IEEE Boston Reliability Seminar 9/11/13

Reliability of Li-ion Batteries

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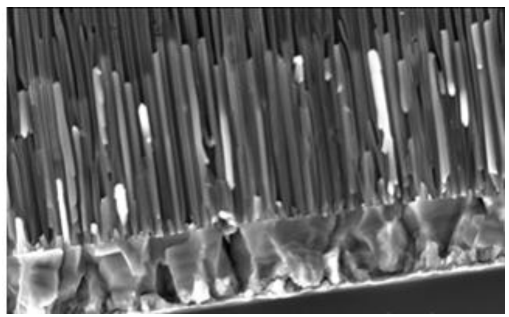
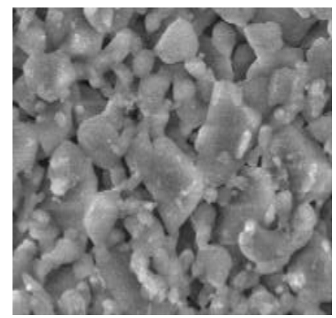
Prior funding (2008-12)

Group Overview

- Nonlinear dynamics of electrochemical systems
- Physics + Mathematics + Engineering
- Theory + experiment

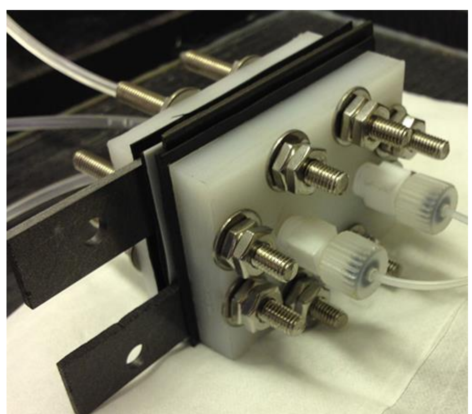
Templated electrodeposition for batteries, nanotechnology





Shock electrodialysis for water desalination, separations

Membraneless HBr flow battery for large scale energy storage

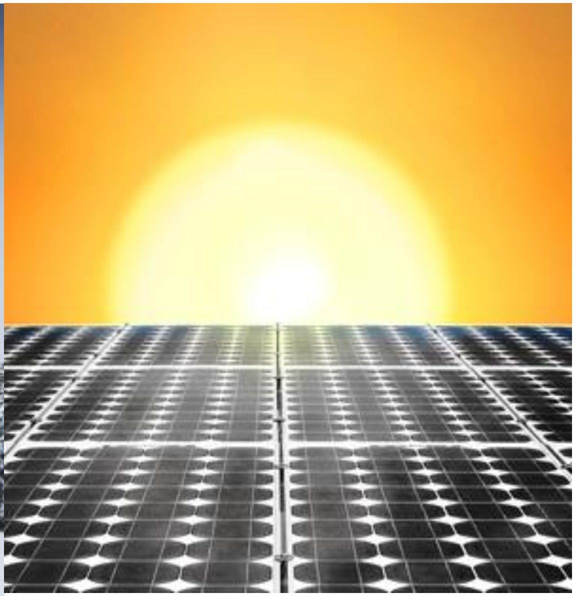


Battery performance and reliability
under diverse operating conditions

Extreme C Rates

Control Failures

Extreme Temperatures



Need for predictive mathematical models

Images: Autoblog Green, Gas 2, Boeing, Reuters
Tory Aardvark, Cosmos Magazine

Multiscale Battery Physics

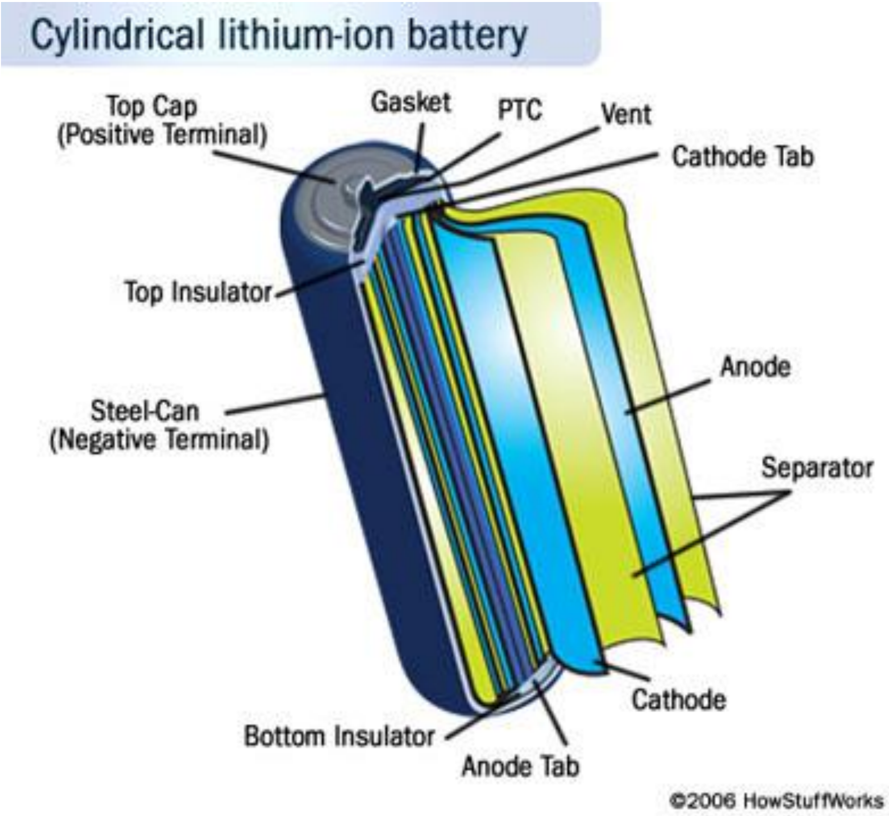
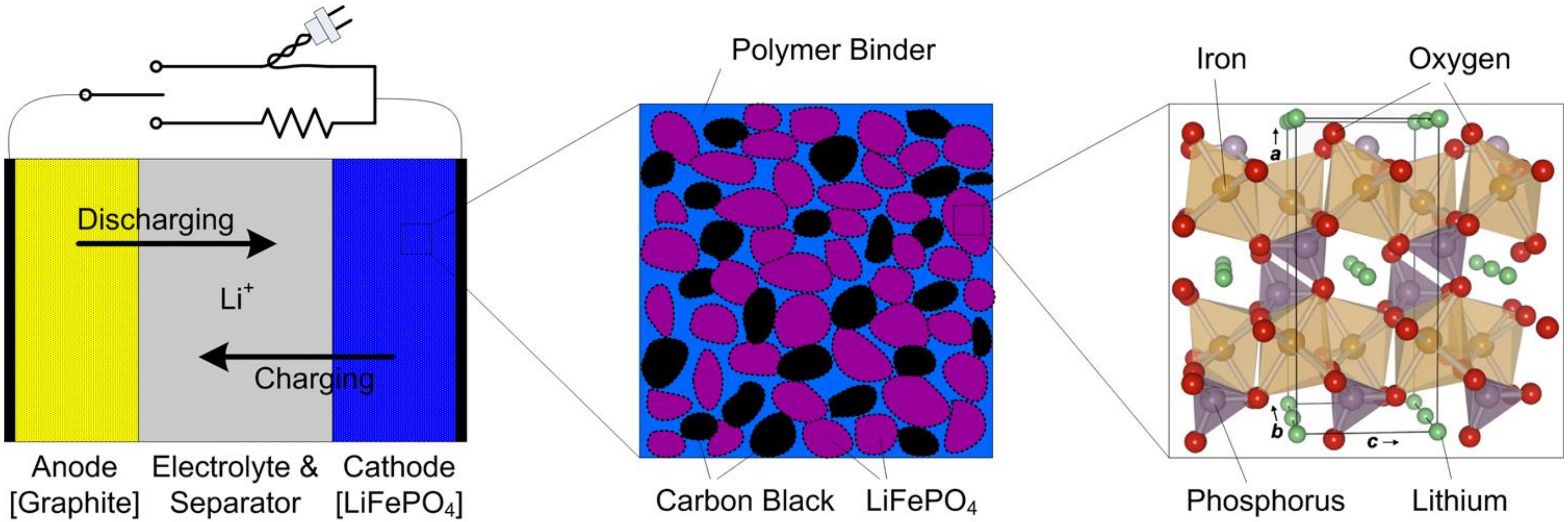


Image: P. Bai, G. Ceder



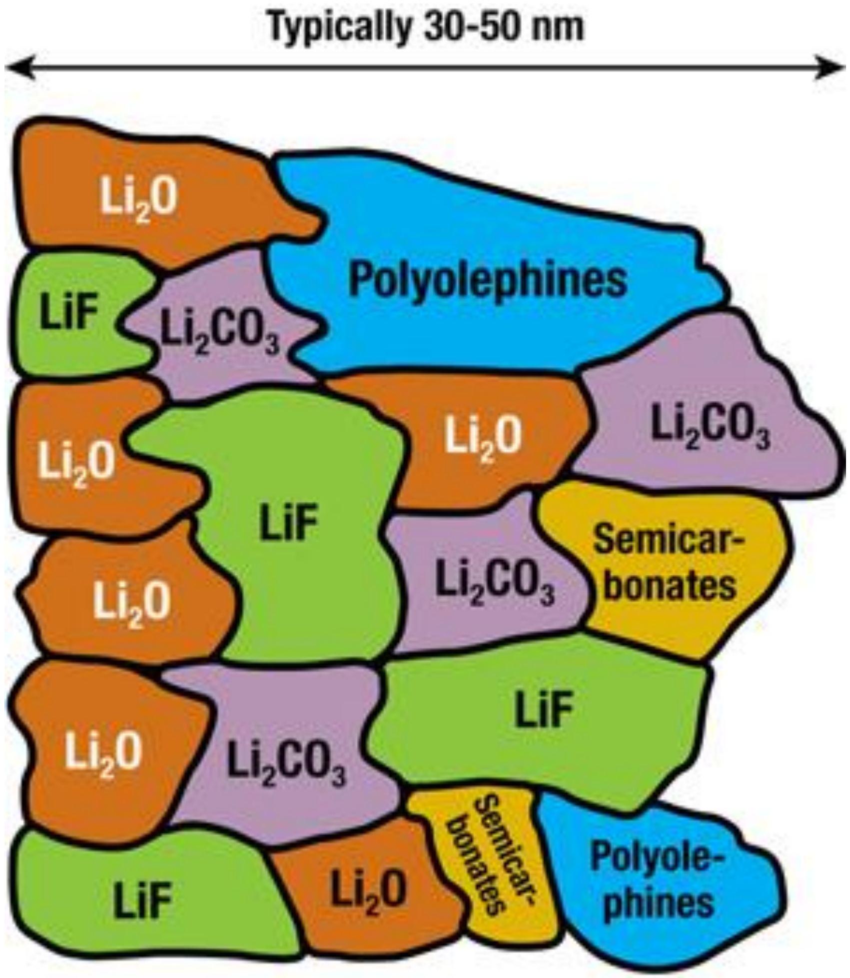
Capacity Fade in Li-ion Batteries

Matthew Pinson (PhD student, Physics)

“Theory of SEI formation in rechargeable batteries: Capacity fade, lifetime statistics, and accelerated aging”, MP & MZB, *J. Electrochem. Soc*. 160, A243 (2013).

“Internal Resistance Matching for Parallel-Connected Lithium-Ion Cells and Impacts on Battery Pack Cycle Life”, R. Gogoana, MP, MZB and S. Sarma.

