Non-equilibrium Thermodynamics of Lithium-Ion Batteries

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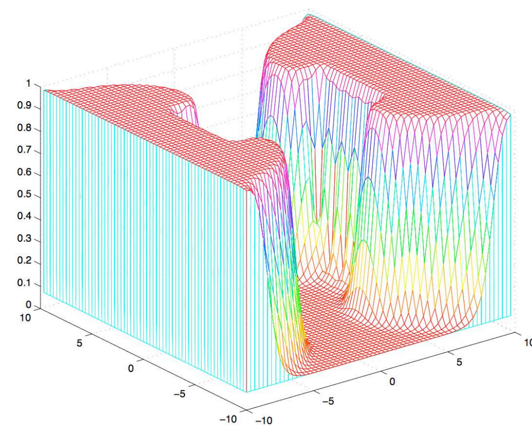
Collaborators: Gerbrand Ceder (MIT, Materials)
Katsuyo Thornton (Michigan, Materials)



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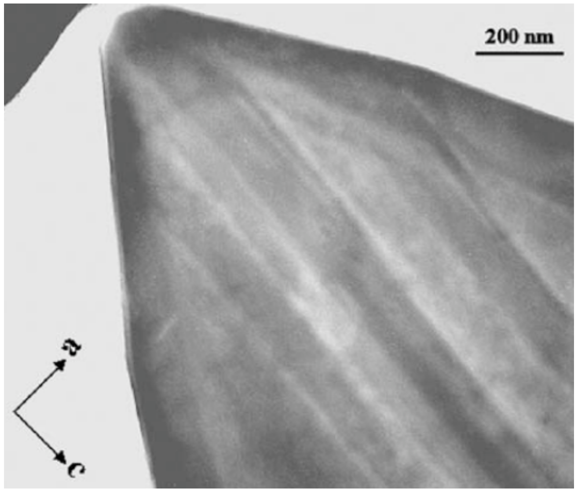
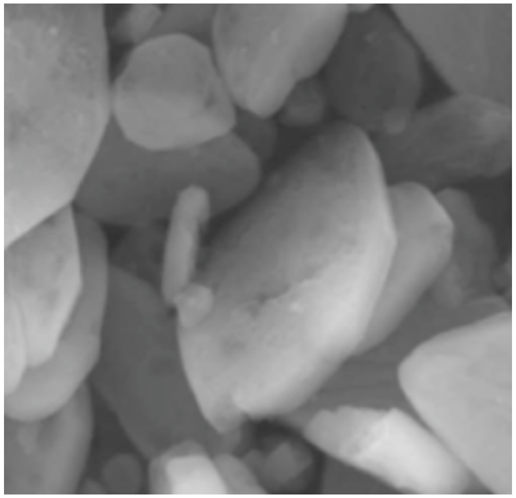
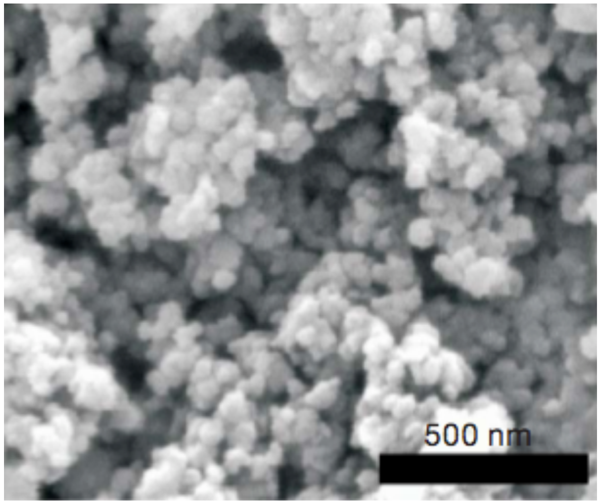
Outline

1. Motivation: Li_xFePO_4
2. Theory of ion intercalation dynamics
3. Phase-transformation waves
4. Composite electrodes





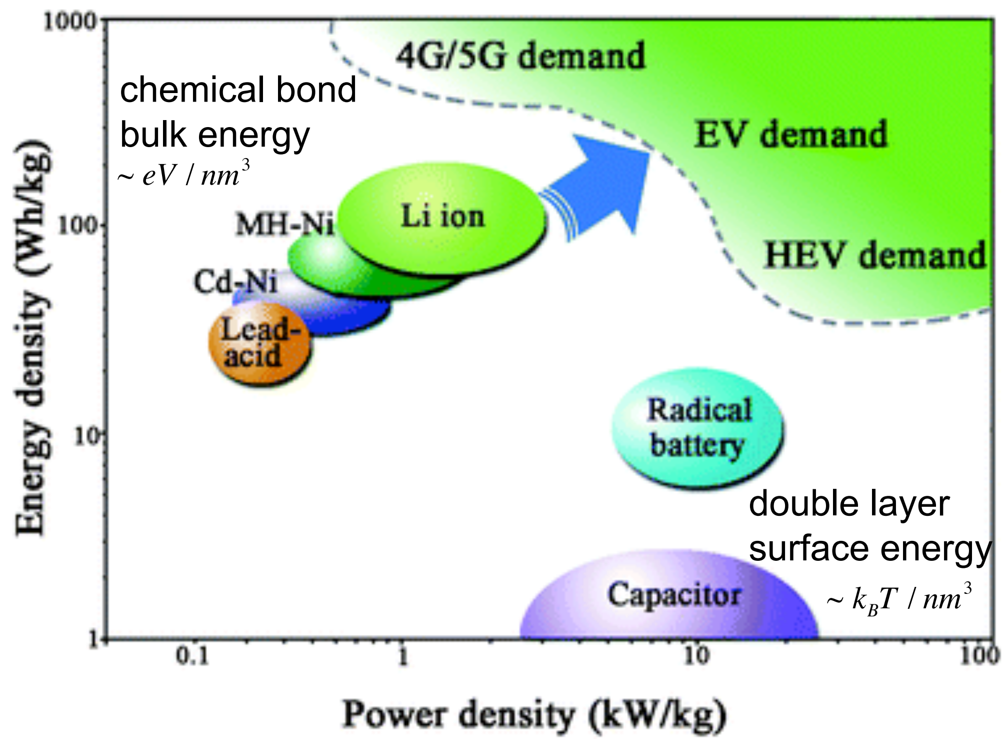
Chen, Song & Richardson, *Electrochem. Sol. State Lett.* (2006)



