

Optimization of the Lithium Insertion Cell with Silicon Negative Electrode for Automotive Applications

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Related Publications

- Single Particle Model

- R. Chandrasekaran, A. Magasinski, G. Yushin, T.F. Fuller,
J. Electrochem. Soc. ,157 (10) A1139-A1151 (2010)

- Li-Silicon/ Separator/ Li Foil Cell Model

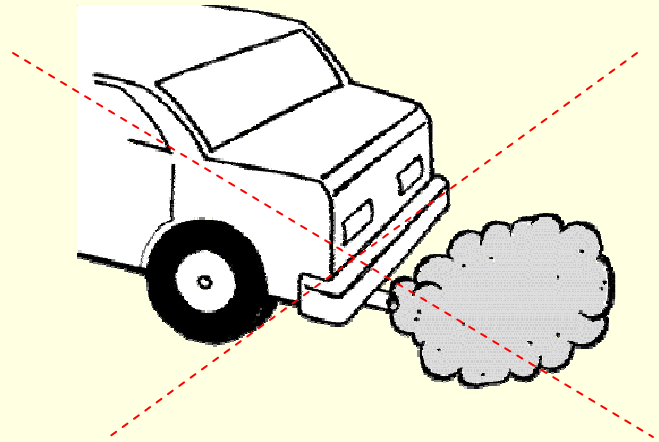
- R. Chandrasekaran, T.F. Fuller,
J. Electrochem. Soc. , 158 (8) A859-A871 (2011)

- Prior work pursued at Georgia Tech, sponsored by NASA Glenn Research Center



Why do we need HEV, PHEV, EV?

- Reduce tailpipe emissions
- Increased fuel economy



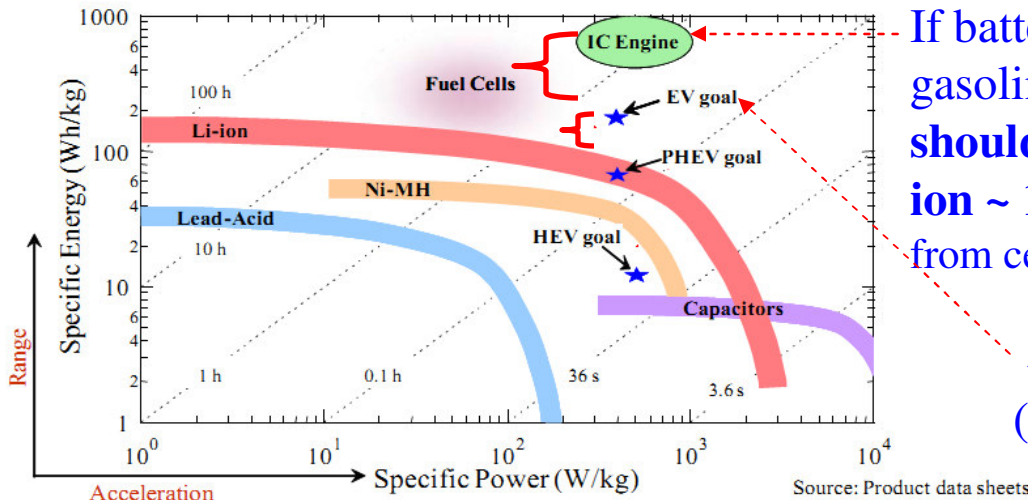
Automotive Adoption Metrics*: Hierarchy of Needs

- **Must work**
 - Performance, life and robustness
- **Must fit (Wh/liter) in the car**
 - Package without compromising crash performance and expected interior utility
- **Must be cost effective**
 - Life of vehicle performance
 - Cost of fuel influence
 - Cost of carbon influence
 - Value based on power and/or energy density
 - Value based on degree of uniformity
- **Must be mass effective (Wh/kg and W/kg)**
 - Increased range



* Courtesy: Ted Miller, Ford Motor Company

Why work on silicon and other new, advanced materials?