- Dominant fade mechanism at high voltage: Solid electrolyte interphase (SEI) growth
- Electrolyte decomposes at the anode (graphite) during recharging (>0.8 V)
- Apply new models to literature data for full cells with graphite, silicon anodes

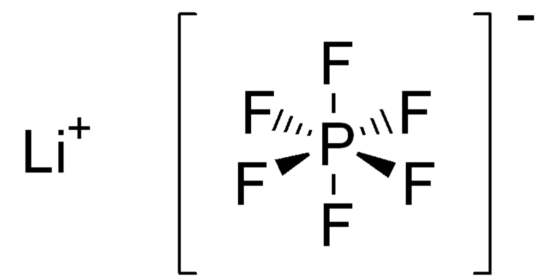


SEI Interface:
Lithium Intercalation into Graphite

Argonne Lab cse.anl.gov

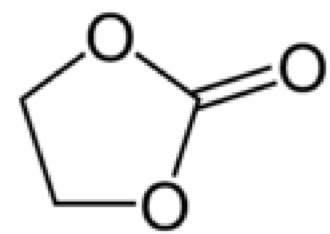
Typical Electrolyte

$LiPF_6$ salt

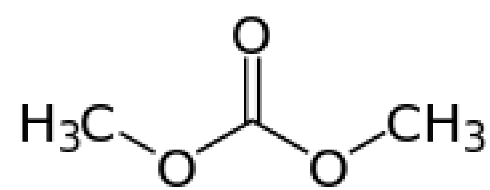


Organic solvents

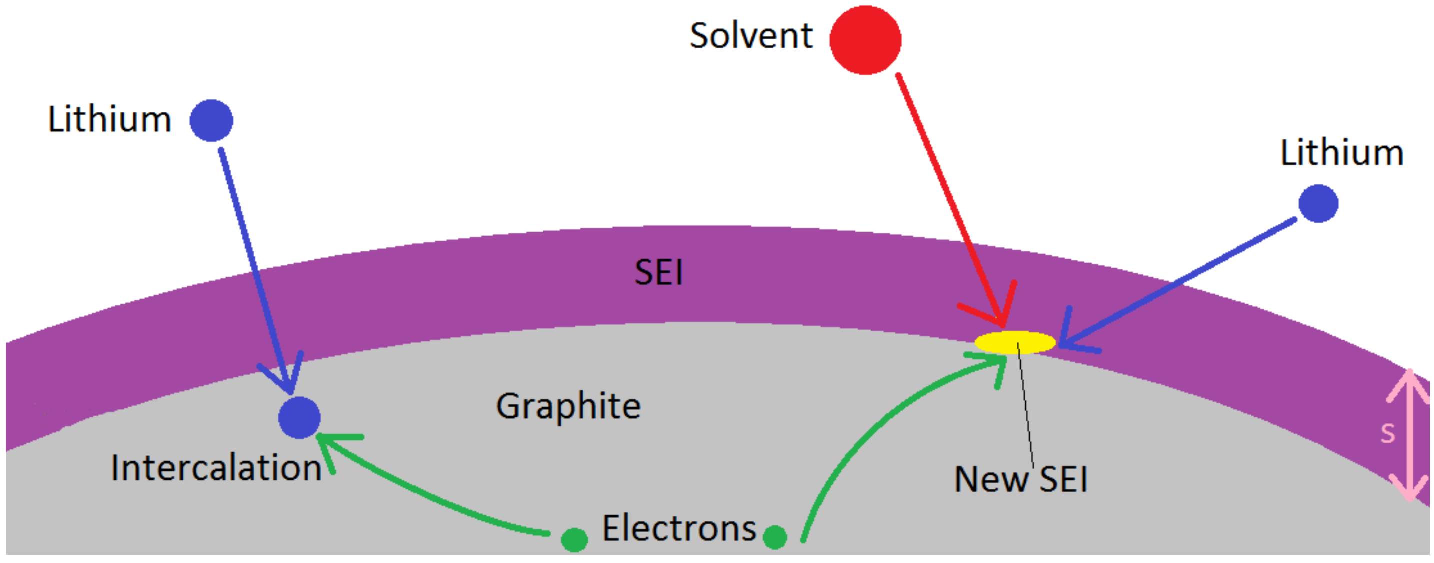
EC



DMC



Simple Model of SEI Growth



$$\frac{r}{m}\frac{ds}{dt} = k(c - \mathrm{D}c) = D\frac{\mathrm{D}c}{s}$$

Two parameters:

k SEI reaction rate

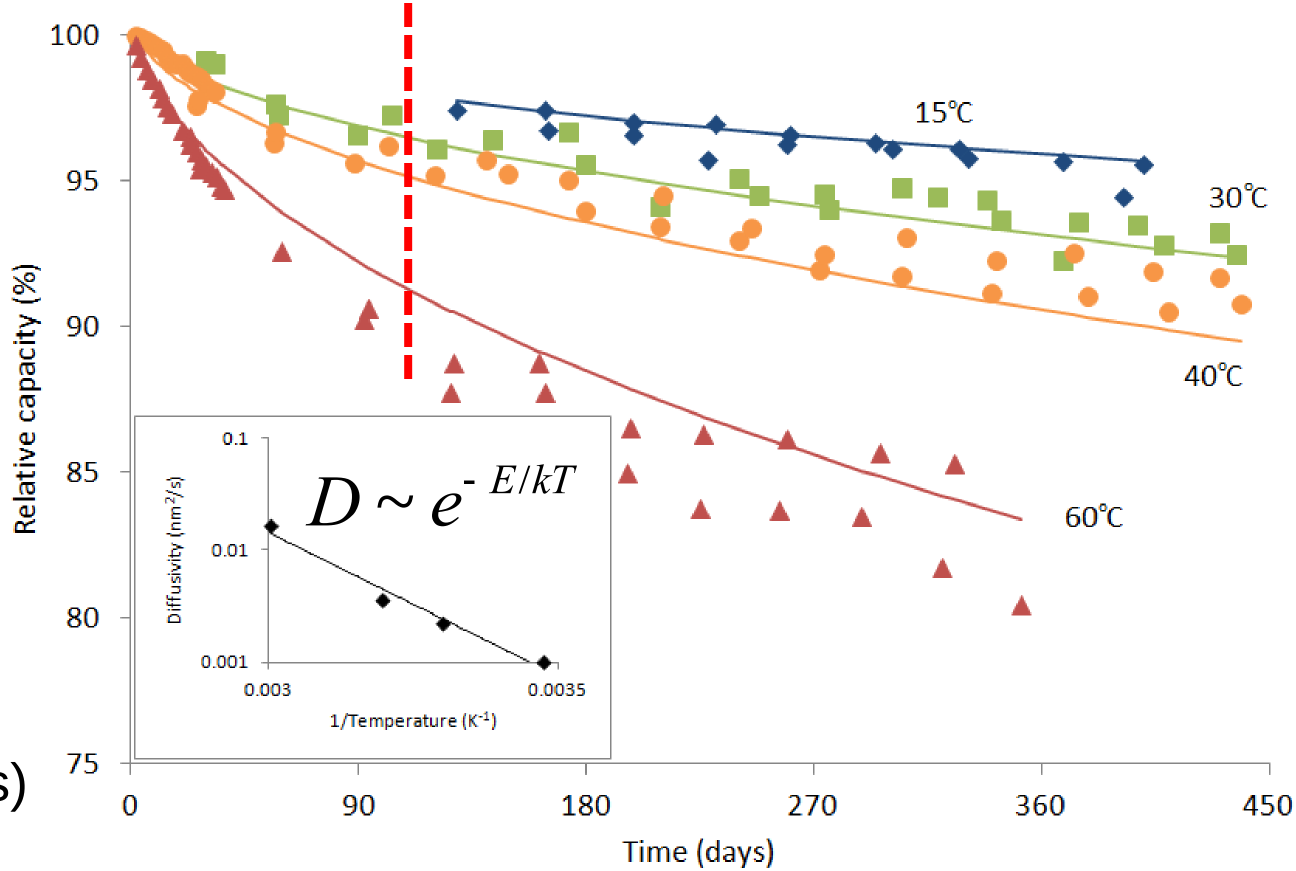
D solvent diffusivity in SEI

$$s \sim \begin{cases} kt & \text{early times} \\ \sqrt{Dt} & \text{late times} \end{cases}$$

Theory of Accelerated Aging

Fit D(T), k(T) over 3 months at 30-60°C

Accurately predict capacity fade over 15 months for 15-60°C

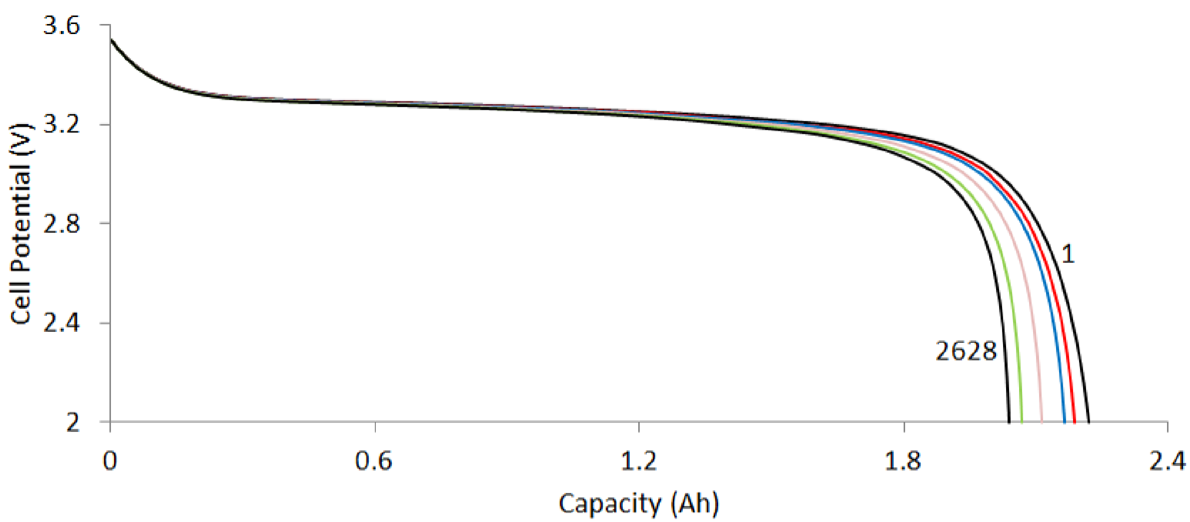


E=0.52V (close to direct expts)

Experimental data of Smith et al, J. Electrochem. Soc. (2011). Graphite/$LiFePO_4$
(Data also fitted for Graphite/$LiCoO_2$)

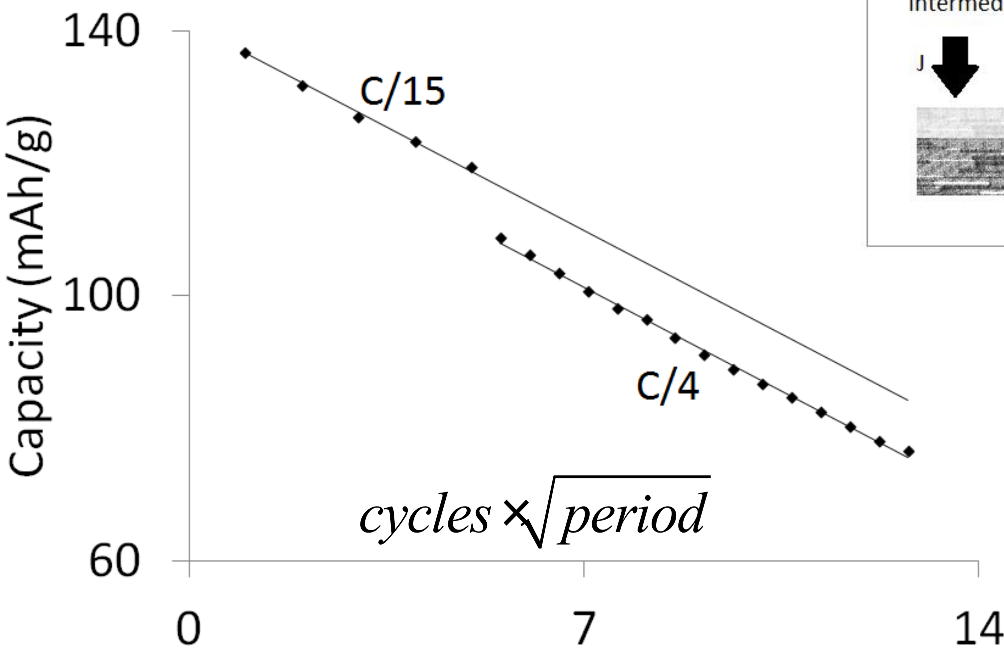
Porous Electrode Model

- Macroscopic mass, charge conservation, Butler-Volmer kinetics for intercalation & SEI growth; Solvent diffusion across SEI layers
- Results
  - SEI grows very uniformly
  - Isothermal fade depends only on cycle time
  - Current dependence due to heating

