Diffusion, growth, and elasticity in batteries

A mathematical modelling perspective

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Lithium-ion Battery

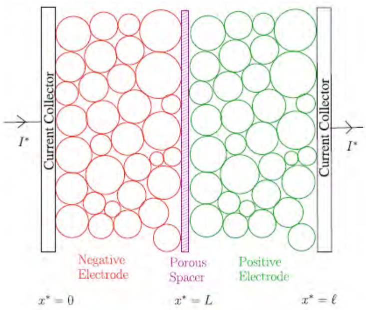
Forerunning energy storage medium for portable electronic devices.

- Lithium is the lightest metal known.
- High energy capacity – run for long periods between chargings.

Biggest challenge: Use them for electric vehicles? Replace fossil fuels?

- Even higher energy capacity needed.
- Search for ‘new’ battery materials ...

Battery materials



Most common commercial battery materials:

Negative electrode (Anode): Graphite

Positive electrode (Cathode): Lithium Cobalt Oxide ($LiCoO_2$)

Electrolyte: Salt of lithium

Figure from G. Richardson, G. Denuault, C. Please, J. Eng. Math **72**, 41 (2012).

Silicon for anodes

Why silicon?

Silicon can accommodate up to 4.4 atoms of Lithium in the fully lithiated state

➥ Theoretical specific capacity value of 4200 mAhg^{-1} (Graphite: 372 mAhg^{-1})

However ...

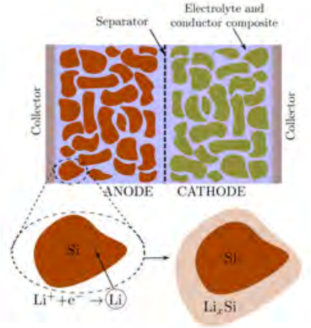
Silicon swells up during lithiation - 310% when fully lithiated

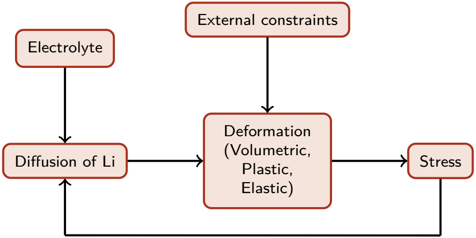
➥ Cyclic charging/discharging leads to mechanical failure (fracture)

A way out ...

Use nanostructured silicon electrode particles

Overview of the problem





Particle Level —Homogenization→ **Electrode Level**

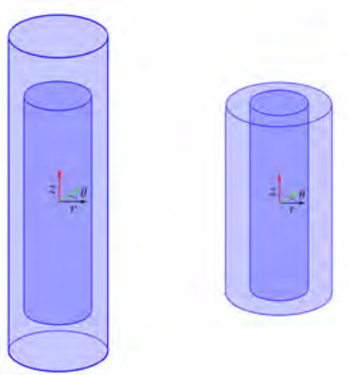


Figure: Left: Unconstrained case. Right: Constrained case – No net axial deformation, edges free to move laterally.

Description of Model

Diffusion

Stress

Plastic stretch

Description of Model

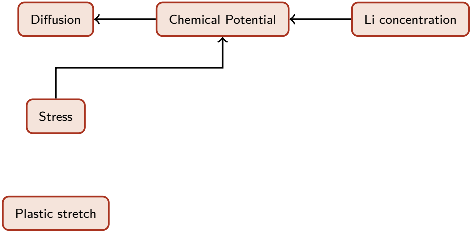
$$\text{Diffusion} \longleftarrow \text{Chemical Potential}$$

$$\boldsymbol{j} = -Dc\boldsymbol{\nabla}\mu$$

Stress

Plastic stretch

Description of Model



$$\boldsymbol{j} = -Dc\boldsymbol{\nabla}\mu$$

$$\mu = \mu_{\text{conc}} + \mu_{\text{stress}}$$

$$\mu_{\text{conc}} = \mu^{0}_{\text{conc}} + \log(\gamma c)$$

$$\mu_{\text{stress}} = \frac{\partial W}{\partial c}$$

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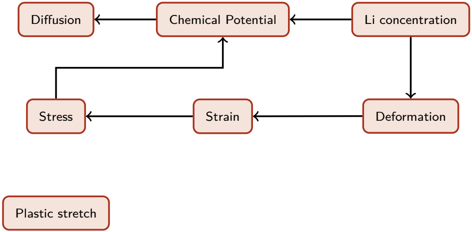