Kang & Ceder, *Nature Materials* (2009)

A Grand Challenge

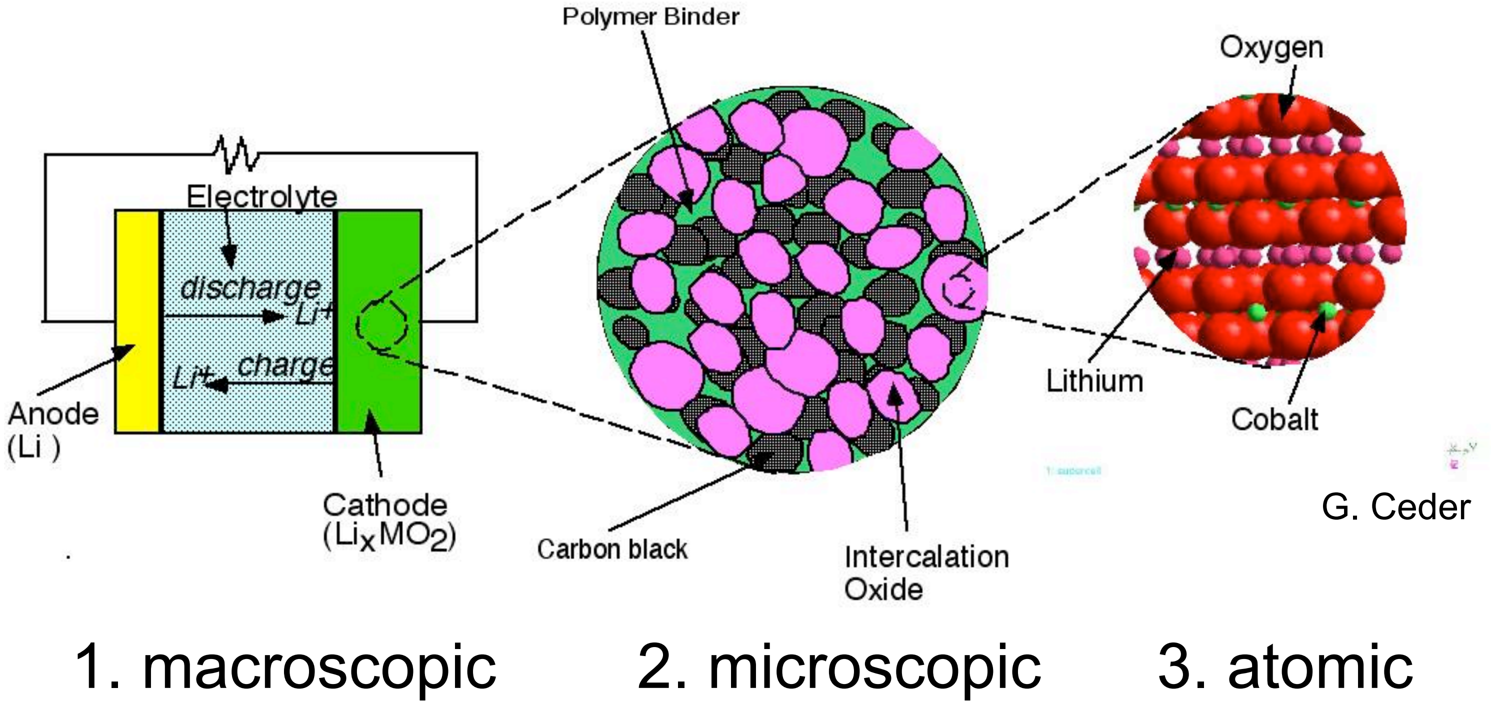
- New applications require better performance (>10x)
- Energy density is nearing theoretical limits (<10x)
- Power density can improve (>>10x?), but must not sacrifice capacity or cycle life
- Predictive mathematical models are needed to interpret data & guide engineering



"Ragone plot" for electrochemical energy storage

Gao & Yang, Energy Environ. Sci. (2010)