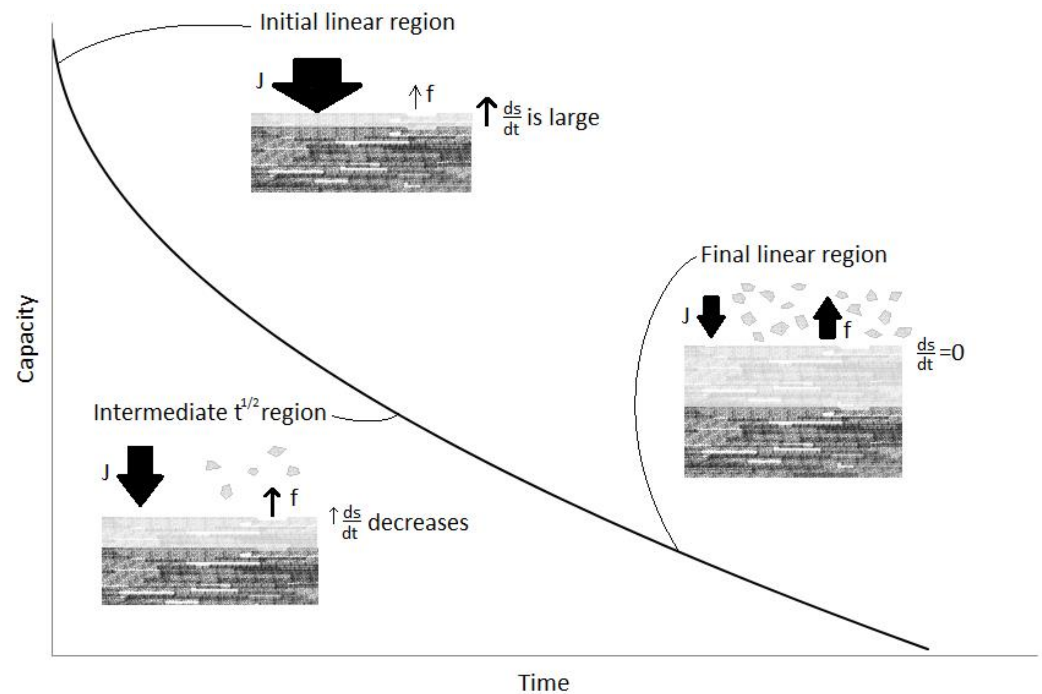


SEI Capacity Fade Mechanisms

Fastest fade (silicon): 300% volume expansion creates fresh area; repeat SEI growth model each cycle



Experimental data for Si cells from Ji et al., *Nano Energy*, 2012.



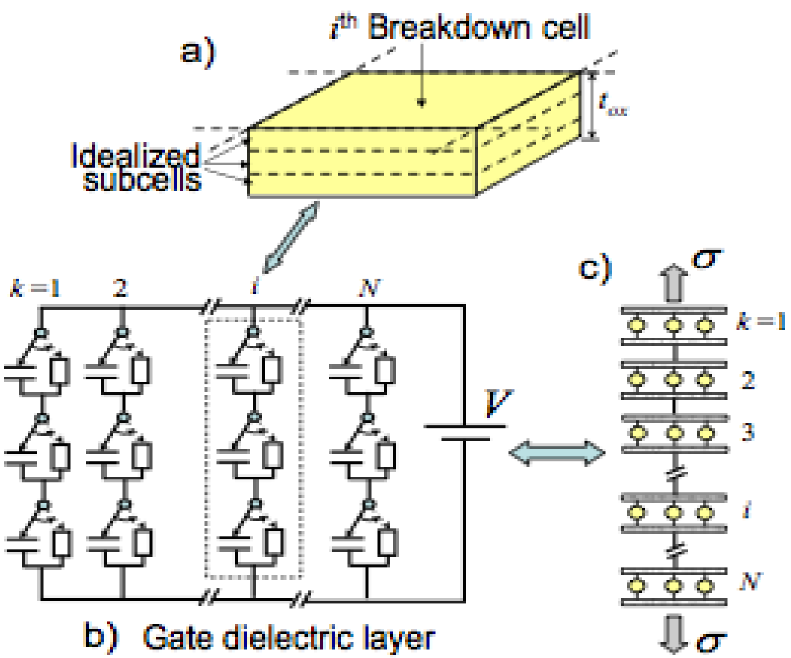
Slowest fade (graphite): Attached SEI

Intermediate fade: SEI delamination

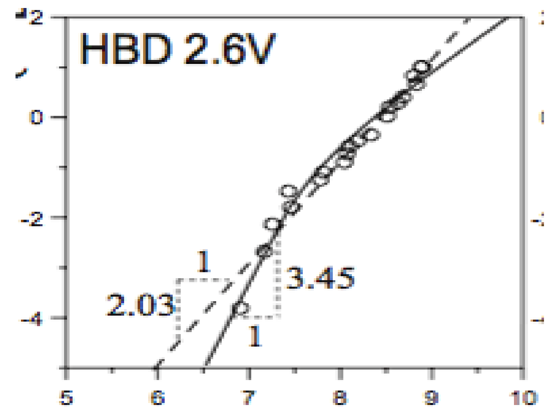
Lifetime Statistics

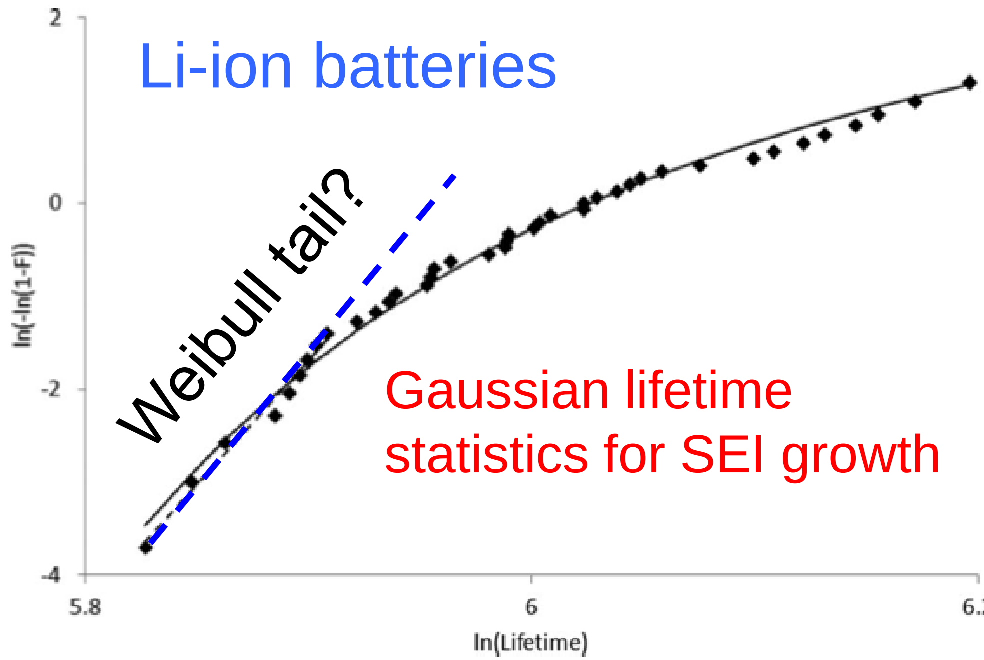
Dielectric breakdown statistical theory

J. Le, ZP Bazant, MZ Bazant, J Appl Phys (2011)



DB of oxide thin films

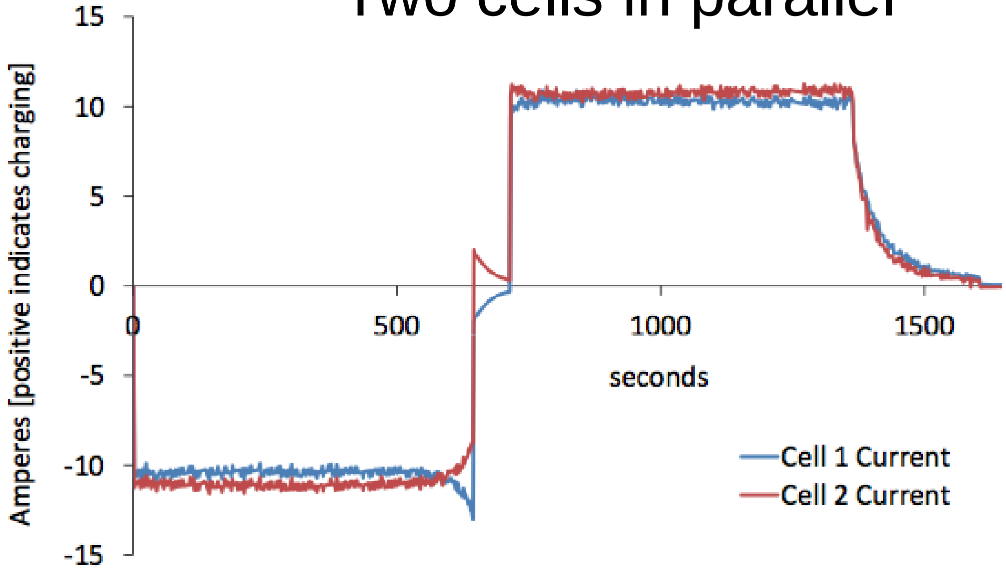


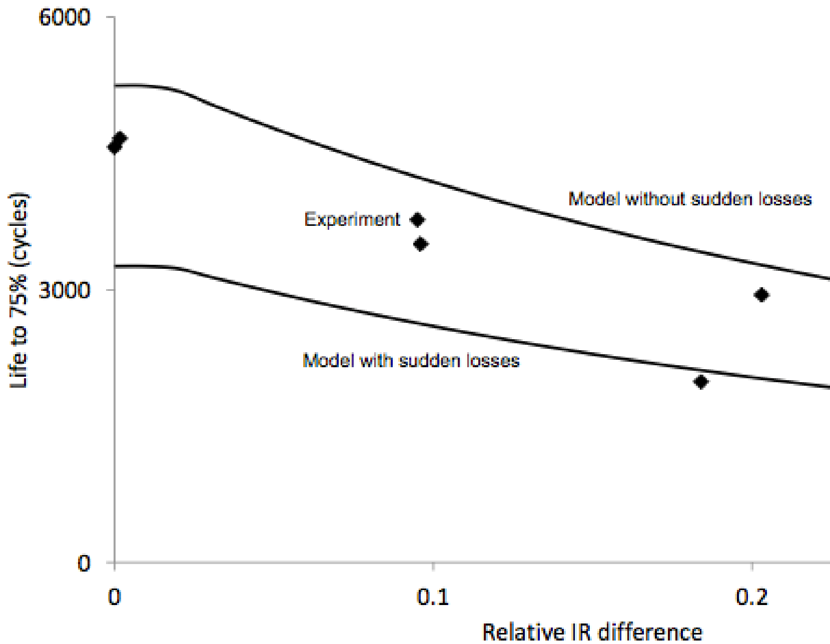


Data: J. I. Park et al, Korean J Systems Eng (2008)