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$$\boldsymbol{\sigma}^0 = \frac{\partial W}{\partial \mathbf{F}} = f(c, \mathbf{E}^e)$$

$$\mathbf{F} = \mathbf{F}^p\mathbf{F}^e\mathbf{F}^c = \mathbf{I} + \boldsymbol{\nabla}\mathbf{u}$$

$$\mathbf{E}^e = \frac{1}{2}\left(\mathbf{F}^{eT}\mathbf{F}^e - \mathbf{I}\right)$$

$$\mathbf{F}^c = (1 + 3\bar{\eta}c)^{1/3}\mathbf{I}$$

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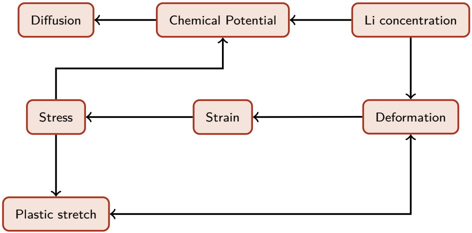

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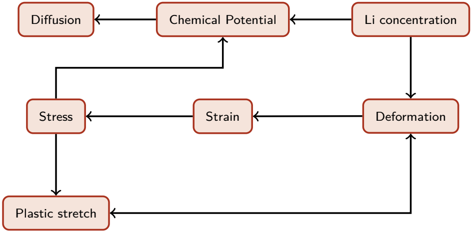
$$\mathbf{F}^p = g(\boldsymbol{\sigma}^{\mathbf{0}})?$$
$$\det(\mathbf{F}^p) = 1$$

Description of Model



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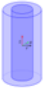
Net axial force is zero.



Net axial displacement is zero.

$$\boldsymbol{\sigma}^0 = \frac{\partial W}{\partial \mathbf{F}} = f(c, \mathbf{E}^e)$$

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Governing equations

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Background

Model

Buckling

Limiting growth

Upscaling

Diffusion:

$$\frac{\partial c}{\partial t} = -\mathbf{Div}\, \boldsymbol{j} \quad \rightarrow \quad \frac{\partial c}{\partial t} = -\frac{\partial j_r}{\partial r} - \frac{j_r}{r},$$
$$c(r,0) = 0, \quad j_r(0,t) = 0, \;\; j_r(1,t) = J_0(1-c)$$

Mechanical equilibrium:

$$\mathbf{Div}\, \boldsymbol{\sigma}^0 = 0 \quad \rightarrow \quad \frac{\partial \sigma_r^0}{\partial r} + \frac{\sigma_r^0 - \sigma_\theta^0}{r} = 0,$$
$$u(0,t) = 0, \quad \sigma_r^0(1,t) = 0.$$

Plastic stretch evolution:

$$\frac{\partial \lambda_{r,\theta}}{\partial t} = \lambda_{r,\theta} \mathrm{Pf} \left(\frac{\sigma_{\mathrm{eff}}}{\sigma_f} - 1 \right)^m \frac{\tau_{r,\theta}}{||\boldsymbol{\tau}||} \; H\left(\frac{\sigma_{\mathrm{eff}}}{\sigma_f} - 1 \right),$$
$$\lambda_{r,\theta}(r,0) = 1.$$

Motivation to study buckling

An empirical evidence

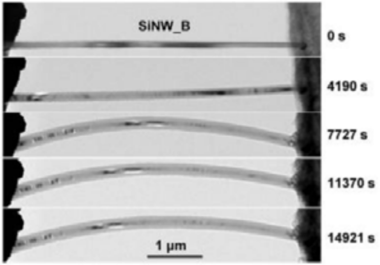


Figure: Buckling of a Si nanowire electrode particle as it undergoes lithiation. (Reproduced from Liu *et al.*, ACS Nano, 7, 1495–1503, 2013.)

Buckling

General Considerations:

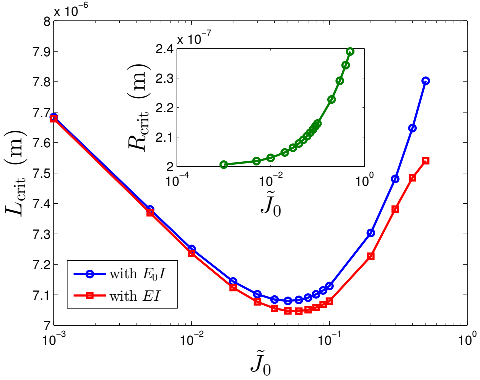
	LOW	HIGH
Length	✓	✗
Radius	✗	✓
Stiffness	✗	✓

For Si electrode particle:

Radius increases ← Increasing Li concentration → Stiffness decreases

↓

Modifications in the classical buckling criterion



- **Competition between growing stress and growing radius**
- **Predominating influence of growing radius**

