaxllc.com/img/LP_B_siliconanode_v02.jpg

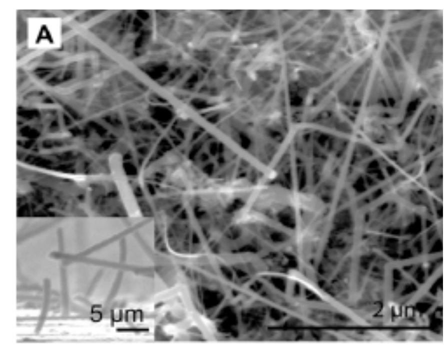






ESL, 7, A44 (2004)

Chan et al. 2007



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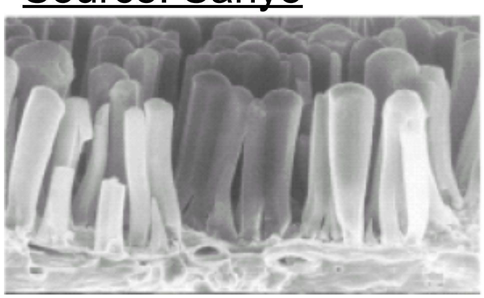
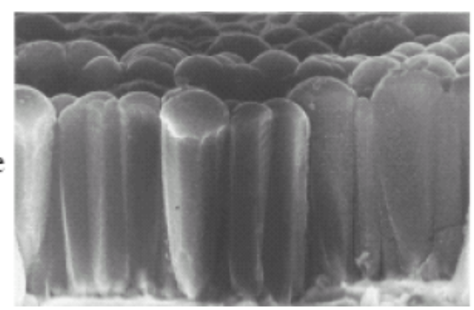
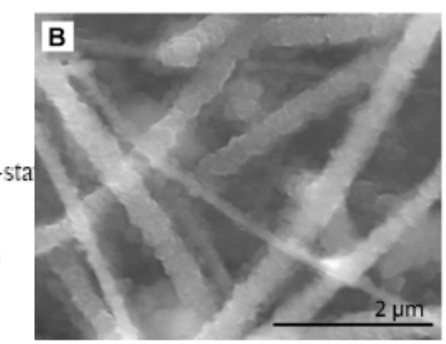