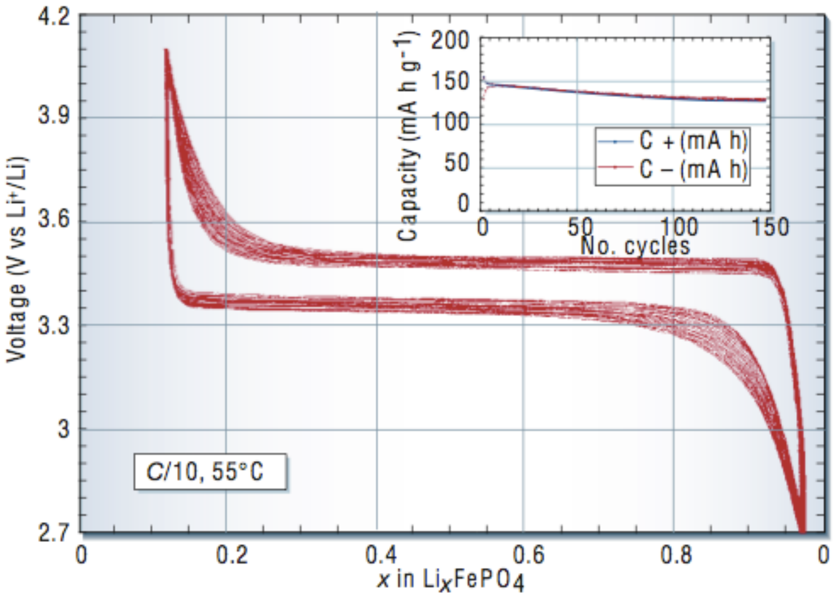
Multiscale Li-ion Battery Physics



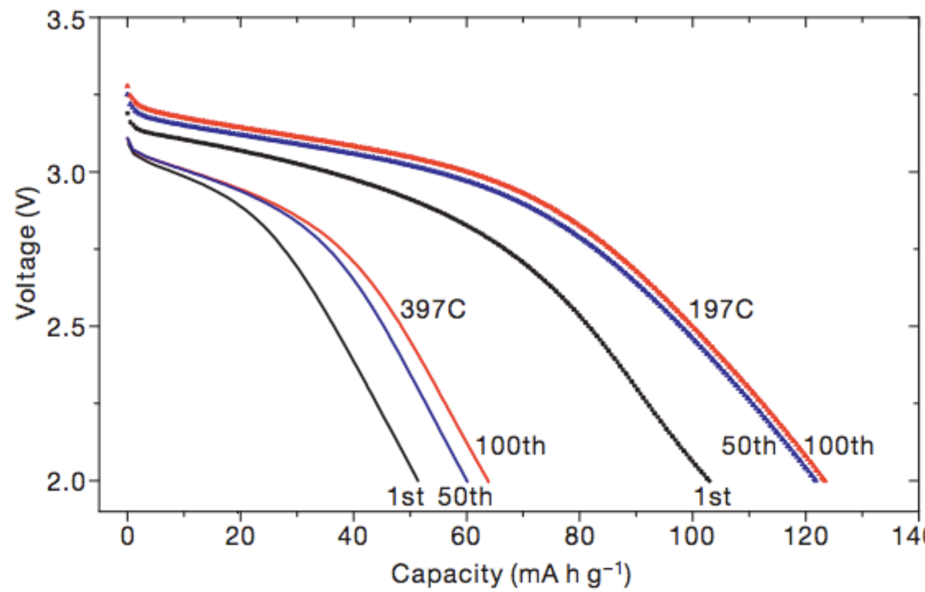
1. Porous electrode theory (J. Newman, Berkeley)
2. ??? (this work)
3. Quantum simulations (G. Ceder, MIT)

Li_xFePO_4

- Advantages: stable, non-toxic, inexpensive, high-rate capability
- “Ultrafast” discharge possible (10 sec!)
- *Phase separating* (voltage plateau)