If battery pack has sp. energy similar to gasoline, then for **500 miles** (~ICE car), we should need **115 kg pack**. With present **Li-ion** ~ **1500 kg pack**-accounting for 30 to 40% loss from cell to pack; **volume also increases!**

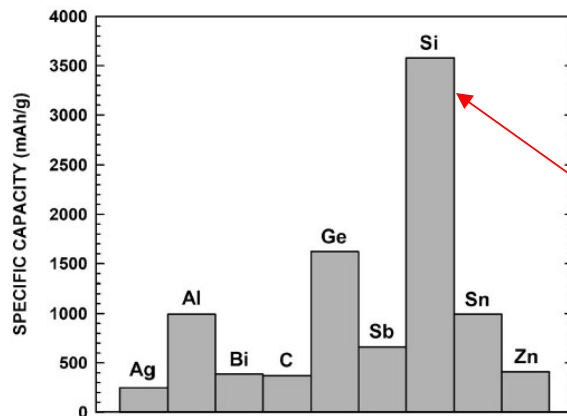
~ For **175-200 miles** ~ **200 kg** (USABC goal: 40 kWh pack)

Source: V. Srinivasan webpage, LBNL

FIGURE 1. Ragone plot (specific power density in W/kg vs. specific energy density in Wh/kg) of various electrochemical energy storage and conversion devices.

Specific Energy (Wh/kg)

= Voltage (V) x Specific capacity (Ah/kg)



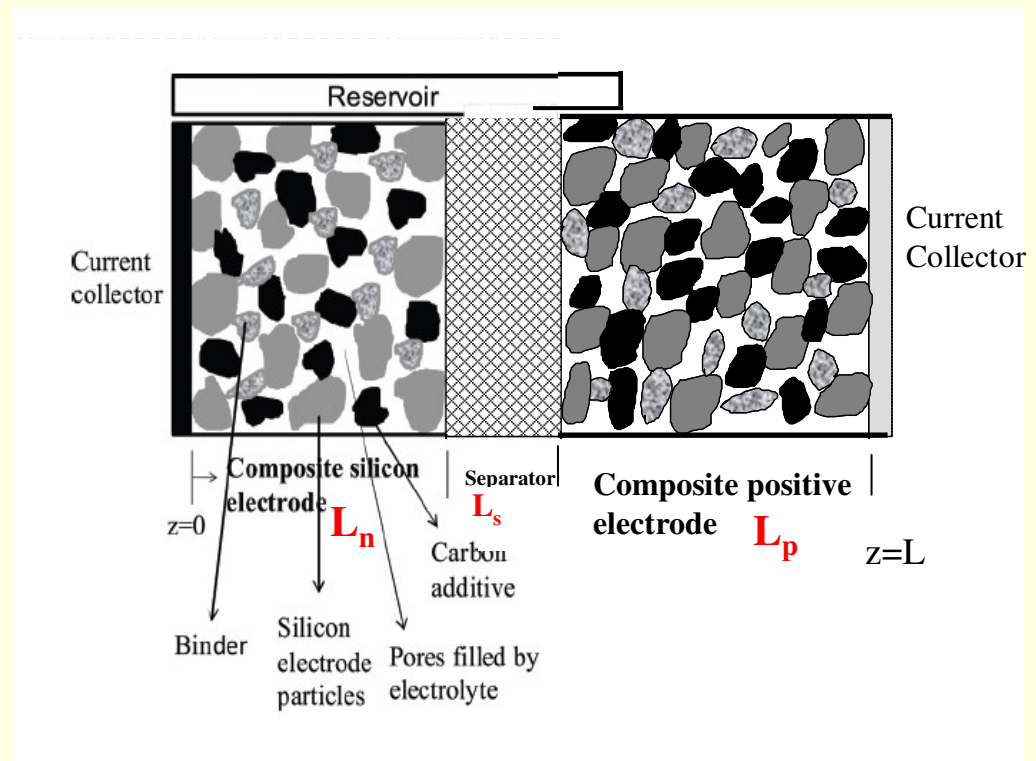
Hence, to increase Wh/kg,

- 1) High voltage positive electrode material
- 2) **Electrode materials with high specific capacity e.g. silicon (for negative electrode)**, undergoes 300% volume expansion

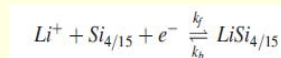


Li-Si/ Separator/ Positive Dual Lithium Insertion Cell

- **Macro-homogenous model**
 - Porous electrode & concentrated solution theory
- **Solved in cell sandwich direction**
 - Within the porous electrode (s), solid phase transport solved in the particle domain
 - Interfacial reaction @ electrode/ electrolyte interface
- **Single particle model** →
 - confirmed that U vs. x curve has path dependence
 - For nanoparticles: OK to use **constant particle size** for solid phase transport & neglect stress
 - **Slow kinetics**
- **Reservoir introduced**
 - Accessed from separator region
 - Mechanical constraint above electrode to maintain rigidity
 - Convection in z -dir
 - **Superficial volume average velocity** as reference



@negative electrode particle/electrolyte interface:








Cell sandwich model development continued...