Effect of Statistical Variability on Reliability of a Battery Pack

Two cells in parallel

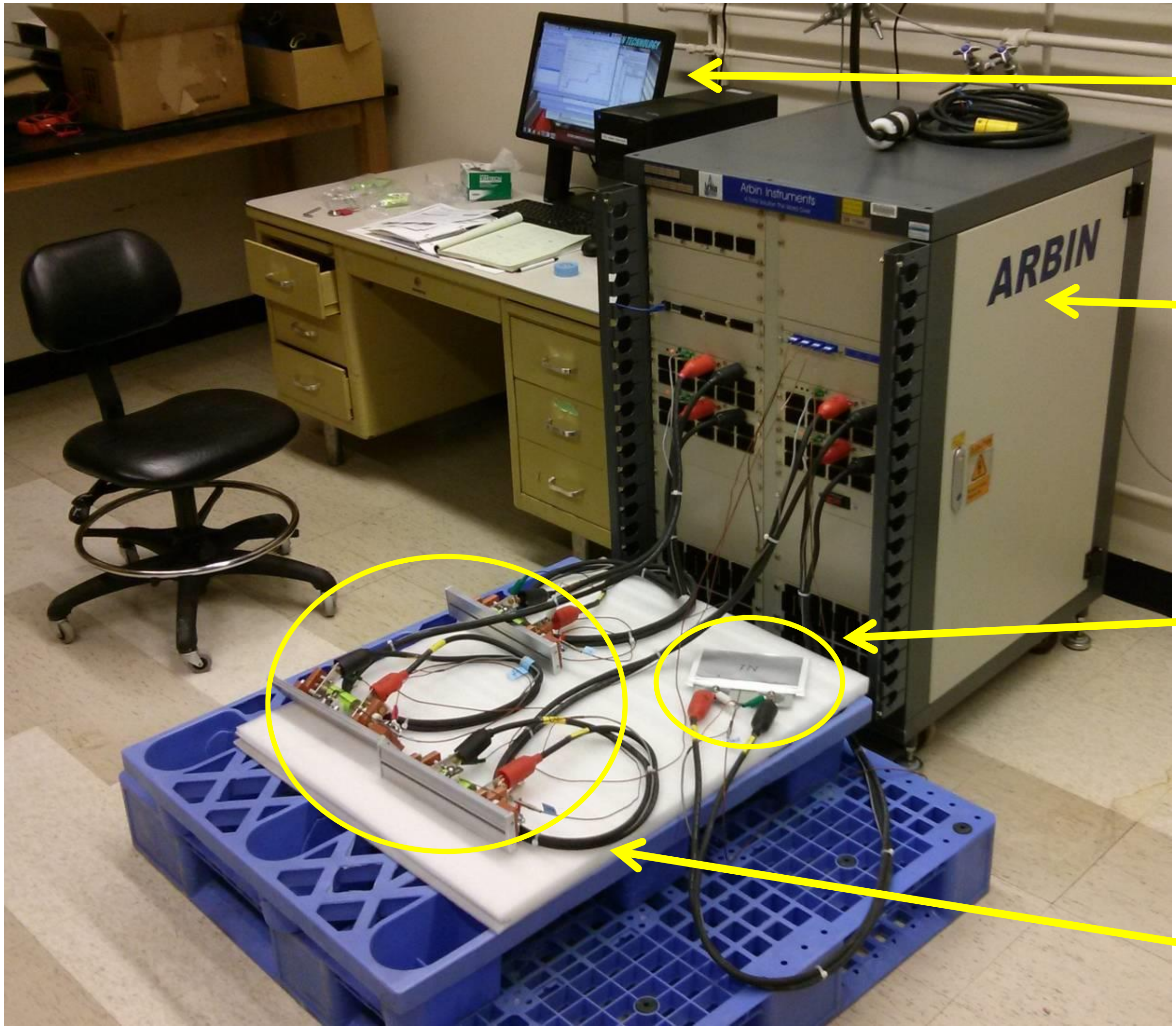




- Rate dependence from localized heating (accelerated aging)
- Resistance variations lower pack cycle life (large max current)
- Test model for A123 battery packs (R. Gogoana, S. Sharma, Mech Eng)

MIT / Lincoln Lab Project

Peng Bai, Alan Millner



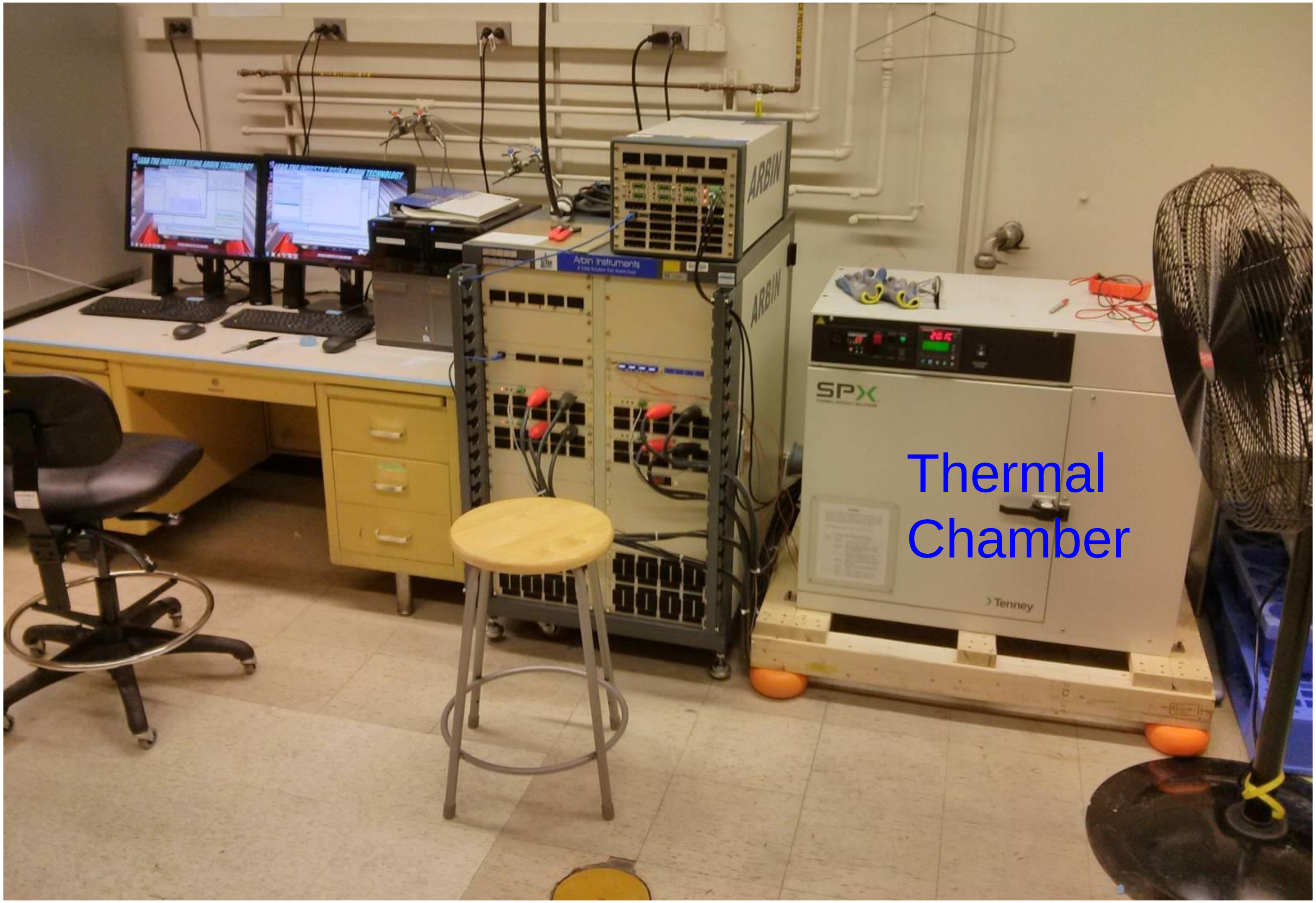
Controlling PC and Testing Interface

Arbin High Current Battery Tester

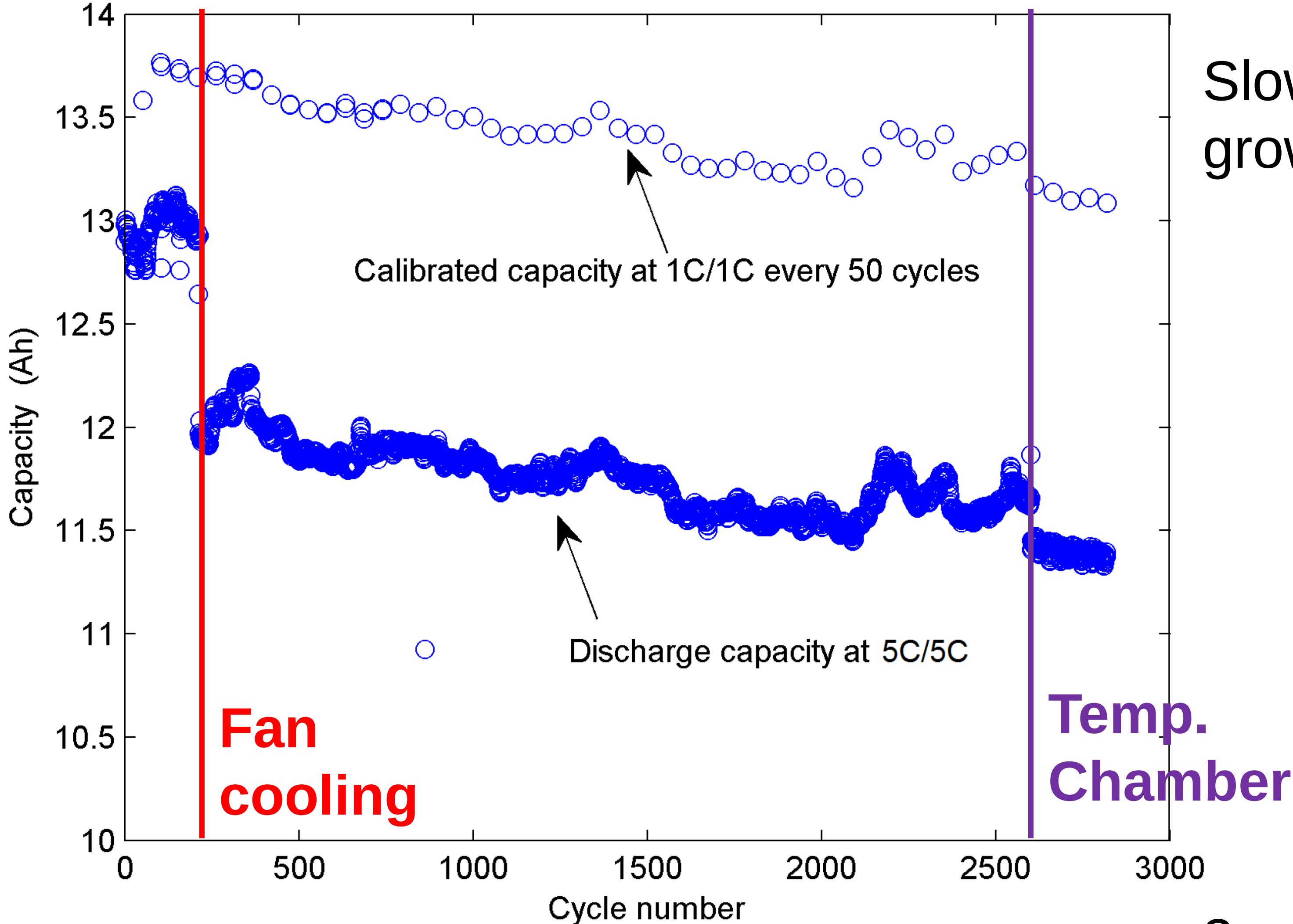
Altairnano 13Ah Prismatic Battery
Titanate anode
Low voltage (1.5-2.8 V)
“strain free”

A123 26650 Cylindrical Cells
Graphite anode

Complete Testing System



Altairnano @5C/5C



Slow SEI growth?

3 months

From Fade to Failure

- Dendritic Li growth (cold, fast charge)
- Thermal runaway, fire… (short)
- Mechanical deformation causing
  - Loss of electric contacts
  - Damage in solid active particles
  - Leakage, contaminant entry
- Side reactions
  - Corrosion (moisture)
  - Leaching cathode ions (Fe, Ni…)

Batteryuniversity.com

Need for physics-based predictive models

Test Case: LiFePO4

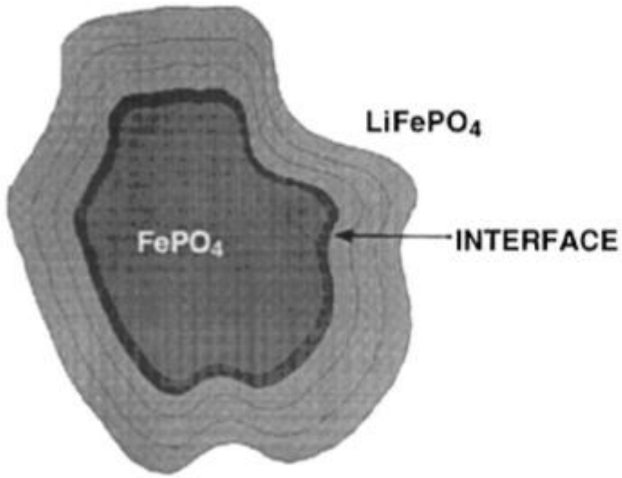
- 1997: "Low power" Li_xFePO_4 (J. Goodenough)
- 2000s: Doping, coatings, nanoparticles… (Y.-M. Chiang)
- 2009: "Ultrafast" 10 sec. discharge (G. Ceder)

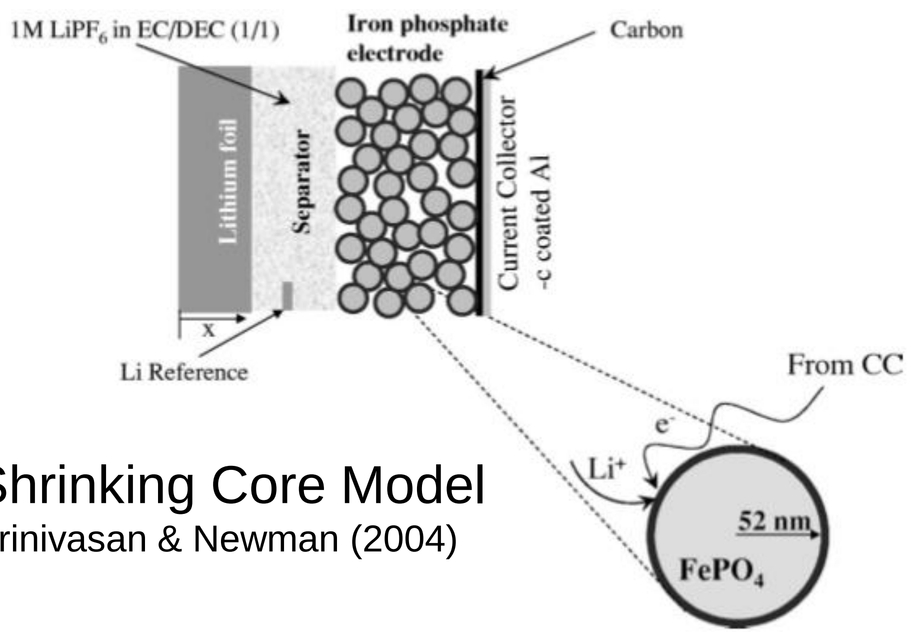
Why is nano so different?