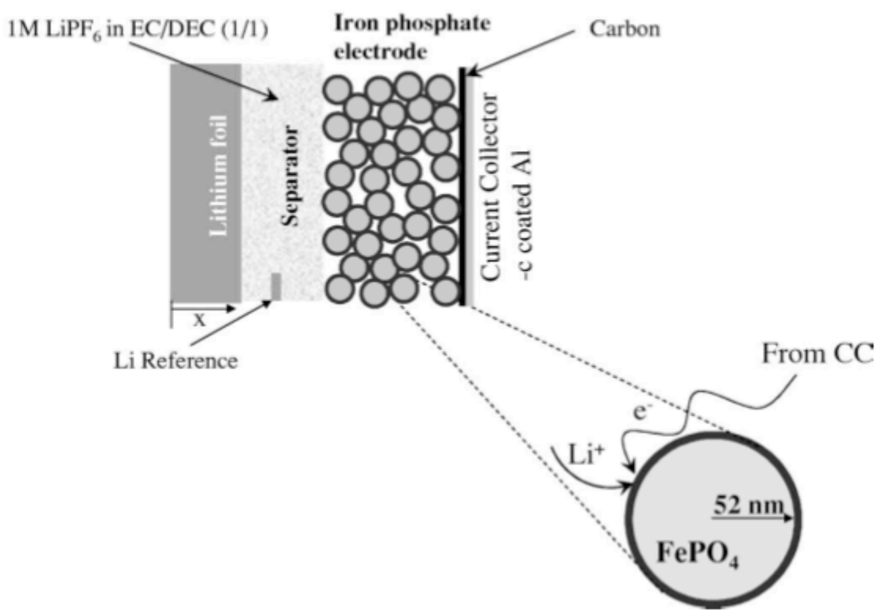
Tarascon & Anand, Nature 2001

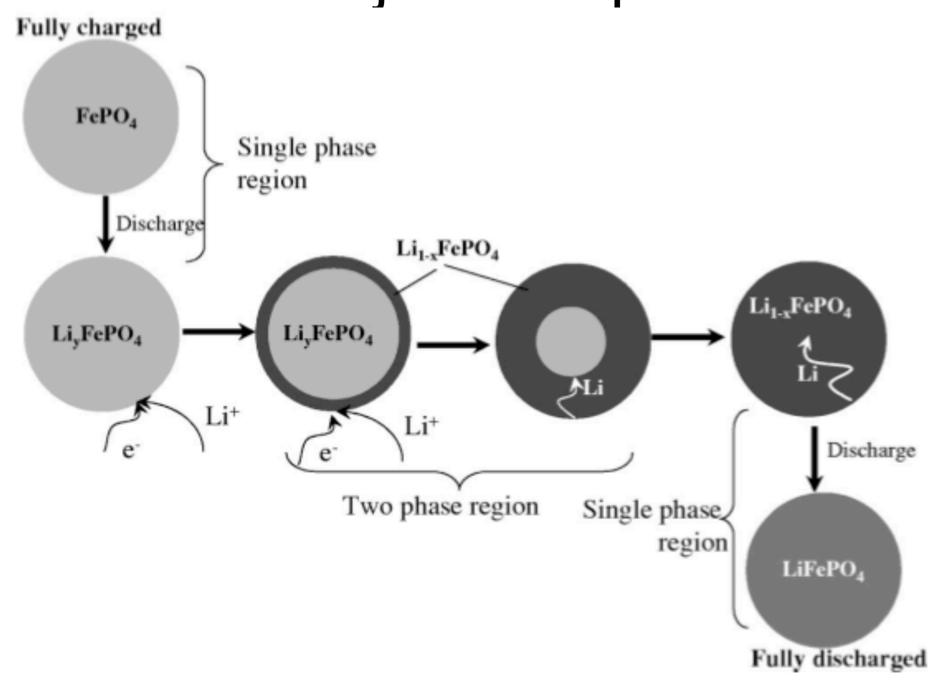


Kang & Ceder, Nature, 2009

Porous Electrode Theory

- Formal volume averaging, overlapping continua for electrolyte (ions) and electrode (electrons)
  - Tobais & Newman (1963), Newman et al 1970s
- Li-ion intercalation: Isotropic diffusion in solid spheres
  - Doyle, Fuller, Newman (1993),
- Li_xFePO_4: "shrinking core model" Srinivasan & Newman (2004)
- $V_{OCV}(x)$, $D(c)$, stable compositions = adjustable params



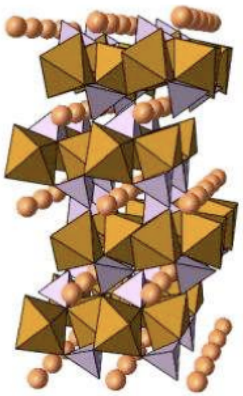


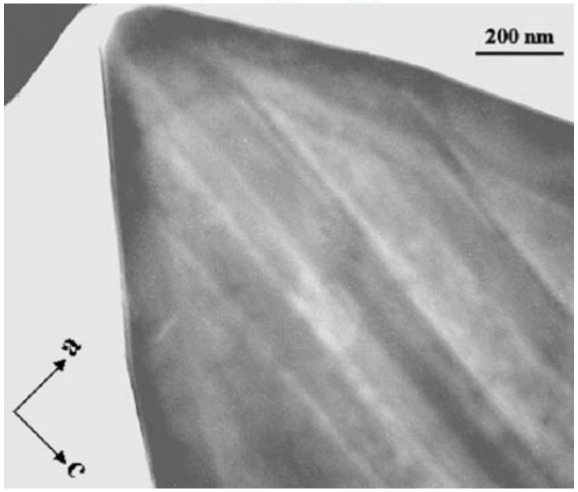
Surprises in Li_xFePO_4

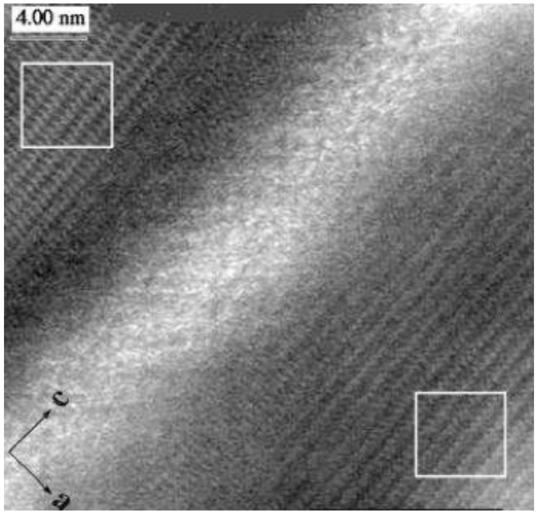
- Atomistic simulations: (Morgan, van der Ven, Ceder, 2004)
  - Fast Li transport in 1D channels
  - Slow 2D electron transport

- Experiments: (Chen et al 2006, Laffont et al 2006, chemical lithiation)
  - No shrinking core
  - Nano-scale phase boundaries, aligned with $FePO_4$ planes
  - Apparent motion along active facet, *perpendicular to Li flux*

Mathematical model???