Modified buckling criteria

$$F_{\text{crit}} = \frac{\pi^2 EI}{(KL)^2}$$

E : Modulus of elasticity

$I = \frac{\pi R^4}{4}$: 2^{nd} moment of area

$$L_{\text{buck}} = \{L : F_{\text{crit}} \text{ exists}\}$$
$$L_{\text{crit}} = \min\left(L_{\text{buck}}\right)$$

Modifications:

$$R = R_0 \left(1 + \frac{\partial u}{\partial r}\right)$$
$$E = E_0 \left(1 + \eta_E x_{\max} c\right)$$

$E_0 I$: Only R changed

EI : Both E and R changed

Ref. : J. Chakraborty et al., Int. J. Solids Struct. **54**, 66–81 (2015).

An estimate for design

Approximate the critical compressive force using the yield stress
➥ Determine critical length

$$\sigma_f \pi R_0^2 = \frac{\pi^2 E_0}{L^2}\left(\frac{\pi R_0^4}{4}\right)$$

$$\text{Or,} \quad L = \frac{1}{2}\sqrt{\frac{E_0}{\sigma_f}}\pi R_0 \approx 8\mu\text{m}$$

Size-effects

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Background

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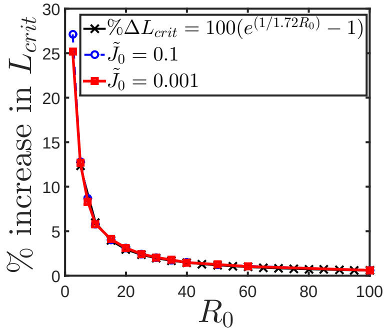
Upscaling

Young's modulus influenced by lithium concentration
Young's modulus *can also* depend on particle size (radius $<$ 30 nm)

$$E = E_0(1+\chi_c)(1+\chi_s)$$

χ_s determined from Bond-Order-Length-Strength (BOLS) theory



Sun et al., J. Phys. Condens. Matt. **14**, 7781 (2002).
Neogi and Chakraborty, J. Appl. Phys. **124**, 154302 (2018).

Limiting axial growth

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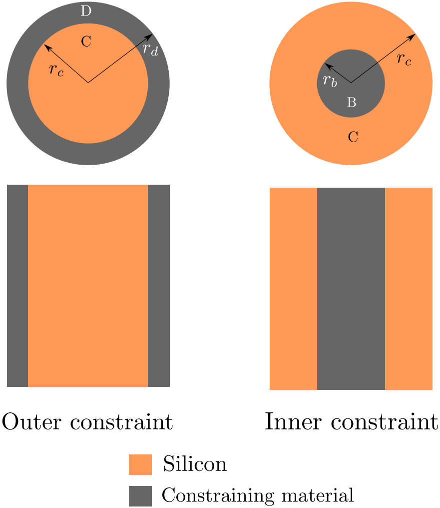
Upscaling

Is there any *simple* way to limit axial growth?

$\downarrow$

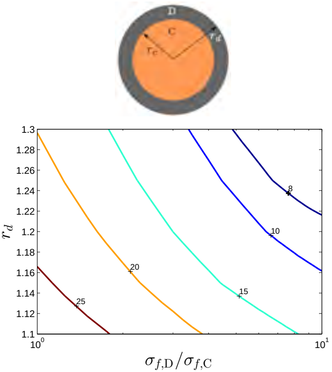
Use constraints

Two configurations

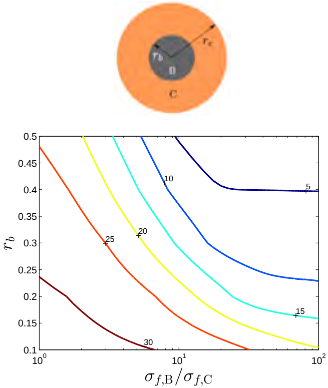


Phase diagrams

From numerical simulations



Outer constraint



Inner constraint

Yield stress of Region D: $\sigma_{f,\mathrm{D}}$ Yield stress of Region C: $\sigma_{f,\mathrm{C}}$ Yield stress of Region B: $\sigma_{f,\mathrm{B}}$

Contour values indicate percentage increase in length

Ref: J. Chakraborty et al., J. Power Sources **279**, 746–758 (2015).

Upscaling

Upscaling

Electrode Particle Level

➥ Full set of equations

↓

Simplified set of equations

↓

Upscale using Homogenization

↓

Battery level

An open question

How can we incorporate large strains in the upscaling steps?
➥ Apply to silicon anodes

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inspire

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Thank You