- Volume changes ~ porosity changes
 - Material balance in matrix phase
 - Electrode dimension changes neglected
 - Depends on extent of reaction
- Transport properties , *i.e.* $D(c)$, $\kappa(c)$, t_+^0
 - Function of concentration
 - Effective properties – function of varying porosity : $D_{\text{eff}}(c)$, $\kappa_{\text{eff}}(c)$, σ_{eff}
- Specific interfacial area (total interfacial area /superficial volume)
 - Function of porosity and varying particle radius*



* Expression from *J. Electrochem. Soc.*, 157, 10, A1139-A1151, 2010.

Outline of Model Equations

Equation type		Phase	Region	Dependent variable
Material balance		Electrolyte	Porous electrode (s) 	c
			Separator	
		Solid	(Negative Matrix) 	ϵ
			Particle* (Both electrodes) 	c_s @ $r = R_p, -D \nabla c = j_n$ @ $r = 0, \nabla c = 0$
		Overall	Negative	v^{\square}
			Separator and Positive	$v^{\square} = 0, \text{ when } \tilde{V}_e = 0$
Charge balance	Ohm's law	Matrix		Φ_1
	Modified Ohm's law	Electrolyte		Φ_2
			Separator	

* Diffusion equation in spherical coordinates



Outline of Model Equations Continued...

Equation type	Phase	Region	Dependent variable
Faraday's law	<i>Relation between divergence of solution phase current (\mathbf{i}_2) & pore wall flux (j_n)</i>		\mathbf{i}_2
	Electrolyte-electrode interface		$j_n = f(\Phi_1, \Phi_2, U(c_s), i_0)$; $i_0 = f(k, c, c_s)$
Butler-Volmer kinetics	For Li-Si/separator/ Li foil cell, electrolyte-lithium foil interface		Φ_2 Boundary condition ($U_{Li/Li^+} = 0, \Phi_1 = 0$)

Also, $\mathbf{i}_1 + \mathbf{i}_2 = I$

→ @ $z=0$ & $z=L$, $\mathbf{i}_1 = I$;

→ Separator region, $\mathbf{i}_2 = I$ & $\mathbf{i}_1 = 0$

@ $x=0$ & $x=L$, $\nabla c = 0$

If against foil cell,

@ Separator/ Li foil interface, $N_+ = I/F$



Present knowledge & intuition for design of Li-Si electrodes

- Low initial porosity

- If both porosity & electrode dimension changes possible/allowed
 - Higher utilization , but short circuit & loss of mechanical integrity
- If only porosity changes
 - Possible that $\varepsilon = 0$, before complete utilization
 - Thinner electrode*

- High initial porosity

- Better utilization & possibly avoid electrode dimensional changes
- Thicker electrodes*

* for a given capacity



Preliminary considerations for design of Li-Si / Separator/ Positive Dual Lithium Insertion Cell

- Charge transfer kinetics @ Li-Si/electrolyte interface slow
 - Limits utilization at medium to high rates in Li-Si/ separator/ lithium foil cell
- High silicon electrode specific capacity → greater mAh/cm² possible (for same thickness as carbon electrode)
 - However, greater current **across separator** → **higher IR drop**
 - **ohmic and transport limitations possible across thick positive porous electrode** (in an attempt to match capacity of Li-Si)

Modeling in COMSOL 3.5a vs. 4.2

■ COMSOL 3.5a

- PDE general form (1D) for
 - charge transport in solid matrix and ionic (electrolyte) phase
 - species transport in electrolyte phase
 - porosity changes
- Diffusion (2D) for solid phase
- Ability to modify equations in the library battery model and build upon it is easier