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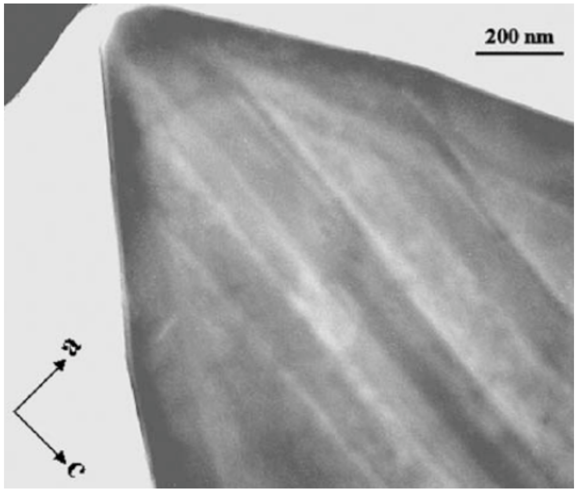
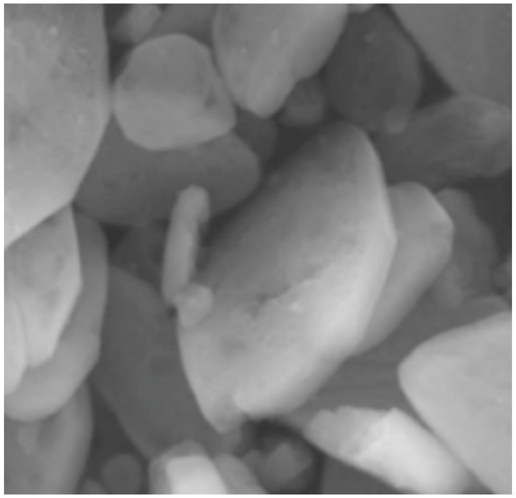
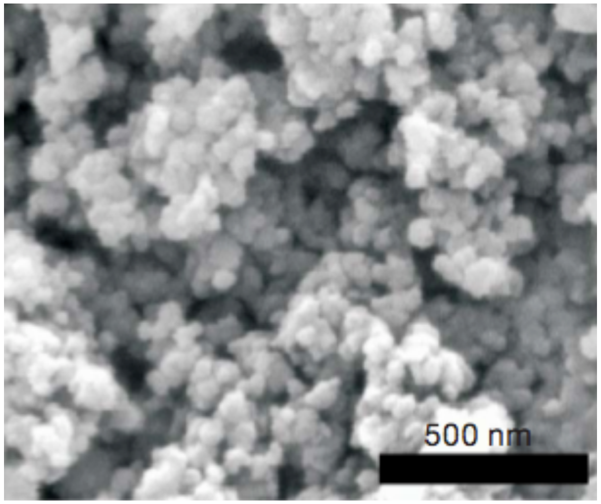


Chen, Song & Richardson, *Electrochem. Sol. State Lett.* (2006)

Kang & Ceder, *Nature Materials* (2009)

Modeling Strategy

Singh, Ceder, MZB, *Electrochimica Acta* (2008)
Burch & MZB, *Nano Letters* (2009)
MZB, *Electrochemical Energy Systems*, MIT course notes (2009-10)

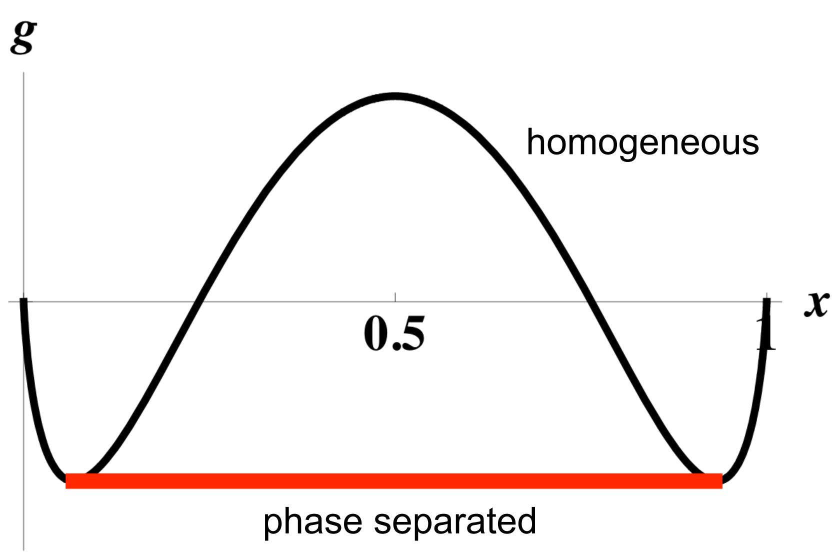
- Focus on *basic physics*: scalings, few params
- Self-consistently *predict* $V_{OCV}(Q,T)$, $D(c,T)$, stable compositions, phase transformations…
- Derive *nonlinear* equations ("beyond 10.50")
- Incorporate *randomness* - nucleation, porous microstructure,…
- Integrate transport and Faradaic reactions with *non-equilibrium thermodynamics*