- Phase separation?
- Role of surfaces?

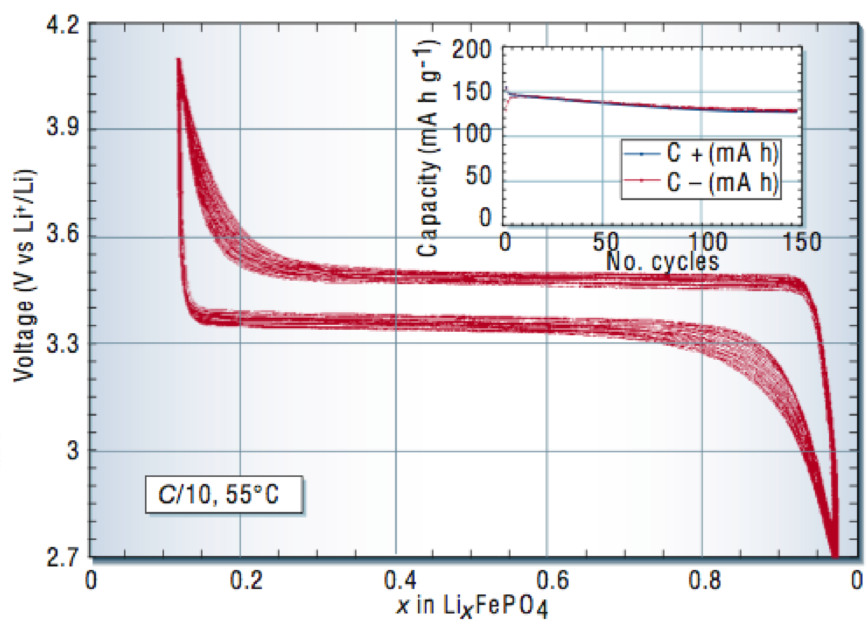
Lithium Iron Phosphate

"This material is very good for low power applications; at higher current densities there is a reversible decrease in capacity… associated with the movement of a two-phase interface." - Padhi, Nanjundaswamy & Goodenough (1997)





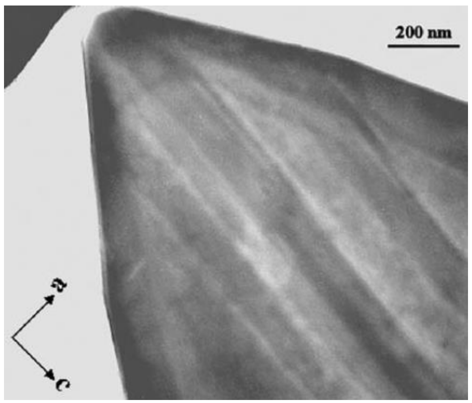
Shrinking Core Model
Srinivasan & Newman (2004)



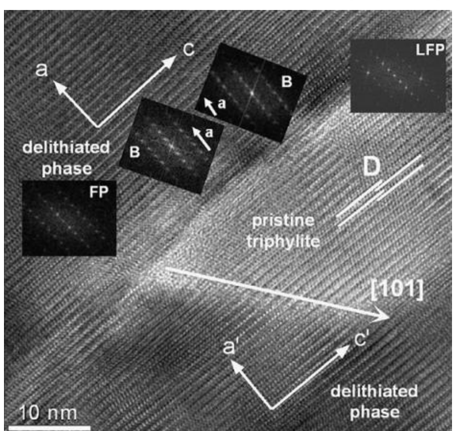
Tarascon et al (2001)

What Shrinking Core?

Phase boundaries along the surface

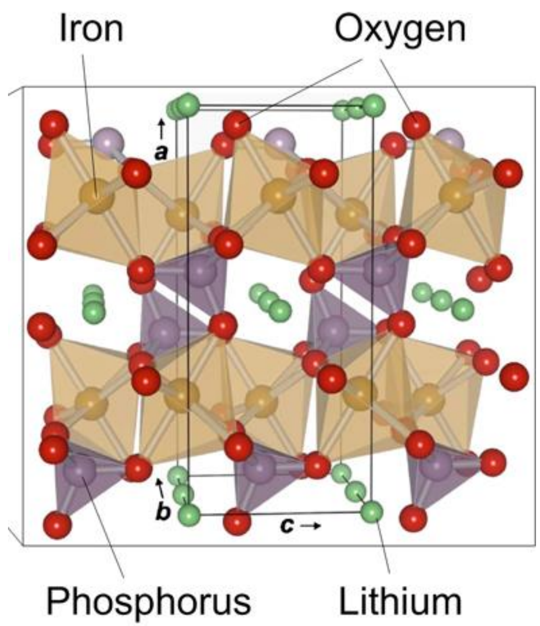


Chen & Richardson (2006)



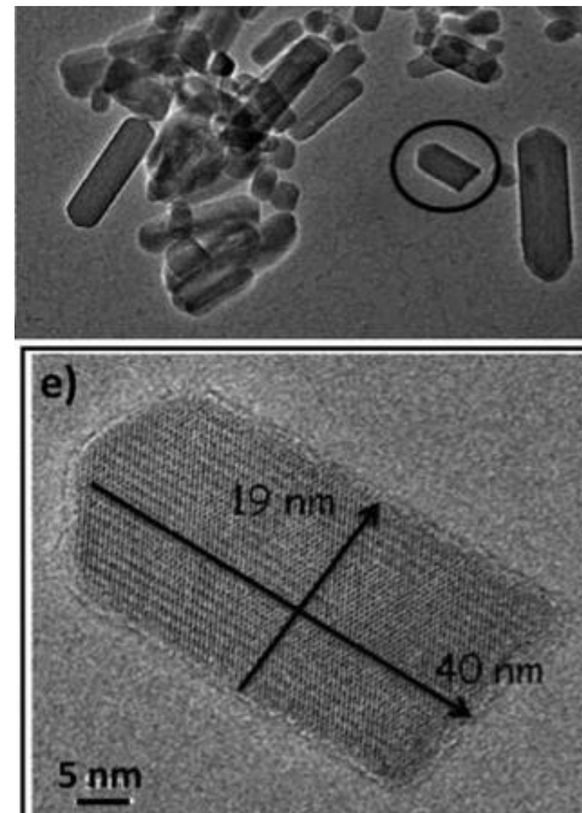
Ramana et al (2009)

1D ion transport



Morgan, van der Ven Ceder (2004)

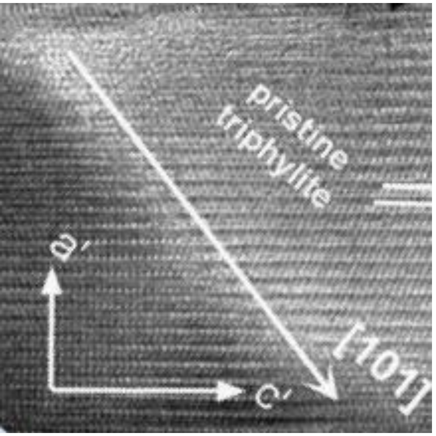
<100nm particles
→fast diffusion (ms)



Badi et al (2011)

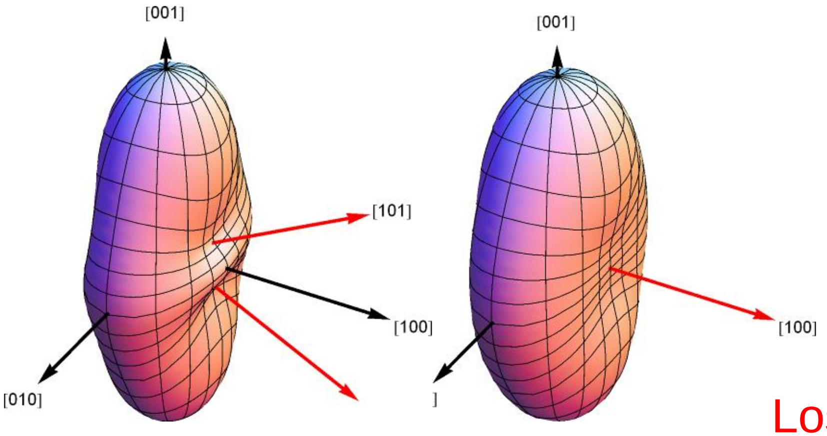
Elastic Coherency Strain

Ramana et al (2009)

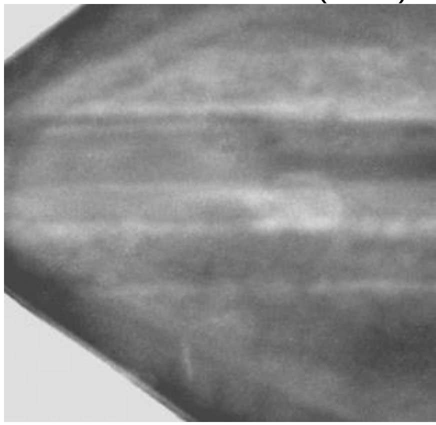


coherent phase separation

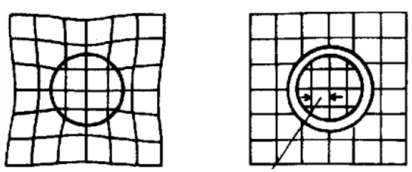
DA Cogswell & MZB, ACS Nano (2012)

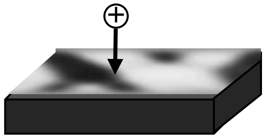


Chen et al (2006)



Loss of c-axis coherency



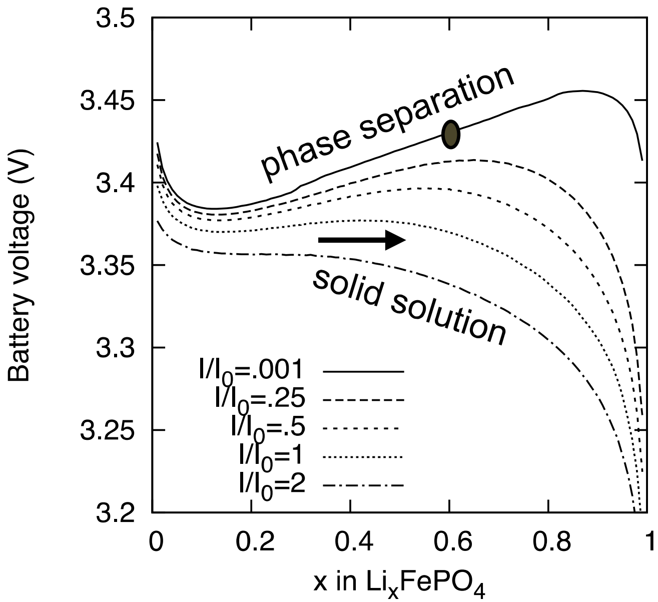


Stripe spacing

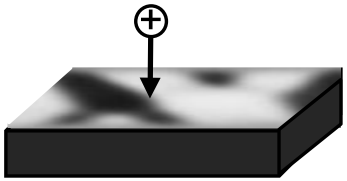
$$l = \sqrt{\frac{gL}{Df}}$$

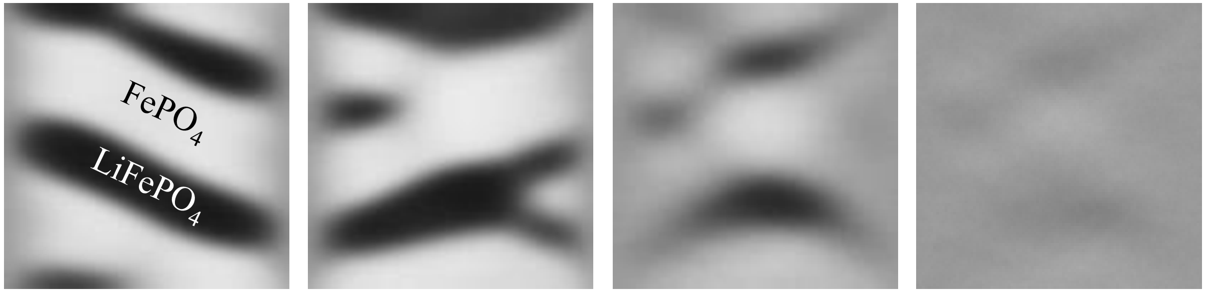
Suppression of phase separation at high rates