■ COMSOL 4.2

- Advantages:
 - ✓ Material properties library available
 - ✓ **Parametric sweep for different electrode thicknesses**
- Option 1: Batteries and fuel cells module → lithium ion battery physics interface → add porous electrode nodes
 - ✓ Study **different particle shapes**
 - ↓ Difficult to introduce additional phenomena or modify existing one in porous electrode node
 - e.g porosity changes, particle growth and (may be stress too), specific interfacial area changes
- Option 2: Use comparatively generic physics interfaces from chemical species transport or the general PDE form



Results from Li-Si/separator/foil cell (Simulations in COMSOL 3.5a)

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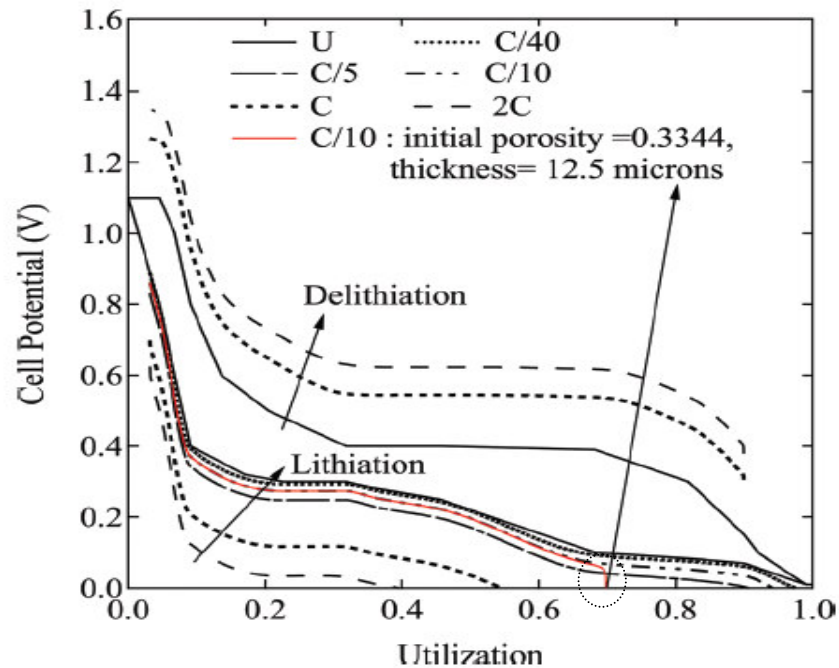