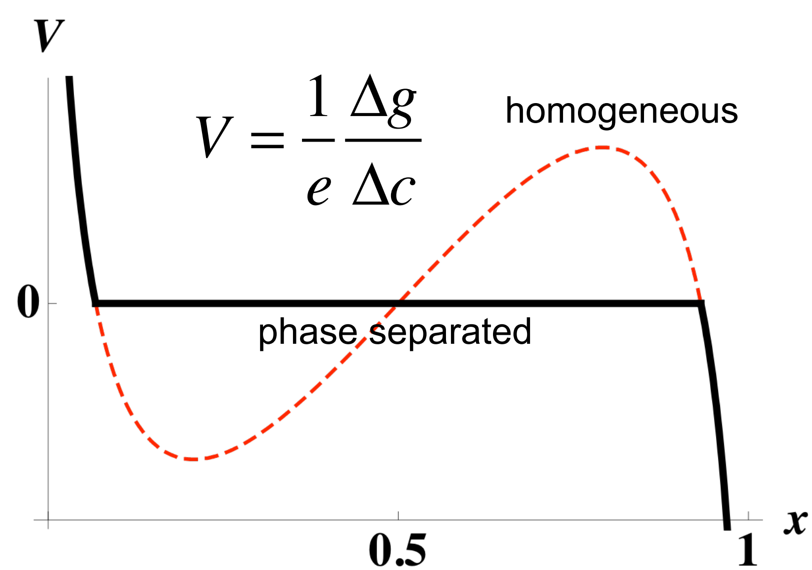
Equilibrium Thermodynamics

Homogeneous free energy density, e.g. regular solution model:

$$\bar{g}(c) = V^{\Theta} c + ac(1-c) + kT[c\log c + (1-c)\log(1-c)]$$

= standard potential + enthalpy density (particle-hole repulsion) + entropy density (ideal mixture of particles and holes)





common tangent $\quad$ $if \quad T < T_c = \frac{a}{k_B}$ $\quad$ voltage plateau

Non-equilibrium Thermodynamics

Singh, Ceder, MZB, *Electrochimica Acta* (2008)

Total free energy (solid phase)

$$G = \int \left(\bar{g}(c) + \frac{1}{2}\nabla c \cdot K \nabla c + \frac{1}{2}\sigma : \varepsilon + \ldots \right) dV + \oint n \cdot \gamma(c)\, da$$

Bulk (diffusional) chemical potential

$$\mu \equiv \frac{\delta G}{\delta c} = \bar{g}'(c) - \nabla \cdot K \nabla c + U : \sigma + \ldots$$

= homogeneous chem. potential + gradient penalty + lattice mismatch strain energy

Cahn-Hilliard Equation (1958)

$$\frac{\partial c}{\partial t} + \nabla \cdot F = 0, \qquad F = -Mc\nabla\mu$$

Variational boundary condition

$$n \cdot (K\nabla c + \gamma'(c)) = 0$$

Intercalation boundary condition (new)

$$n \cdot F = R(c, \mu, \mu_e)$$

Reactions in Concentrated Solutions

MZB, *Electrochemical Energy Systems*, MIT course notes (2009-10) + papers to follow…

Chemical potentials $\mu = k_B T \ln a = k_B T \ln(\gamma c) = k_B T \ln c + \mu^{ex}$

Reaction rate: state 1 ←(activated state)→ state 2

$$R = R_0 \left(c_1 e^{(\mu_a^{ex} - \mu_1^{ex})/kT} - c_2 e^{(\mu_a^{ex} - \mu_2^{ex})/kT} \right) = \frac{R_0}{\gamma_a}(a_1 - a_2)$$

Basic idea: the reaction complex diffuses over an activation barrier (>>kT) between two local minima (states 1,2) in a *landscape of excess chemical potential*

Note: we cannot simply "replace concentrations with activities"

Equilibrium Voltage

Faradaic reaction: reduced state ←→ oxidized state + n e$^-$

Chemical potentials

$$\mu_1 = \mu_R = k_B T \ln(\gamma_R c_R) + q_R \phi$$

$$\mu_2 = \mu_O + n\mu_{e^-} = k_B T \ln(\gamma_R c_R) + q_O \phi - ne\phi_e$$

Charge conservation

$$q_R = q_O - ne$$

Interfacial voltage

$$\Delta\phi = \phi_e - \phi \qquad \Delta\phi = \Delta\phi_{eq} \Leftrightarrow \mu_1 = \mu_2$$

Nernst equation

$$\Delta\phi_{eq} = \frac{k_B T}{ne} \ln \frac{a_O}{a_R}$$

Theory of Electrochemical Reactions in Concentrated Solutions

"Butler-Volmer hypothesis":
electrostatic energy of transition state
= weighted average of states 1 and 2

$$\mu_a = k_B T \ln \gamma_a + \alpha q_R \phi + (1-\alpha)(q_O \phi - ne\phi_e)$$

Overpotential

$$\eta = \Delta\phi - \Delta\phi_{eq} = \mu_2 - \mu_1 = \Delta\mu$$

Butler-Volmer equation

$$J = neR = J_0 \left(e^{(1-\alpha)ne\eta/kT} - e^{-\alpha ne\eta/kT} \right)$$

Exchange current density

$$J_0 = neR_0 c_R^{\alpha} c_O^{1-\alpha} \left(\frac{\gamma_R^{\alpha} \gamma_O^{1-\alpha}}{\gamma_a} \right)$$

Note: we recover classical Butler-Volmer kinetics only in a *dilute solution*, where all activity coefficients = 1