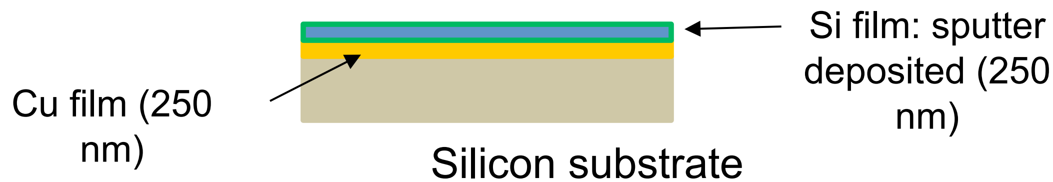
(a)Discharged-state
10µm

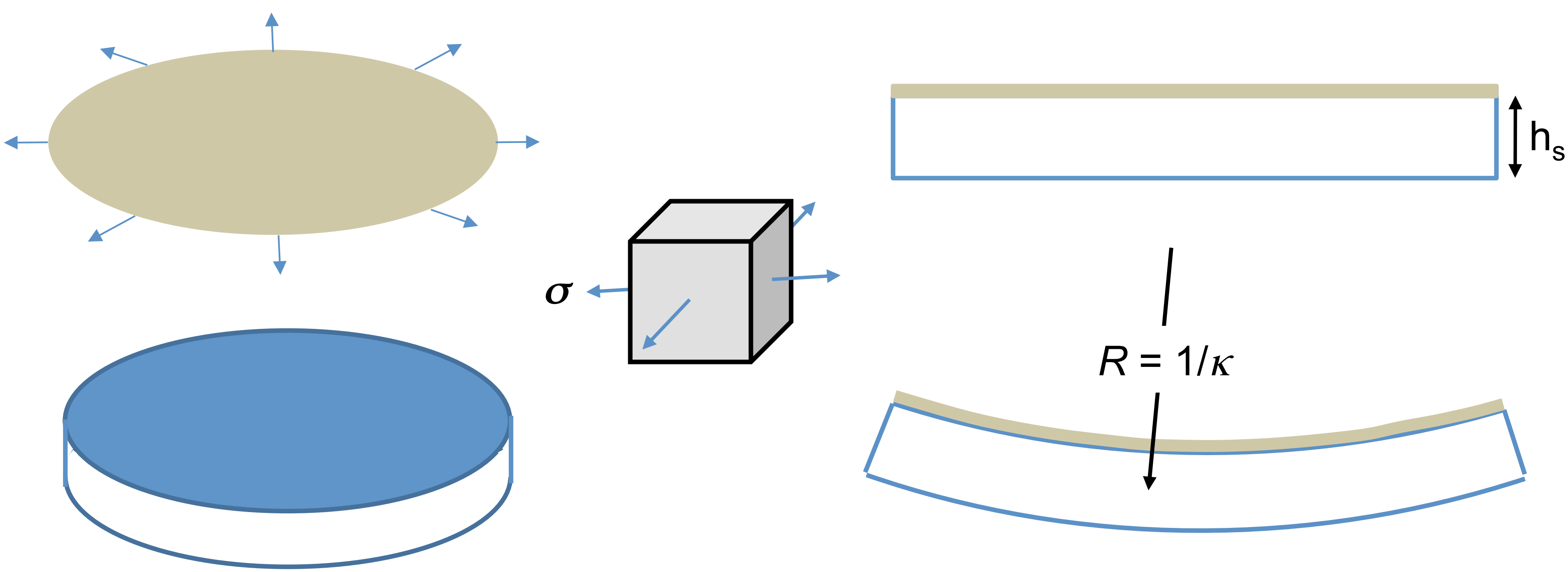


(b)Charged-sta
10µm



Thin film stress and wafer curvature





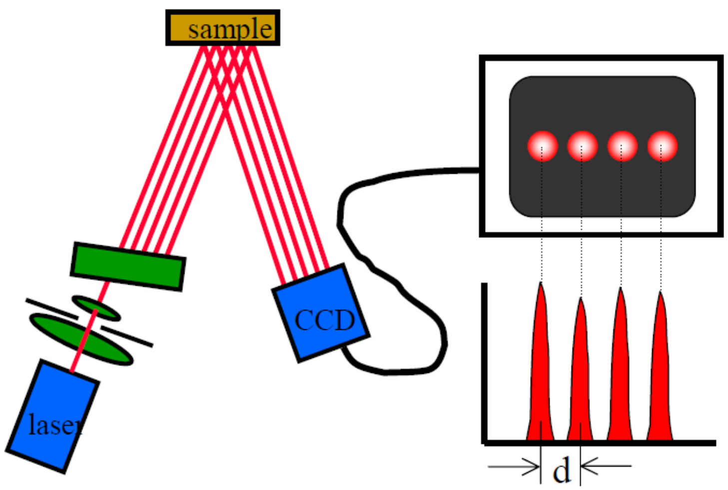
Stoney Equation

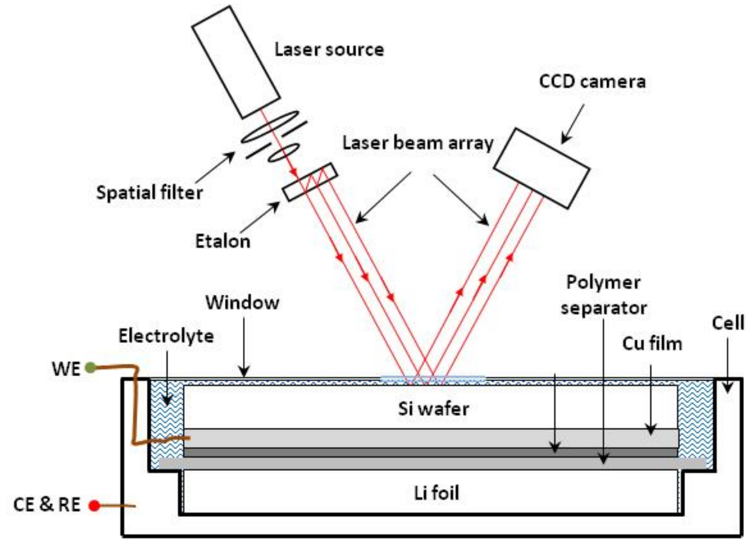
$$\kappa = \frac{6\sigma h_f}{M_s h_s^2}, \quad M_s = \frac{E}{1-\nu}$$

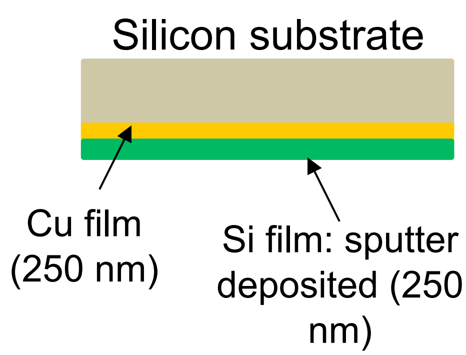
For h_s = 430 μm
E = 150 GPa, ν = 0.25
h_f = 250 nm, σ = 1 Gpa
κ = 0.04 m^{-1} or R = 25 m

Wafer Curvature Measurement

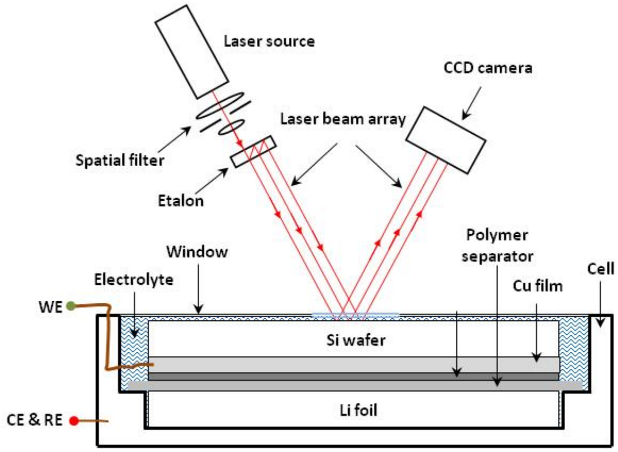
MOS – Multi-beam Optical Sensor; Measurement sensitivity: R ~ 10,000 m