Potential vs. utilization in a Li-Si/ separator/Li foil cell @ different rates

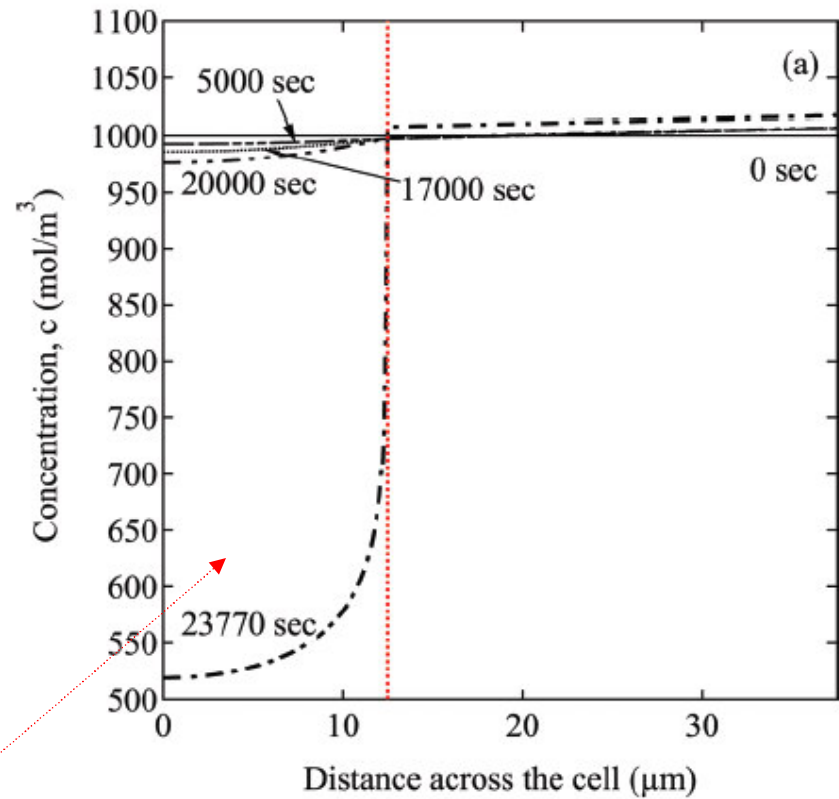
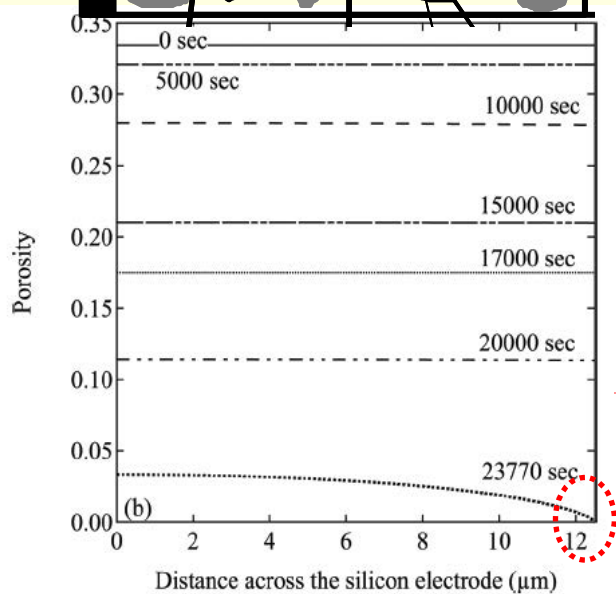
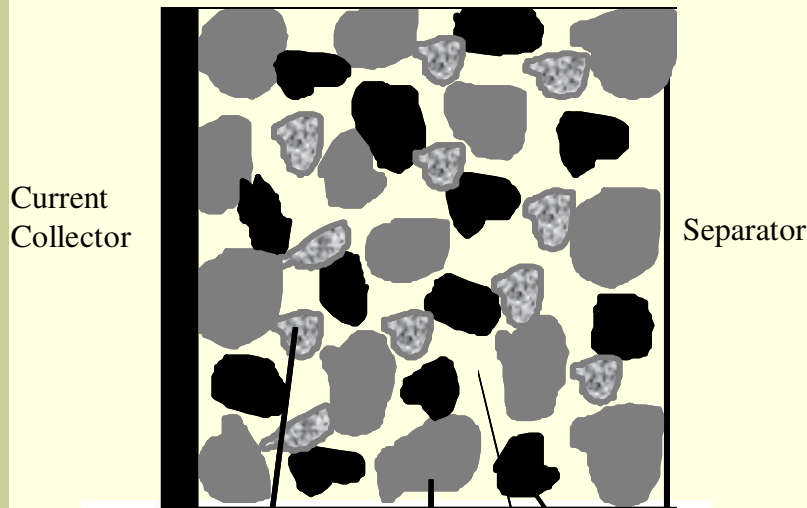
$$u = \frac{\int_0^{L_c} soc_{avg} dx}{\int_0^{L_c} dx}$$

$$soc_{avg} = \frac{c_{s,avg}}{c_{max}}$$

$$c_{s,avg} = \frac{\int_0^{R_s} c_s r^2 dr}{\int_0^{R_s} r^2 dr}$$



Porosity & Concentration Profile for $\epsilon=0.33$, 12.5 μm @ C/10 rate



- 70% utilization only



Trade-off between utilization (@ different rates) & volumetric energy density – Optimization of thickness of the electrode

- For slow kinetics
 - Lithiation @ $\geq C$ -rate:
 - Capacities $\neq f$ (electrode thickness); Lower utilization
 - Lithiation @ $\leq C/2$ rate:
 - Thinner, less porous electrodes: capacity obtained limited by plugging of the pores
 - Thicker, porous electrodes: Capacity obtained is higher and remains invariant
- If kinetics improved \rightarrow better performance esp. at medium to high rates.