Dan Cogswell & MZB, ACS Nano (2012)



$$Li^+ + FePO_4 + e^- \rightarrow LiFePO_4$$

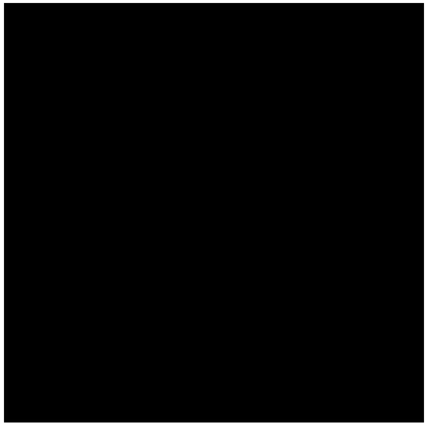




$\tilde{I} = 0.001$ $\tilde{I} = 0.01$ $\tilde{I} = 0.033$ $\tilde{I} = 0.05$

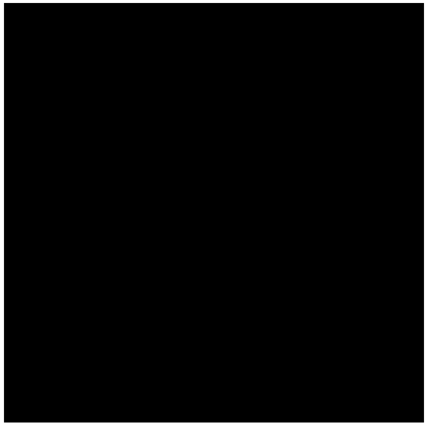
quasi-solid solutions at X=0.6 with increasing current

Slow discharge
I/I_0=.001
~C/50



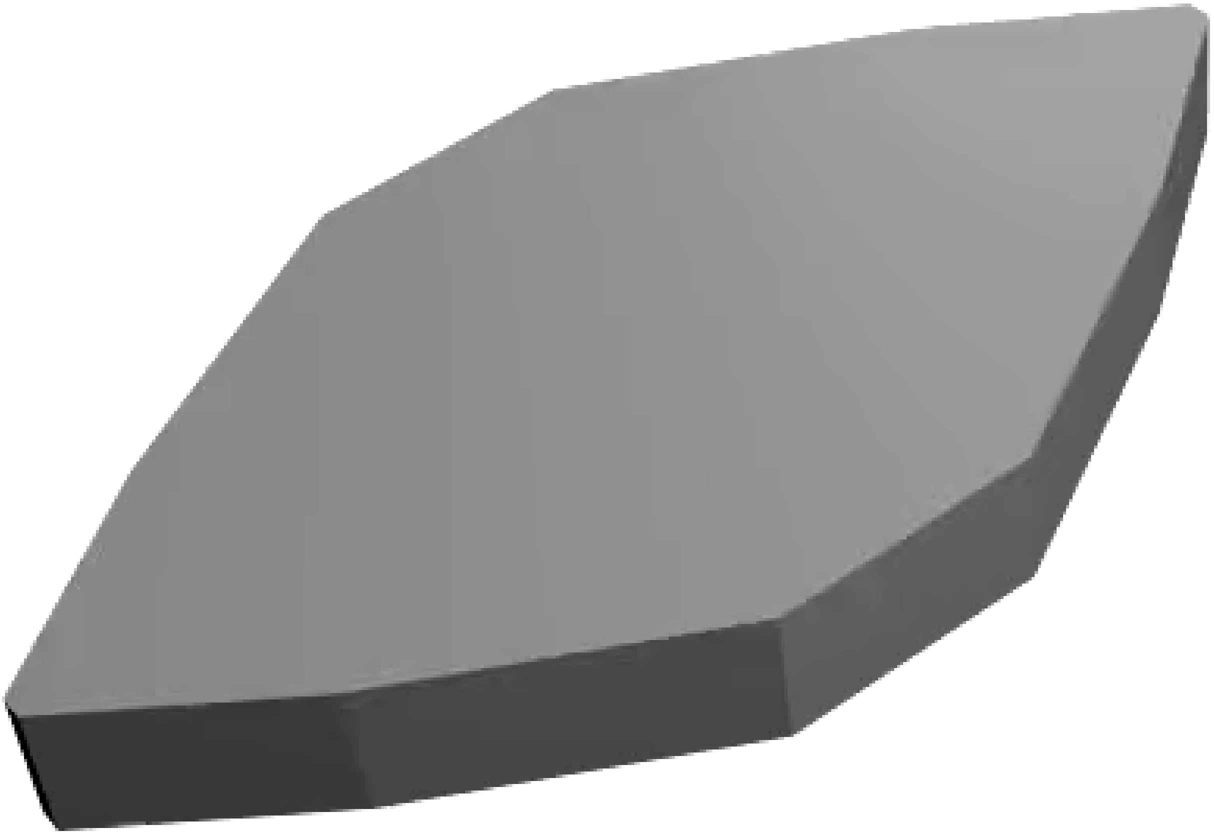
100x100 nm

Fast discharge
I/I_0=.3
~7C



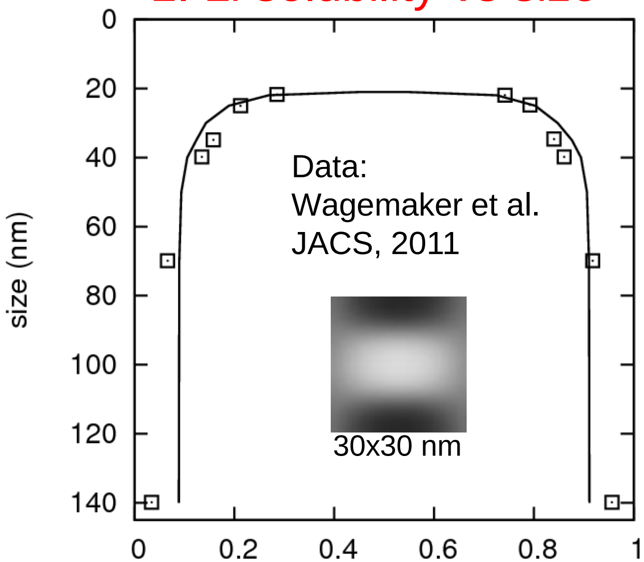
Nucleation at Nanoparticle Surfaces

Dan Cogswell & MZB, Nano Letters (2013)



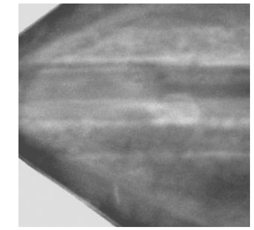
Accurate Model of Li_xFePO_4

1. Li solubility vs size



Dan Cogswell, MZB, ACS Nano (2012)

3. Stripe spacing

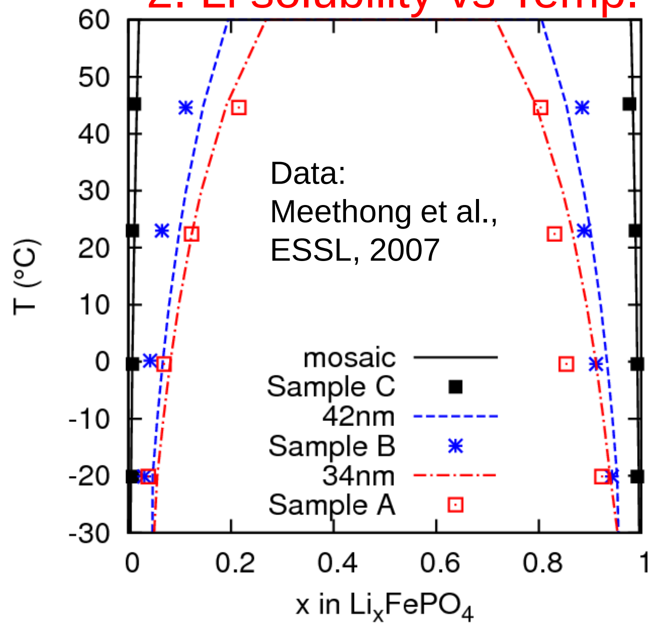


- *Ab initio* elastic constants, misfit strain, surface energies (Ceder)
- Only 2 fitting params

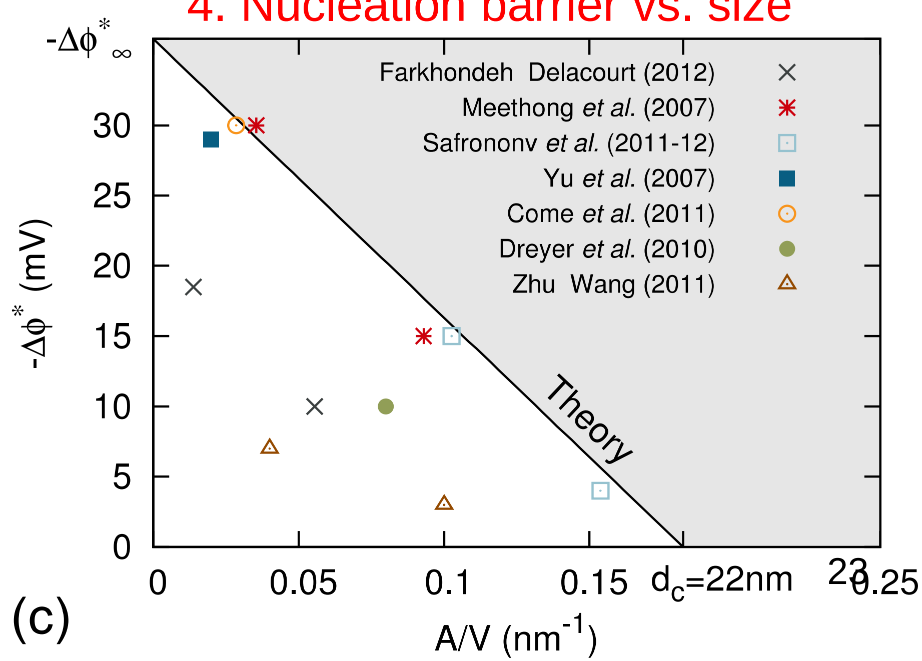
$$\tilde{W} = 4.51, \tilde{\kappa} = 8.90$$