Models for Ion Intercalation Kinetics

Example: Lithium intercalation $Li_{(s)} \leftarrow\rightarrow Li^{+}_{(l)} + e^{-}$

$$\mu_1 = \mu_{Li(s)} = k_B T \ln\left(\frac{c}{1-c}\right) + a(1-2c) - \nabla \cdot K\nabla c$$

Cahn-Hilliard
in the solid phase

$$\mu_2 = \mu_{Li^+(l)} + \mu_{e^-} = k_B T \ln c_+ + e(\phi - \phi_e) = \mu_{ext}$$

$$\gamma_a = \frac{1}{1-c}$$

only excluded volume
in transition state

Symmetric Butler-Volmer

$$J = 2J_o \sinh\left(\frac{e(\mu_2 - \mu_1)}{2k_B T}\right)$$

$$J_0 = eR_0\sqrt{c_+ c(1-c)}\exp\left(\frac{-2ac - \nabla \cdot K\nabla c}{2k_B T}\right)$$

Reaction rate depends strongly on concentration… and on *concentration gradients*!

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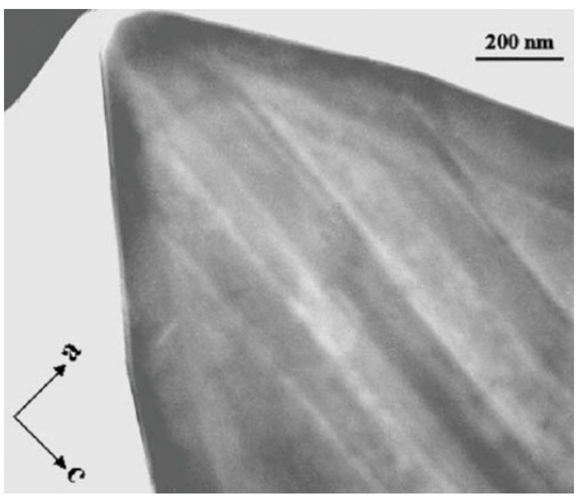
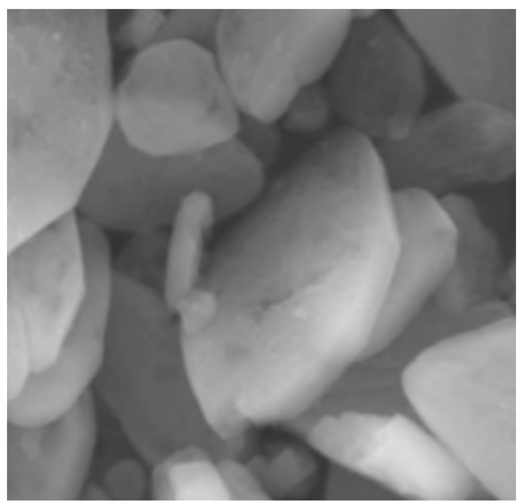
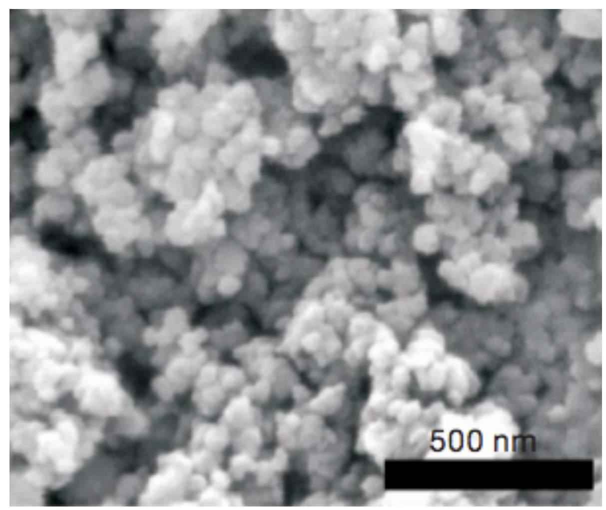


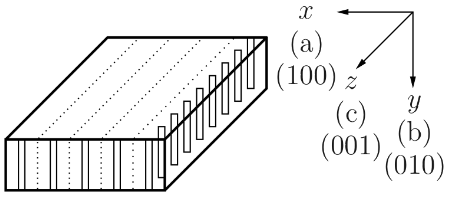


Chen, Song & Richardson, *Electrochem. Sol. State Lett.* (2006)



Kang & Ceder, *Nature Materials* (2009)

Reaction-limited Intercalation in Anisotropic Nanocrystals



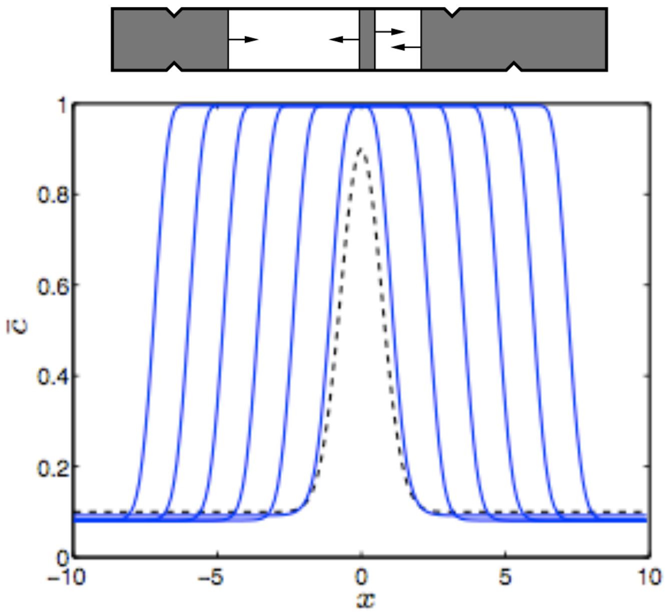
- Assume for Li_xFePO_4
  - no phase separation, fast diffusion in y direction (Da_x<<1)
  - strong phase separation, slow diffusion ($Da_{x,z}$<<1)
- 2D nonlinear “forced Allen-Cahn” equation

$$\frac{\partial c}{\partial t} = R(c, \nabla \cdot K \nabla c) \propto \sinh\left(\mu_{ext} - \mu\right)$$