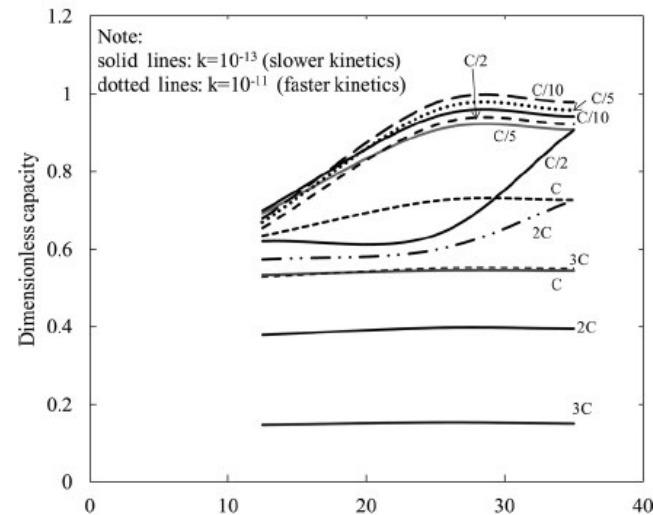


Figure 7. Dimensionless capacity vs. thickness of the electrode (i.e. initial porosity is varied to maintain the same theoretical capacity). The three thicknesses modeled are 12.5, 25 and 35 μm .

Variation of specific interfacial area during lithiation

- Why is 'a' important?
 - Li-Si system- kinetics dominate
 - Low temperature performance

$$a = 3 \frac{(1 - \varepsilon - \varepsilon_{bf})}{R_{sp}}$$

- ε decreases, R_{sp} increases \rightarrow 'a' decreases and then increases
- At higher rate of lithiation, largest change occurs at the separator / electrode interface (due to larger local reaction rate).

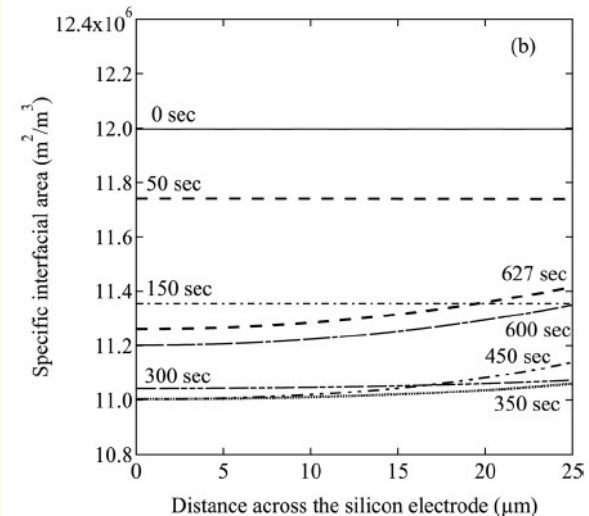
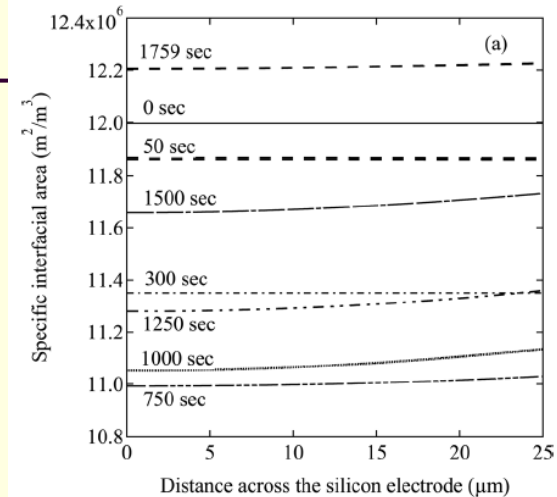


Figure 8. Variation of specific interfacial area across silicon electrode during lithiation for non-ideal electrolyte for the case of varying transference number (Appendix A) at (a) C-rate (b) 2C-rate.

During de-lithiation @ C-rate...