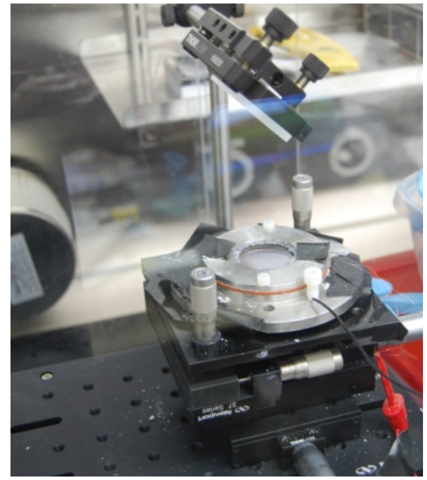


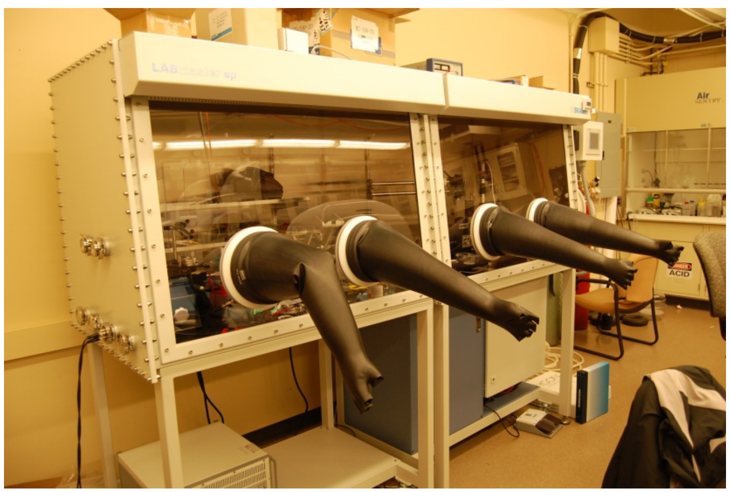


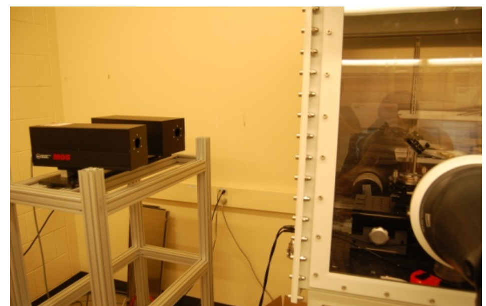


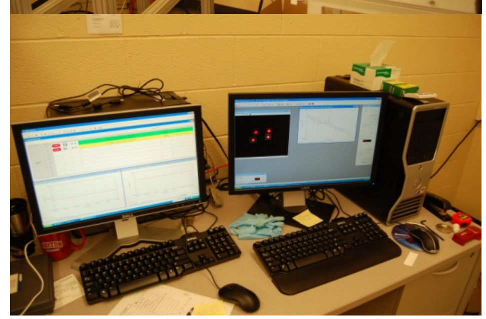
Experimental Setup





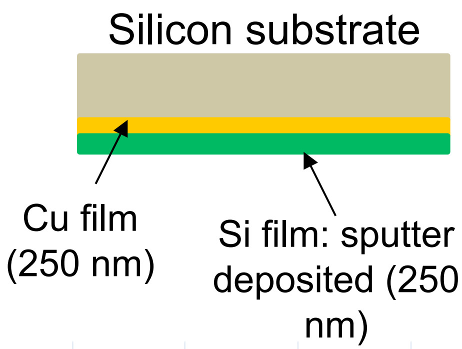


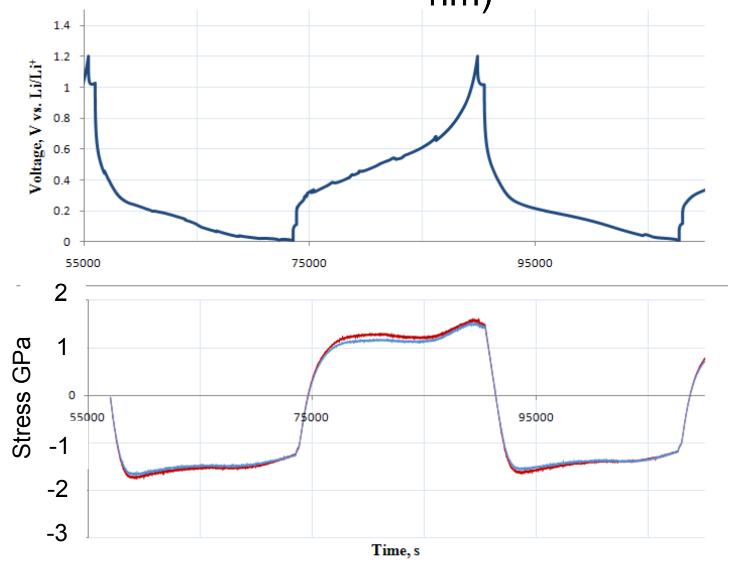


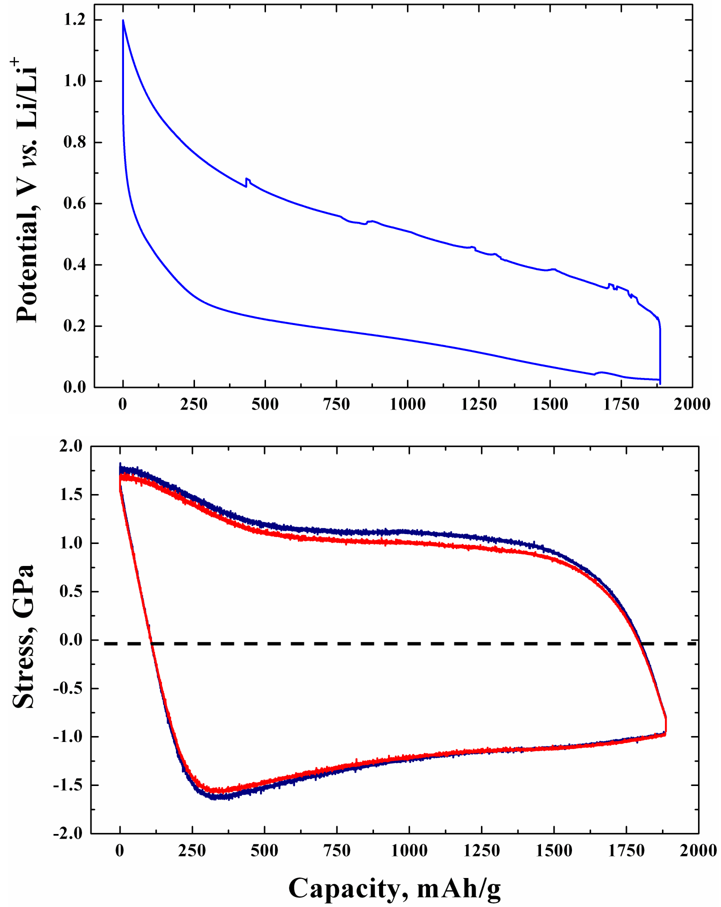


MOS setup integrated with the glove box

In situ measurement of stress in silicon anodes during electrochemical cycling







- Area under V vs. t plot: Electrical work
- Area under stress vs. time plot: mechanical dissipation due to plasticity
- Energy dissipation due to “plasticity” – affects energy recovery efficiency

Energy dissipation during lithiation and de-lithiation

Energy balance during lithiation

$$W_\mu = W_c^l + W_m^l + W_p^l$$

$$W_c^l = I\int V d\tau \qquad W_m^l = 2\nu\int \sigma_f d\dot{\varepsilon}$$

Energy balance during delithiation

$$W_c^d = W_\mu + W_m^d + W_p^d$$

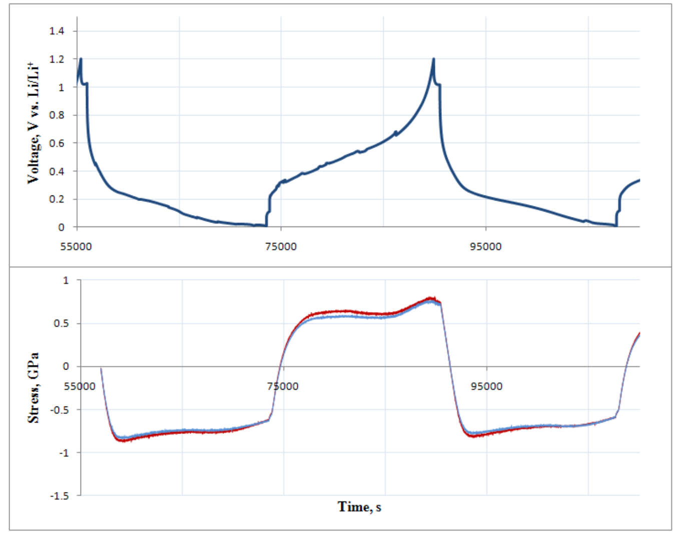
$$W_p^l = W_p^d$$

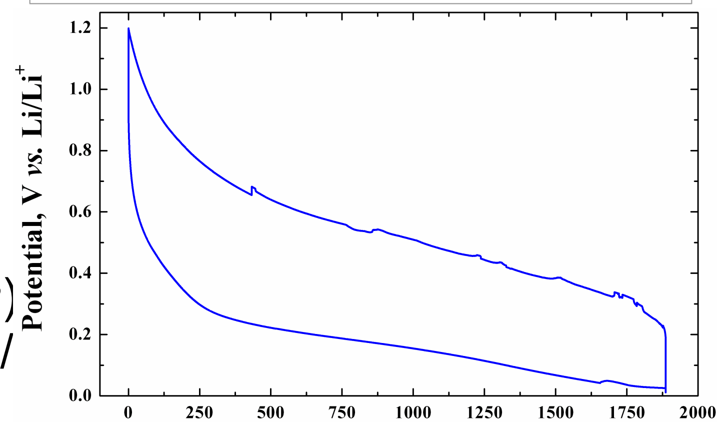
mechanical dissipation

During lithiation ~ 0.65 J (1.2 GJ/m^3)