$$l = \sqrt{\frac{gL}{Df}}$$

2. Li solubility vs Temp.



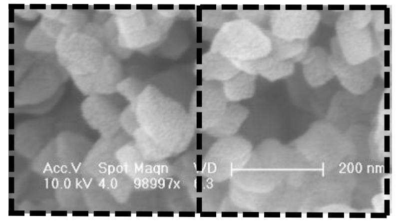
4. Nucleation barrier vs. size

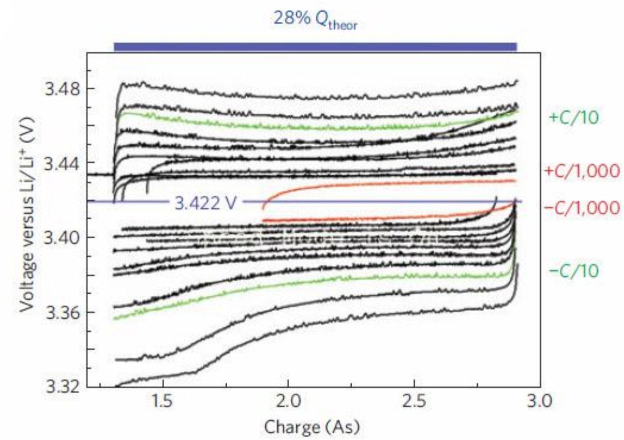


Porous Electrodes

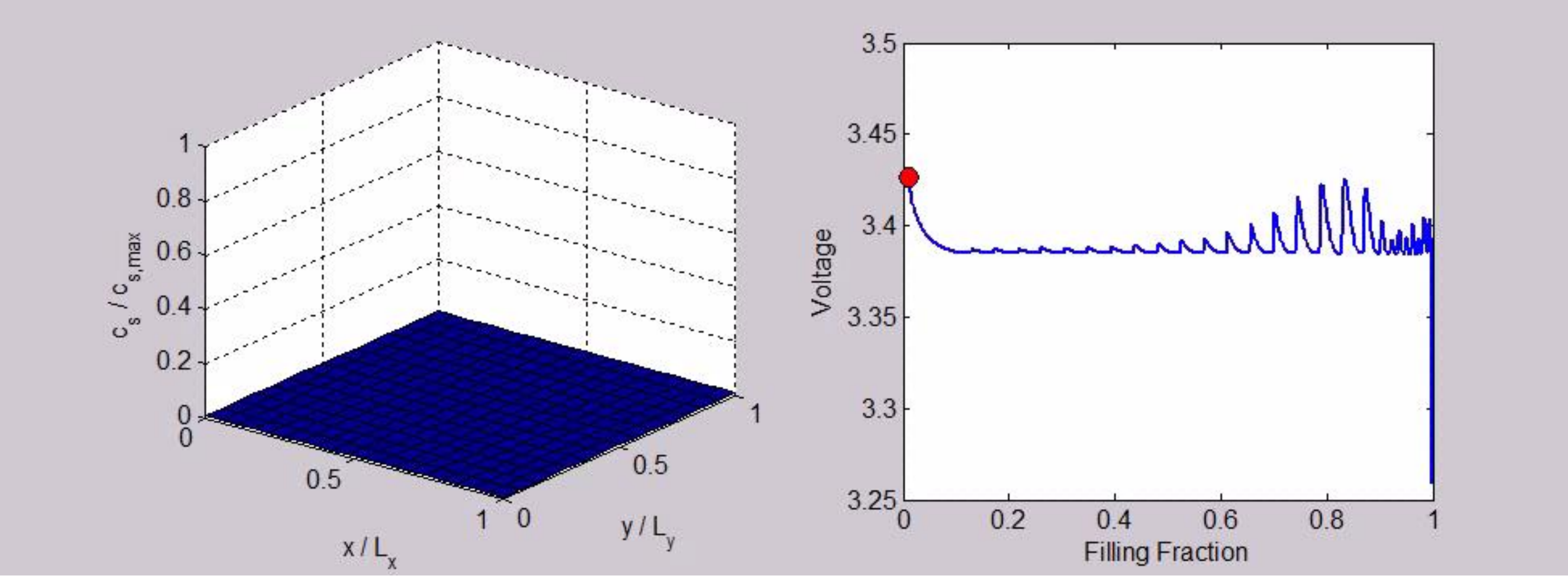
Todd Ferguson and MZB,
J. Electrochem Soc (2012)

- Low current (i/i_o=0.01, ~C/2)
  - narrow reaction front
  - mosaic instabilities



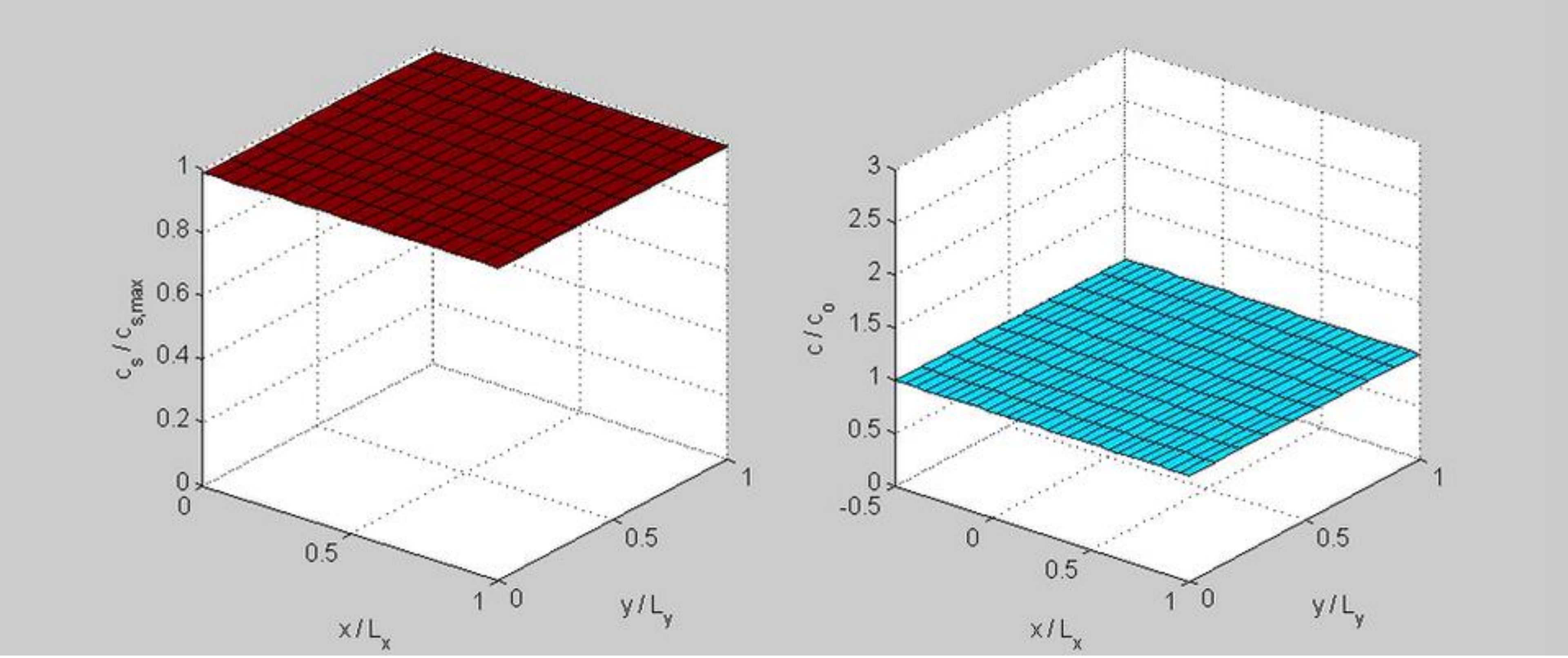


Dreyer et al, Nature Mat. (2010)



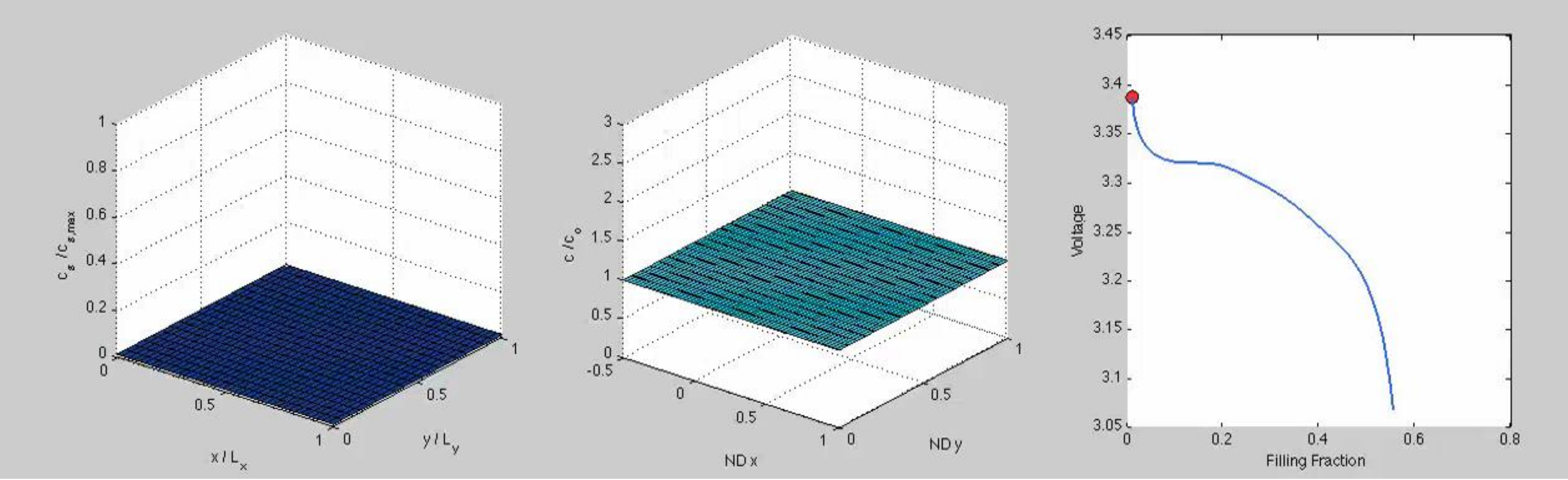
Small voltage step

$C_{solid}(x,y,t)$ $C_{electrolyte}(x,y,t)$



Fast Discharge

- Large current (i/i_o = 4, ~80C)
  - Suppressed *macroscopic* phase separation
  - Electrolyte depletion leads to capacity loss

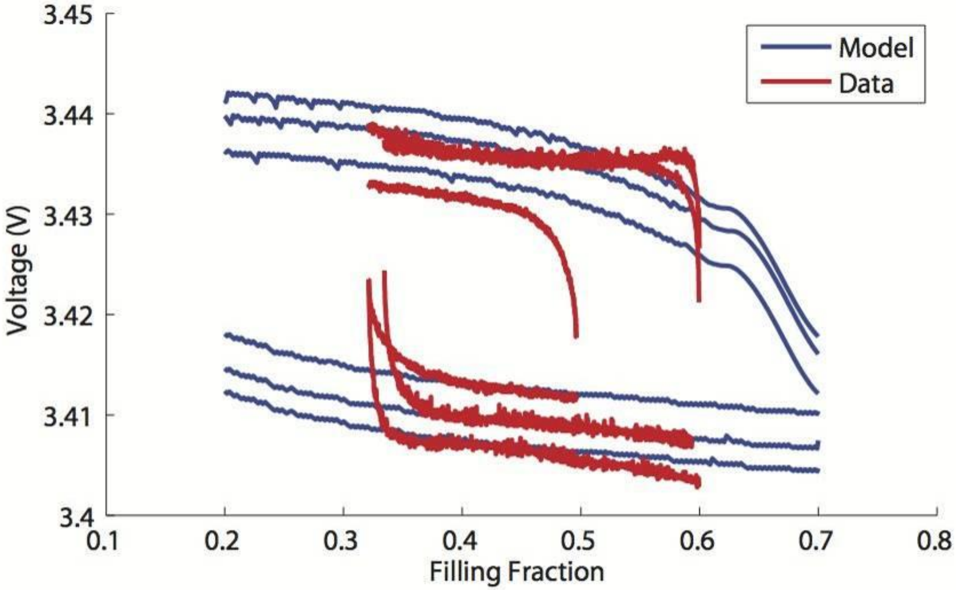


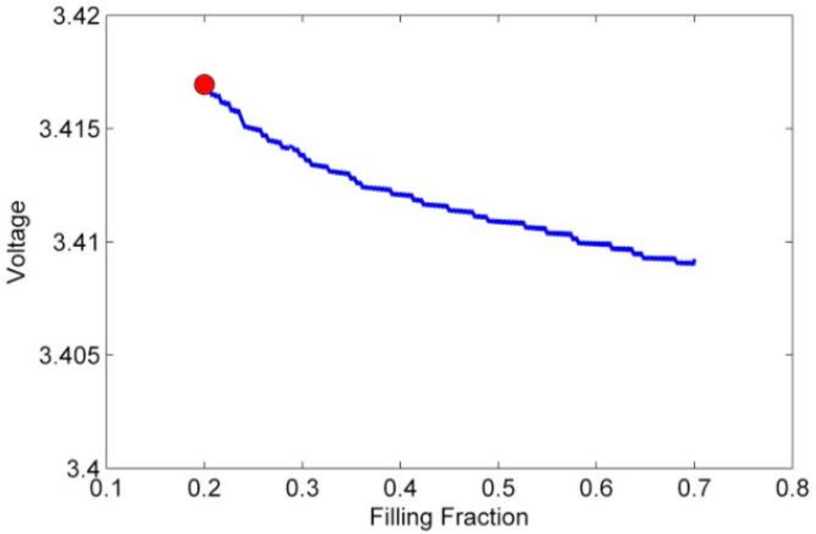
Solid concentration | Electrolyte concentration | Voltage