- **Short times** : Low porosity → transport limitations → Li^+ concentration increases with time in silicon porous electrode
- **Medium/Long times**: Porosity increases → Gradients relax → Li^+ concentration decreases with time in silicon porous electrode*
- Performance limited by initial SOC (that attained from previous lithiation step) & final porosity possible from electrode design

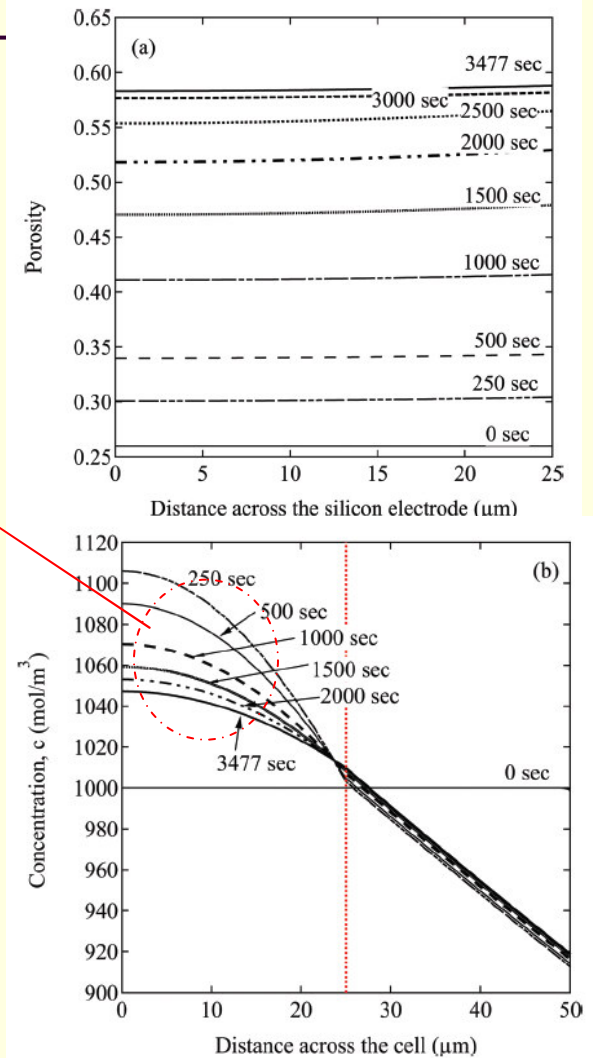
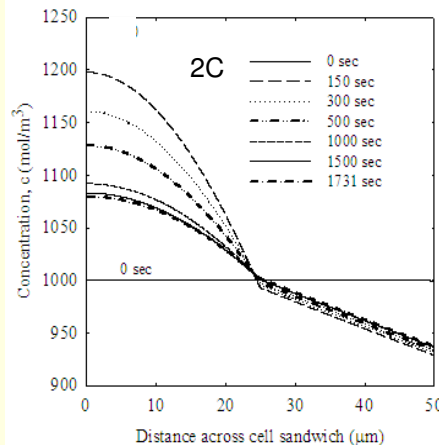


Figure 9. (Color online) (a) Porosity and (b) concentration profiles during delithiation of the silicon electrode for the case of varying transference number in non-ideal electrolyte (Appendix A) at C-rate.



* Accompanied by slight increase in the separator region.

Conclusions from Li-Si/separator/Li foil cell

- Developed one-dimensional flow model for lithium-silicon composite electrode/ separator/ lithium foil cell
 - Includes porosity changes ; reservoir to accommodate displaced electrolyte
 - (Slow) charge transfer kinetics dominate
- First time, application-based designing of silicon electrodes suggested

Application	High Initial Porosity	Low Initial Porosity ⁺
Low-rate* (C/10)	Better utilization (~ 95%)	Plugging of pores → sharp reduction in cell potential → cell performance limited to ~ 70%
High-rate* (≥ C/2)	System Limited by kinetics Utilization of active material limited; similar performance for thick and thin electrodes (of same capacity , i.e. different porosities)	

- If kinetics improved, utilization increases, esp. at medium to high rates; Then initial porosity & thickness decide performance
- Lithiation limits silicon electrode performance vs. lithium foil
- Nano-electrode particles – no solid phase limitations



* Lithiation of silicon electrode

⁺Same capacity as the high initial porosity → thickness varied

Ongoing work

- Analysis of limitations in the Li-Si/separator/positive insertion electrode cell under different conditions
- Any other troubleshooting as required with COMSOL 4.2!

Thank you!!

- Prof. Thomas F. Fuller (PhD Thesis Advisor)
- Mr. Ted Miller (manager)
- **AUDIENCE**
- Family