During de-lithiation ~ 0.5 J (1.05 GJ/

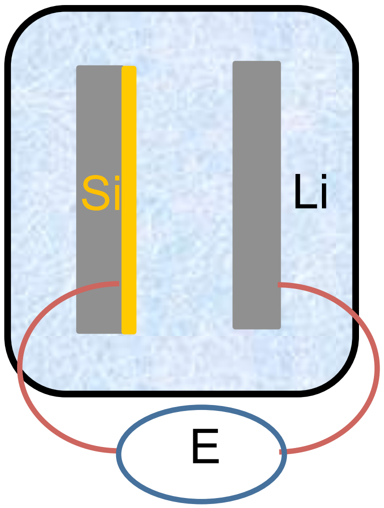
Polarization loss: 0.75 J (~ 400 J/m^2)





Mechanical dissipation is 60% - 80% of the polarization loss. It is significant and needs to be taken into account.

Stress-potential coupling in electrode materials



Li (Si) → Li⁺ (elec) + e⁻ (Si)

At equilibrium $\sum \nu_i \tilde{\mu}_i = 0 \qquad \tilde{\mu}_i = \mu_i + z_i e\phi$

$$\tilde{\mu}_{Li}(Si) = \tilde{\mu}_{Li^+}(elec) + \tilde{\mu}_{e^-}(Si)$$

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

$$\mu = \mu_0 + kTlog(\gamma c / c_0) - \frac{\Omega\eta}{3}\sigma_{kk} - \Omega\beta_{\mathrm{ijkl}}\sigma_{\mathrm{ij}}\sigma_{\mathrm{kl}}$$

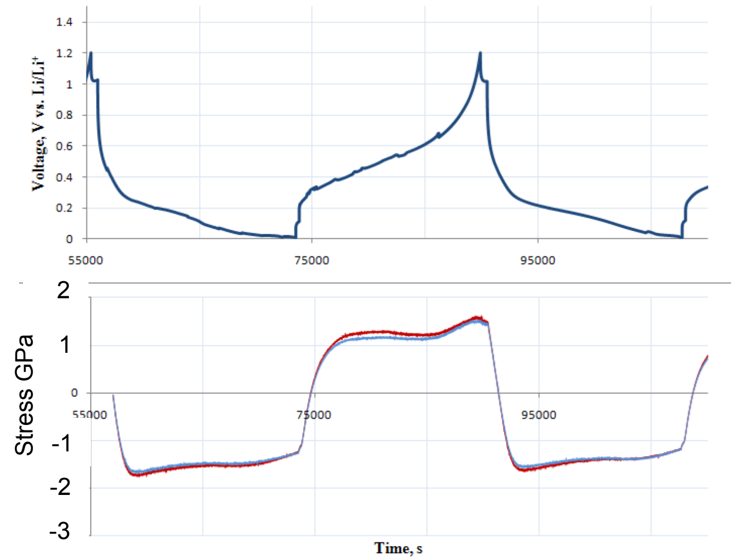
$$\eta = \frac{\partial \varepsilon_v}{\partial c}, \ \varepsilon_v : \text{volumetric strain} \quad \sigma_{ij} : \text{stress tensor}, \ \beta_{\mathrm{ijkl}} = \frac{\partial S_{\mathrm{ijkl}}}{\partial c}$$

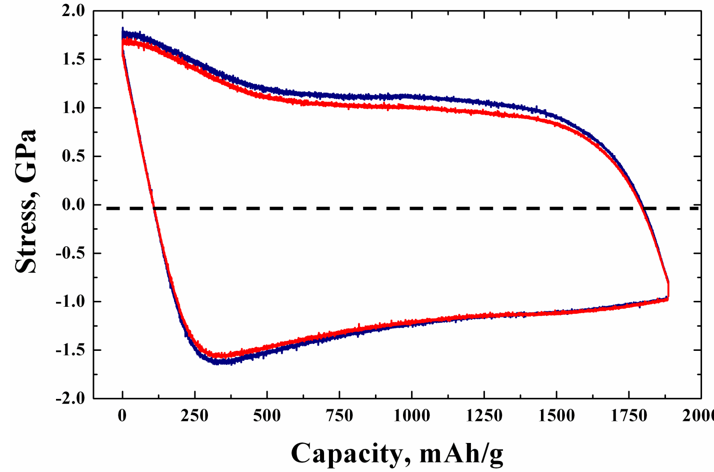
$$eE_0 = \mu_{elec} - \mu'$$

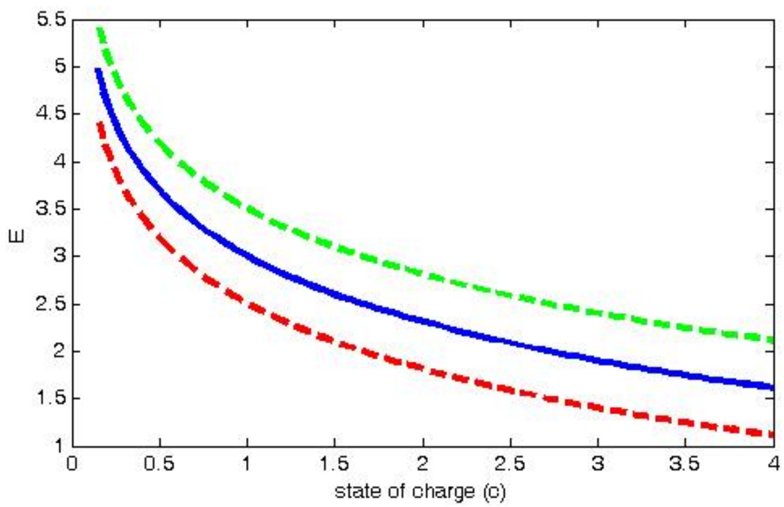
$$\mu' = \mu^0_{Li}(Si) - \mu^0_{e^-}(Si) + kT\log\left(\gamma_1 \frac{c}{c_0}\right) - \frac{\Omega\eta}{3}\sigma_{kk} - \Omega\beta_{ijkl}\sigma_{ij}\sigma_{kl}$$