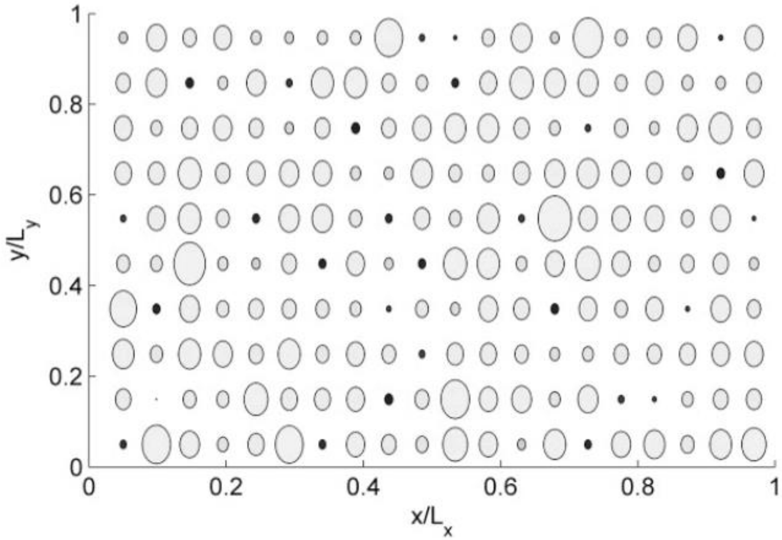
Size-Dependent Nucleation

Todd Ferguson

Only fit variance of particle size



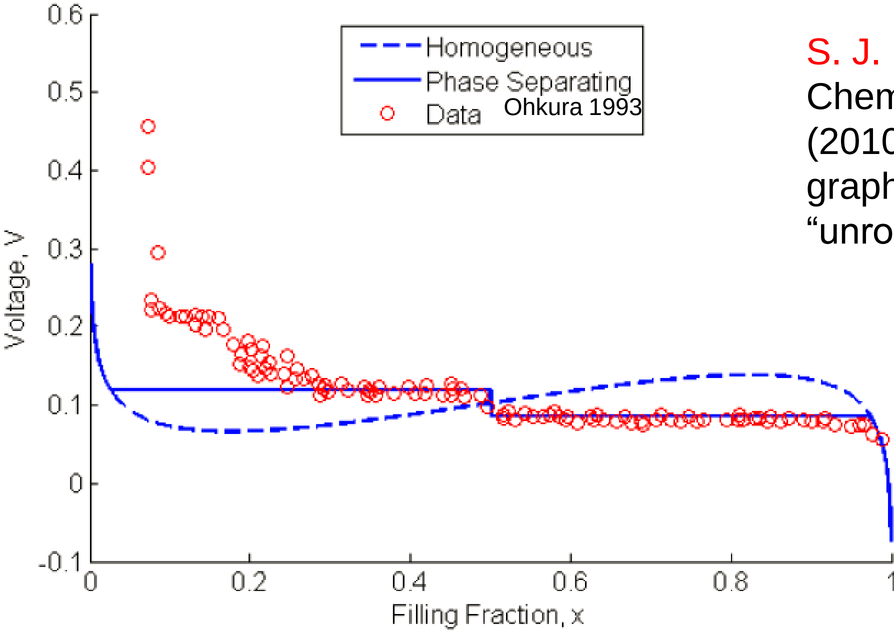




- Downward tilted voltage plateau
- Excellent fit to Dreyer (2010) data
- Next: Chueh et al (2012) data

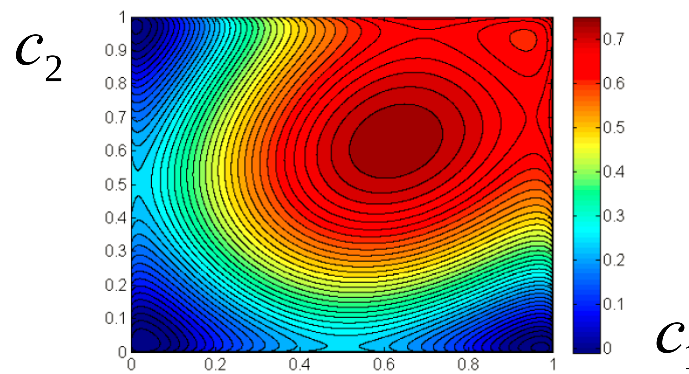
Three Stable Phases:

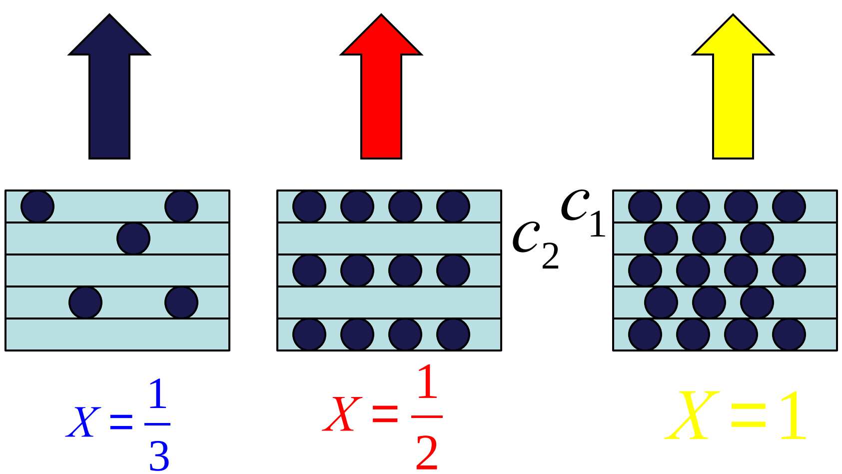
Li_xC_6 (Graphite)



S. J. Harris et al, Chem Phys Lett (2010)
graphite electrode "unrolled"

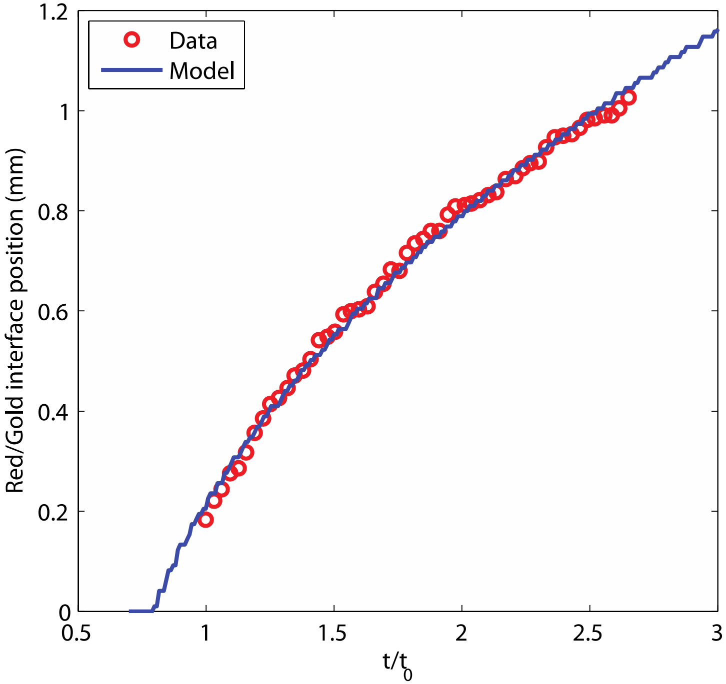
http://lithiumbatteryresearch.com/

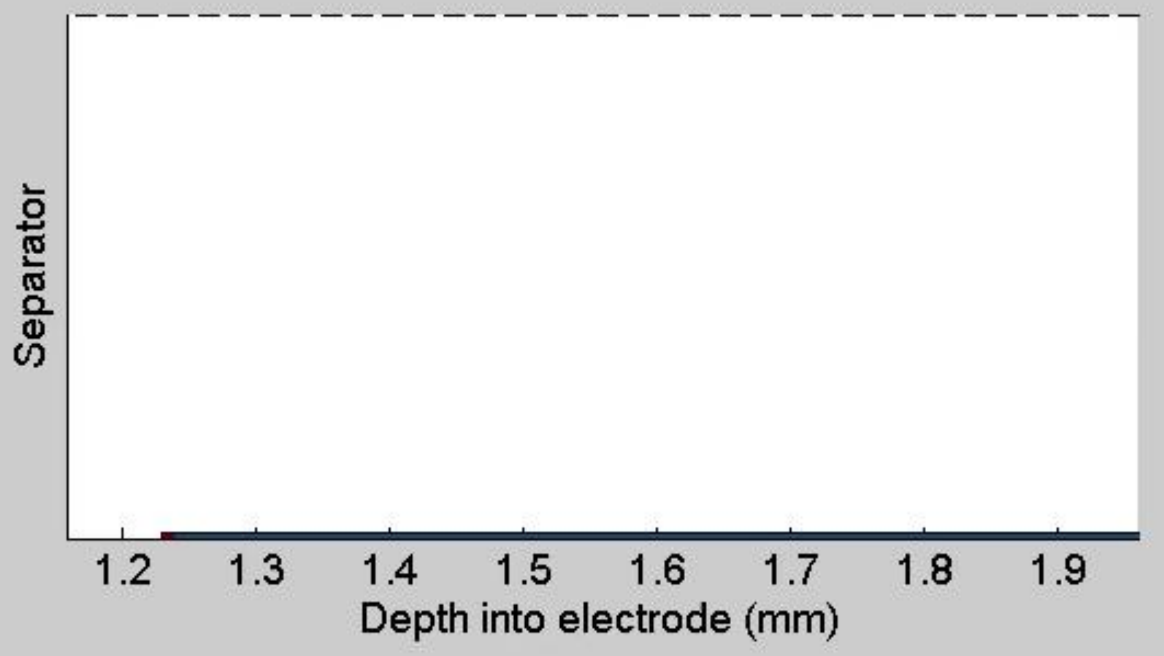




Model: Two periodic layers,
4 species regular solution

Simulation vs. Experiment



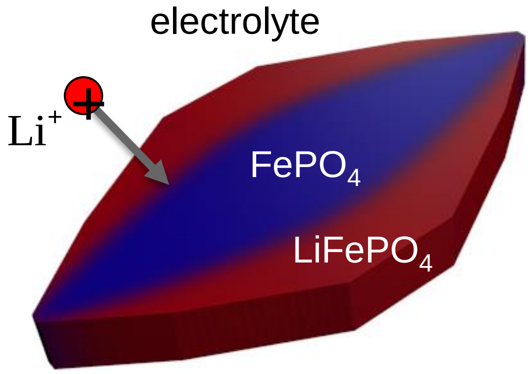


Only fitting parameter
Tortuosity = 0.4

T. Ferguson, MZB (2013)

Conclusion

- New physics-based models can inform:
  - Performance and reliability prediction
  - Battery design
  - Characterization and testing
  - Control systems
- Must capture:
  - Nonequilibrium thermodynamics
  - Reaction kinetics
  - Electrolyte side reactions



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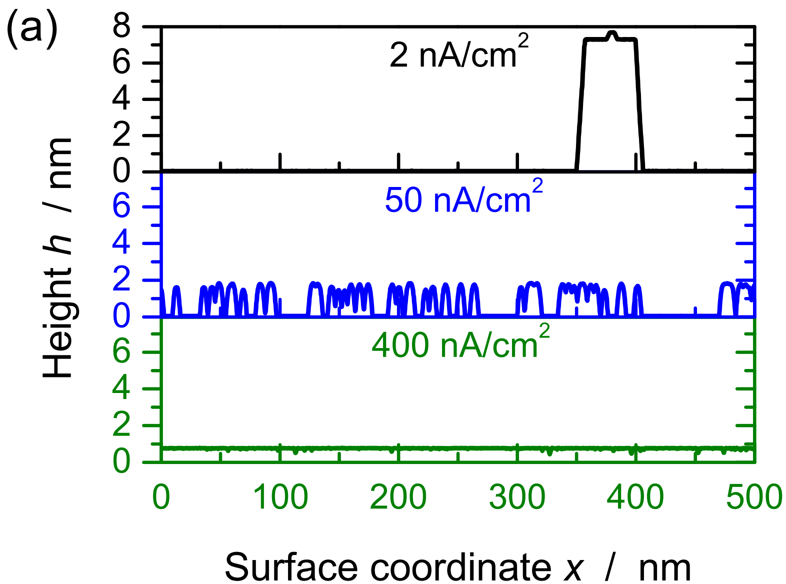
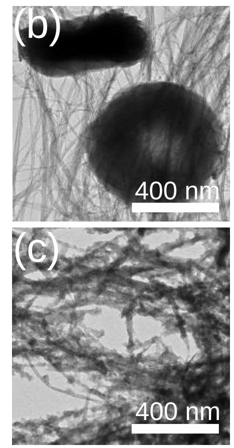
Rate-Dependent Morphology of Li_2O_2 Growth in Li-air batteries





B. Hortsmann, B. Gallant, R. Mitchell, Y. Shao-Horn, MZB (2013)