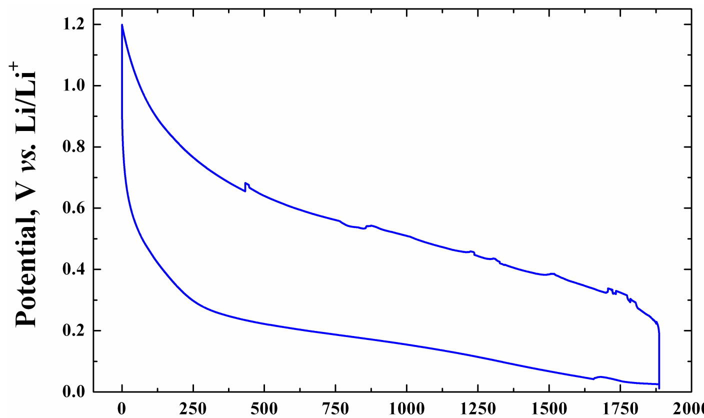
Mechanics and electrochemistry are coupled naturally through solution thermodynamics

Equilibrium potential during lithiation-delithiation with stress effects

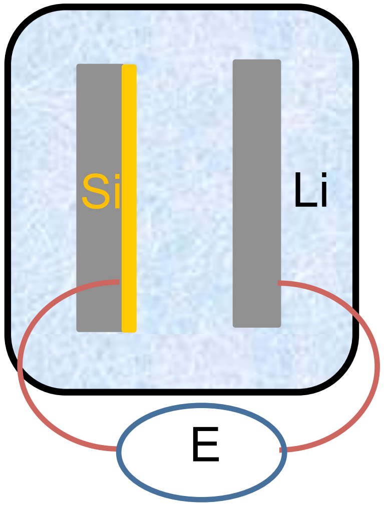








How strong is the stress-potential coupling?



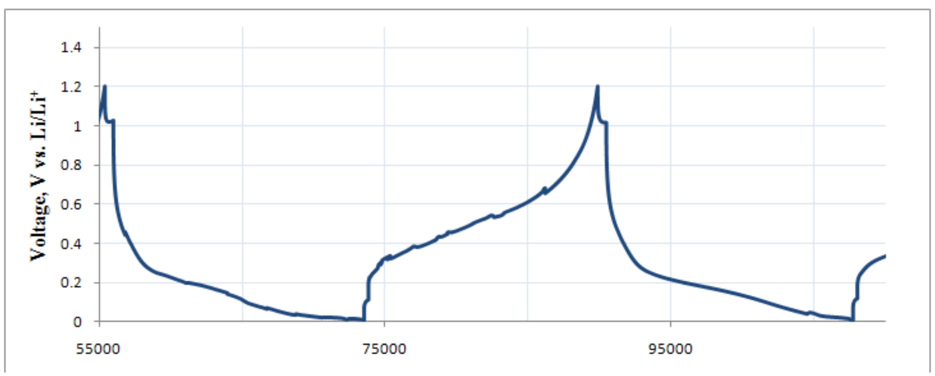
Equilibrium potential

$$eE_0 = \mu_{elec} - \mu'$$

Ignore this term for now

$$\mu' = \mu^0_{Li}(Si) - \mu^0_{e^-}(Si) + kT\log\left(\gamma_1 \frac{c}{c_0}\right) - \frac{\Omega\eta}{3}\sigma_{kk} - \Omega\beta_{ijkl}\sigma_{ij}\sigma_{kl}$$

$$\Delta E_0 = \frac{\Omega\eta}{3e}\Delta\sigma_{kk}$$

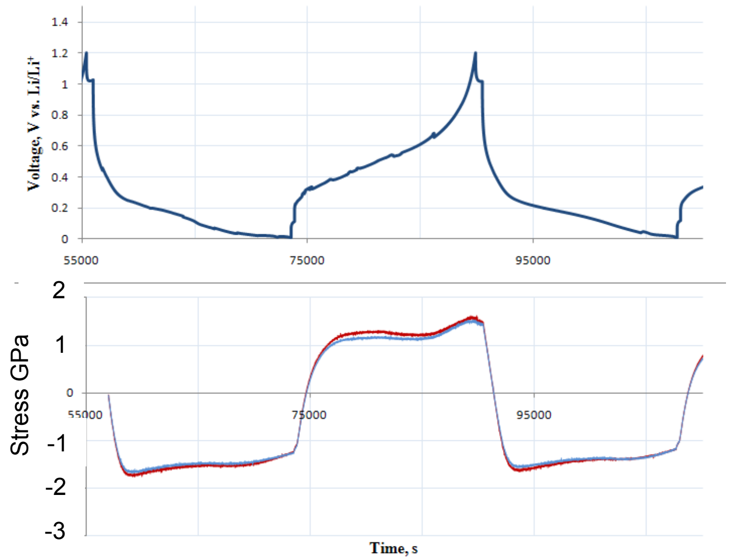


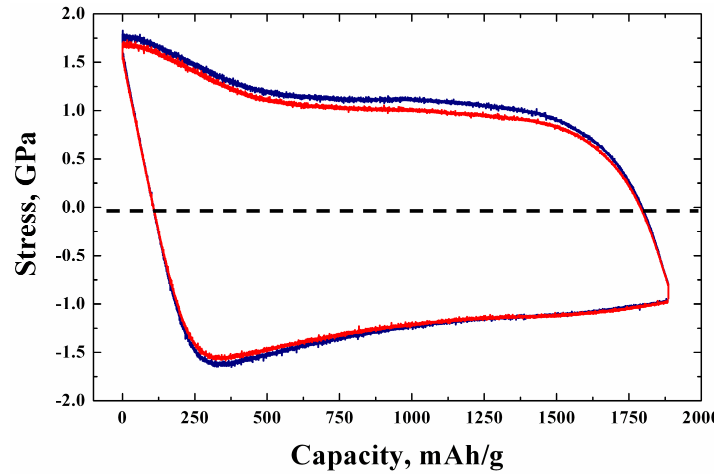
W~ 2 x 10^{-27} m^3/atom; η ~ 0.75;
e = 1.6 x 10^{-19} C; σ_{kk} ~ 2 GPa

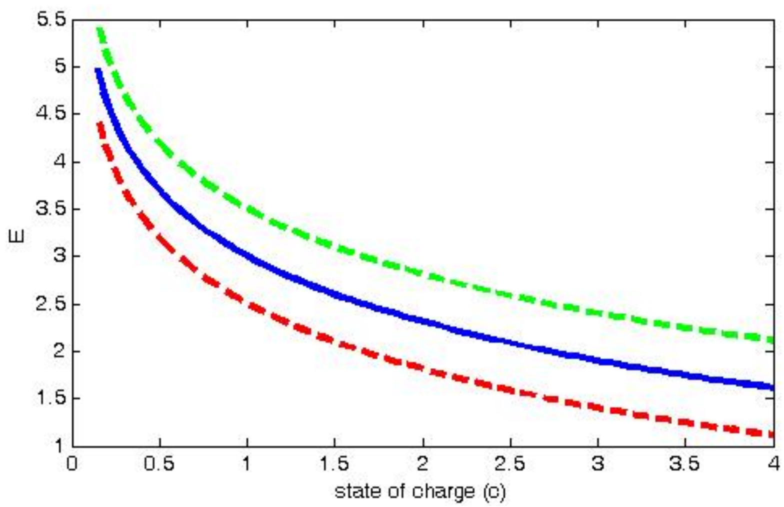
$\Delta E_0 \approx 63$ mV

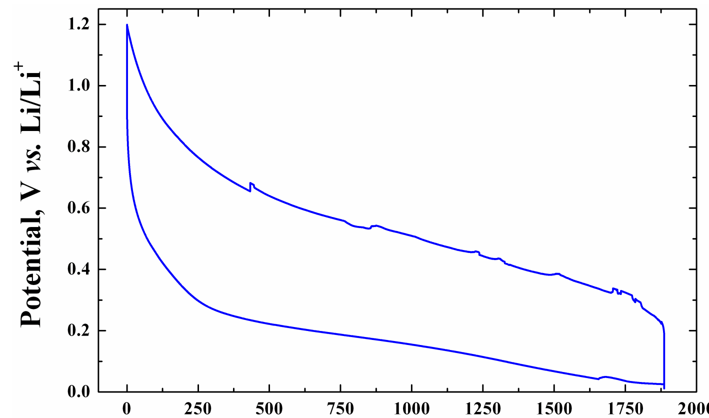
The effect of stress is substantial in all materials that can sustain high stresses! It should be taken into account in battery modeling.

Equilibrium potential during lithiation-delithiation with stress effects

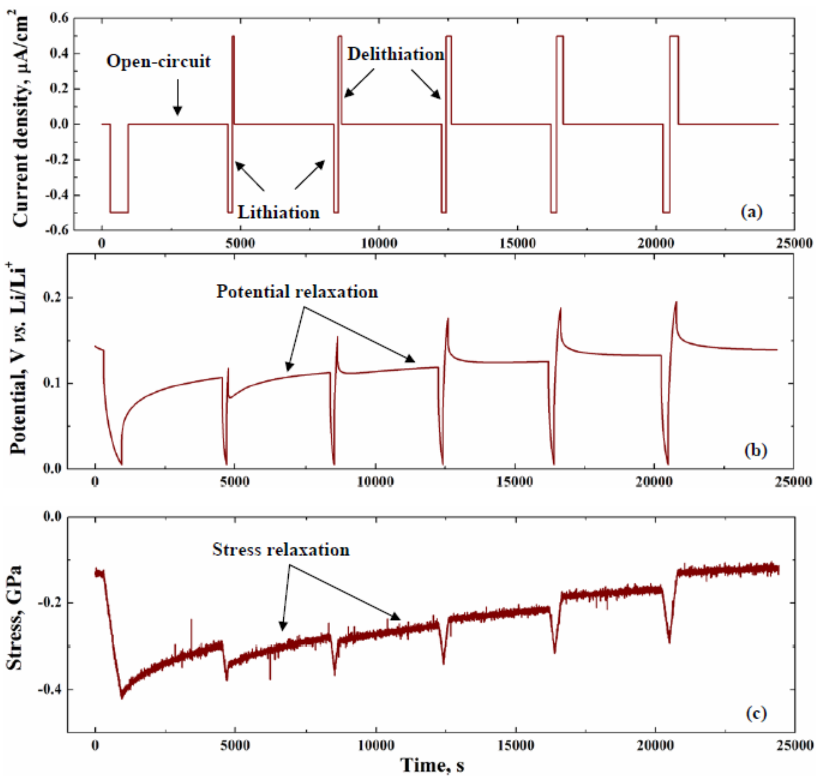


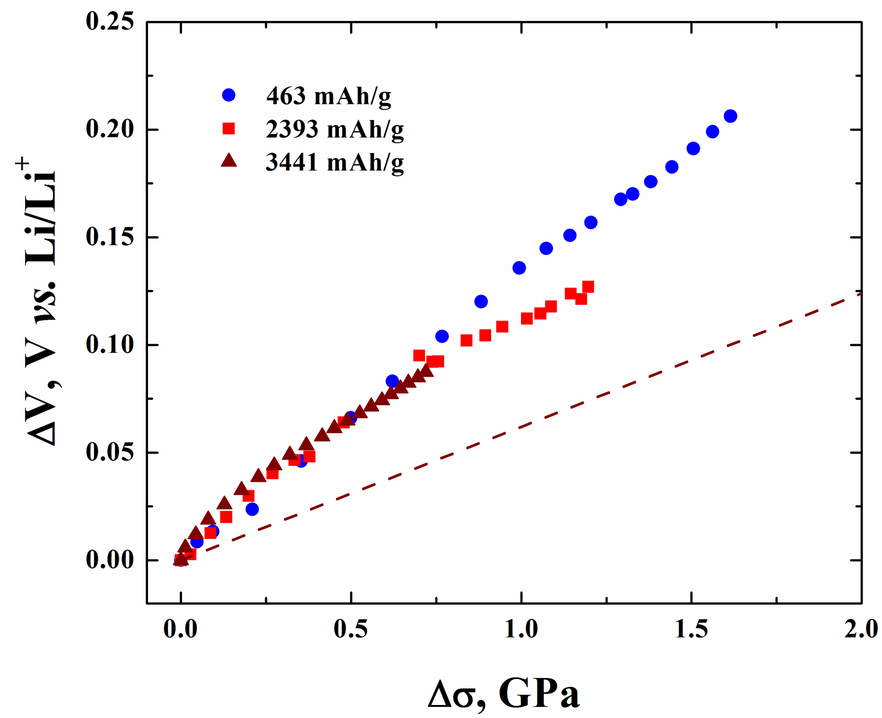






Measurement of Coupling between stress and anode potential

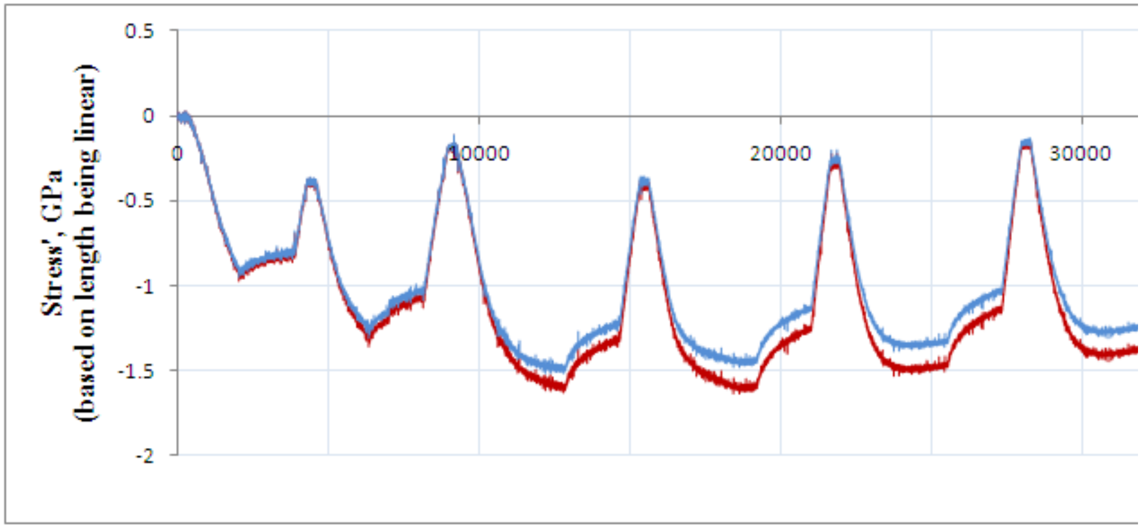


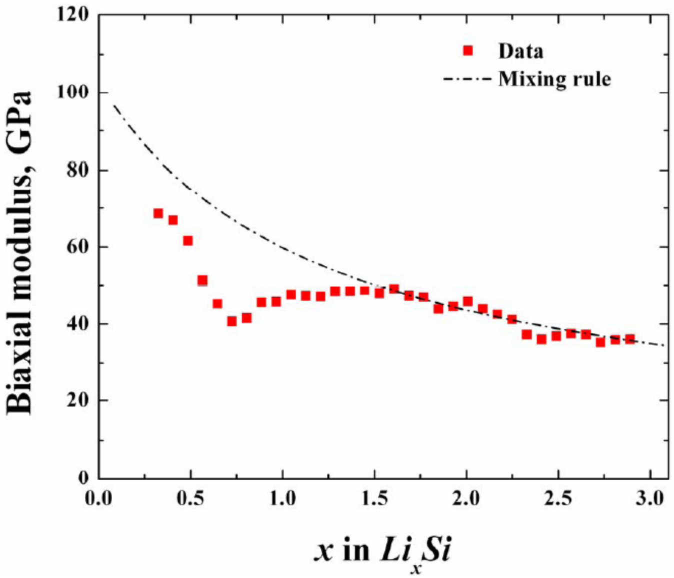


- Measured stress – potential coupling 98-105 mV/GPa
- Agrees reasonably well with the back of the envelope calculation of 63 mV/GPa
- First time observation of this effect – needs to be explored further
- Potentially important factor in silicon anode modeling

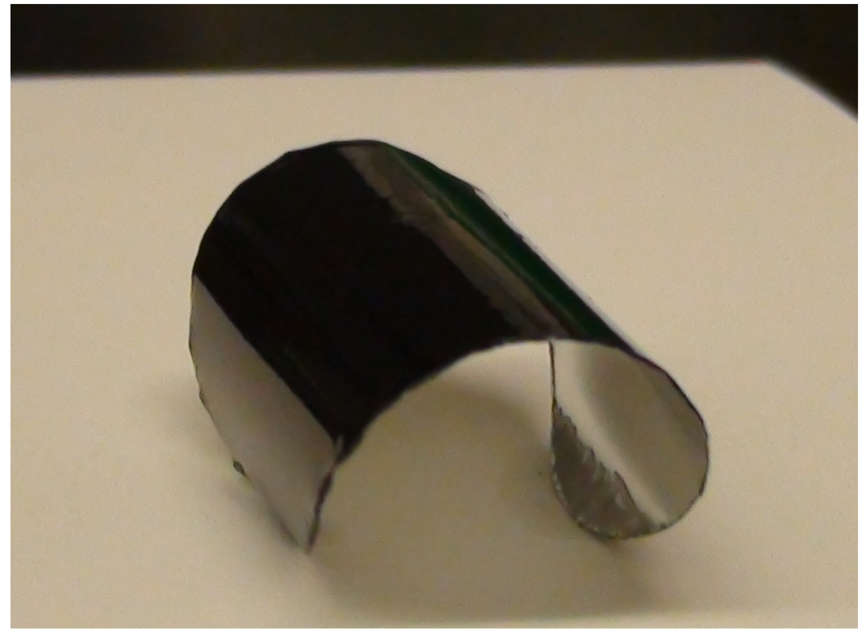
Characterization of elastic modulus of lithiated silicon

Measurement of biaxial modulus with lithiation



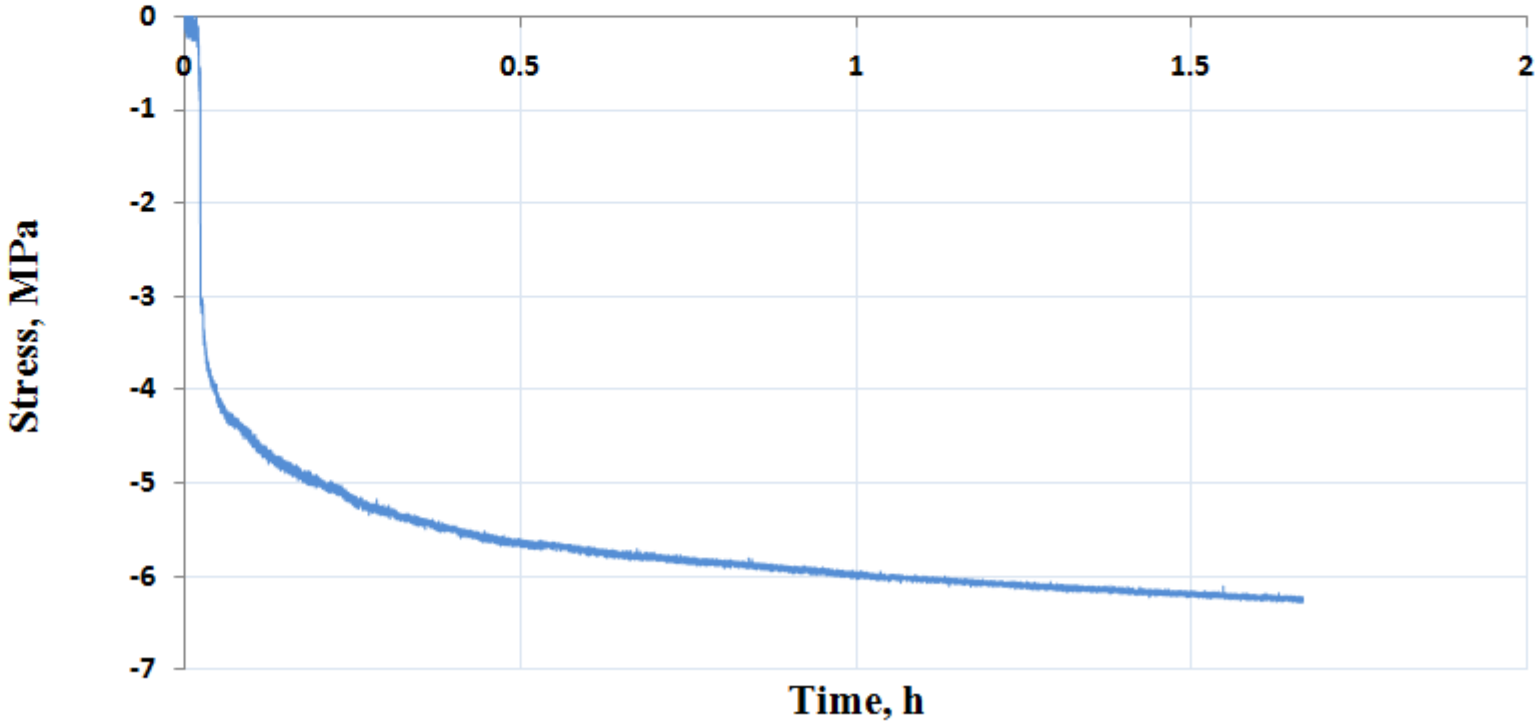


Electrode curls upon electrode-wetting PHEV baseline cathode (Argonne National Lab)



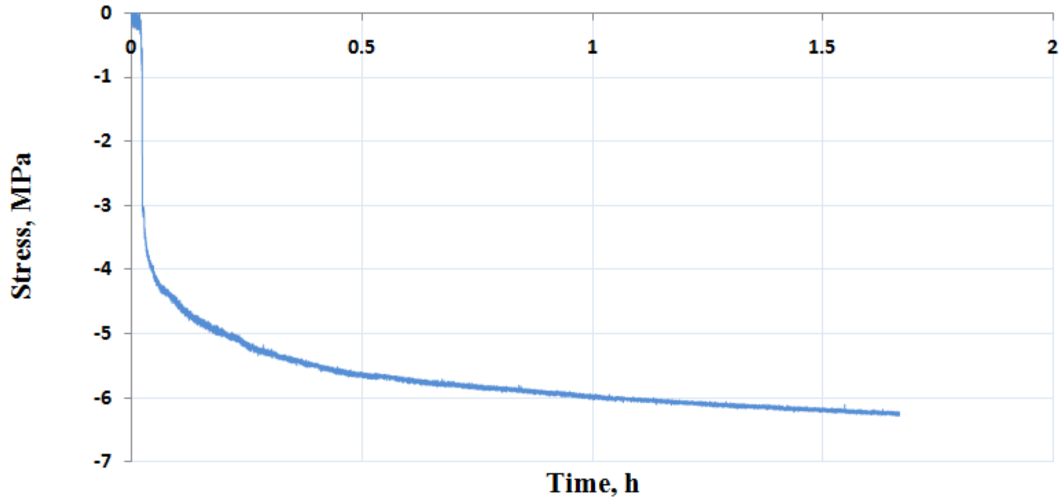
Source: Daniel Abraham, Argonne National Lab

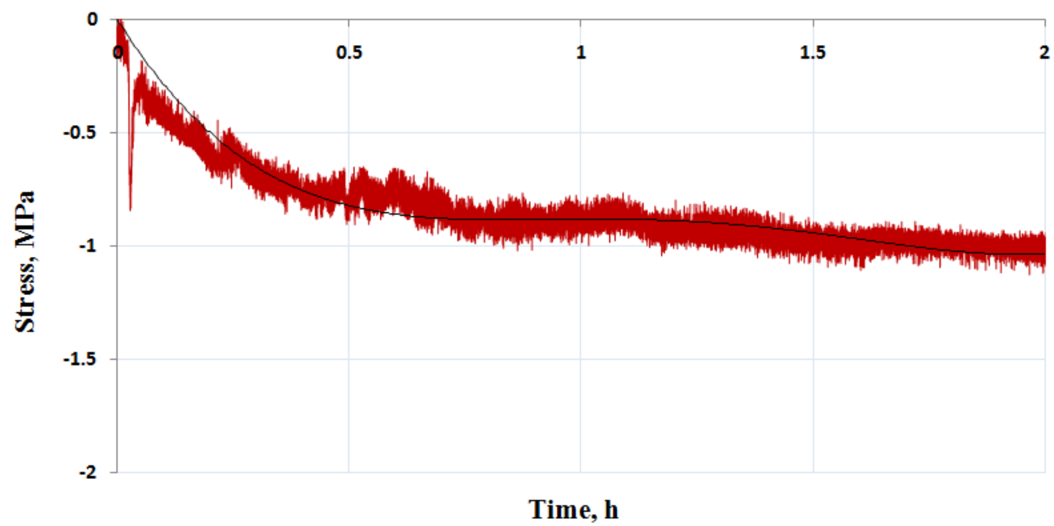
Stress evolution upon electrode-wetting PHEV baseline cathode (Argonne National Lab)



Cathode composition: 84% $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, 4% SFG-6 graphite, 4% Super P Conductive Carbon Black, 8% PVDF
Electrolyte: 1.2 M $LiPF_6$ in EC:DEC

Stress evolution upon electrode-wetting PHEV baseline cathode (Argonne National Lab)





Summary

- Developed a method to measure electrode stress in situ during electrochemistry.
- Demonstrated that mechanical dissipation in silicon anodes due to plasticity is comparable to polarization losses
- Based on solution thermodynamics, we predict coupling between stress and anode potential. Experimentally verified this coupling.
- Measured the elastic modulus of lithiated silicon as a function of lithium concentration. Such data is very important for modeling the cycle life of silicon anodes.
- Characterized stress due to first cycle phase transformation in silicon.
- Effect of self-discharge on stress evolution is characterized.