- Predicts travelling waves, instabilities…
- (This new model may also describe electrophoretic deposition, nanoparticle adsorption in double layers…)

Prediction: Intercalation Waves

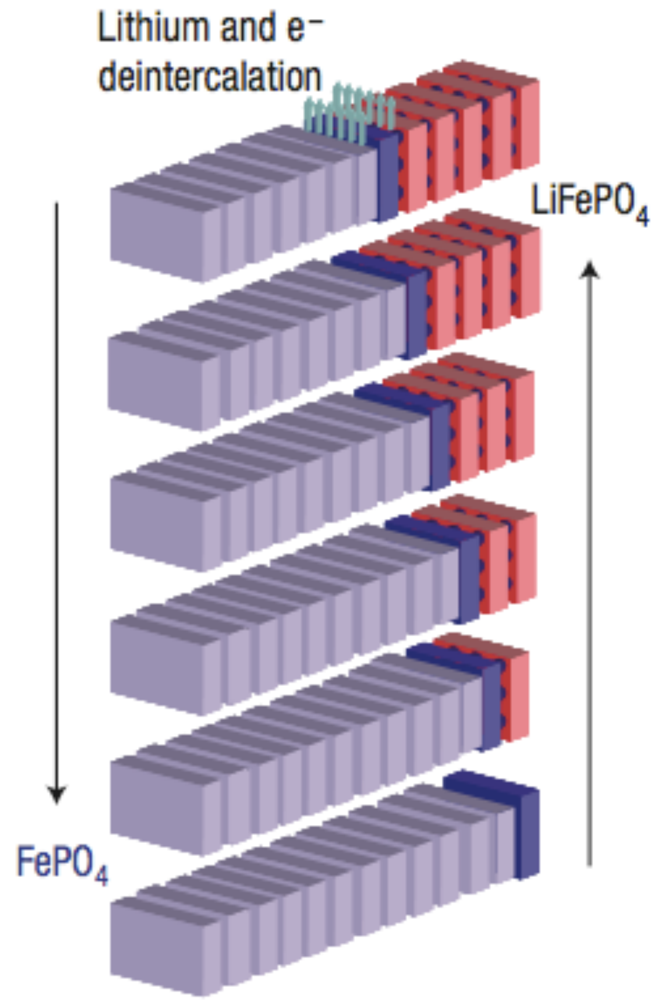
Singh, Ceder, MZB, *Electrochimica Acta* (2008)



insertion wave

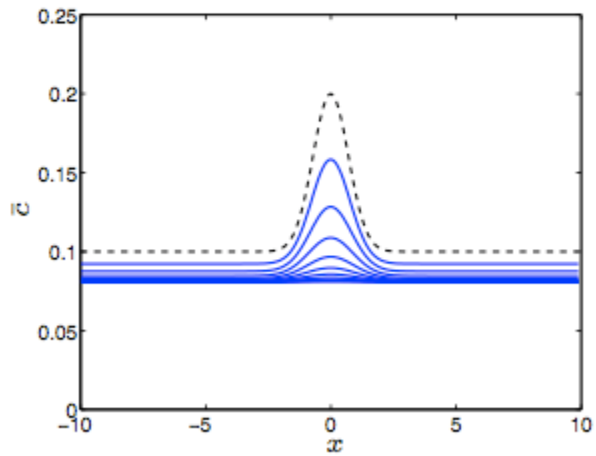
$$\frac{\partial c}{\partial t} = R(c, \nabla^2 c; \mu_{ext})$$ Nonlinear wave equation

- layer-by-layer insertion/extraction
- reaction limited (D irrelevant!)
- nucleation required

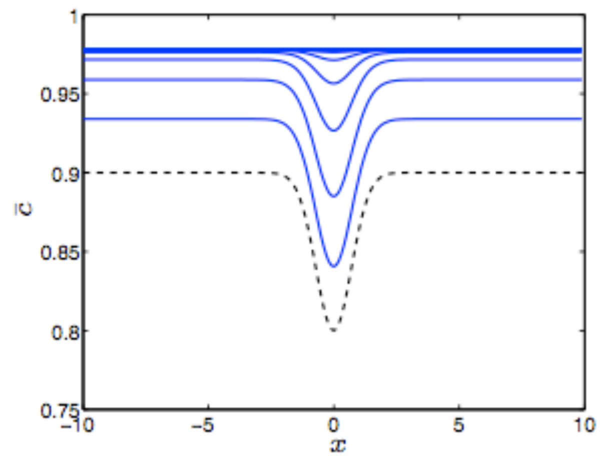


Delmas et al, *Nature Materials* (2008)
"domino cascade model" (no math)

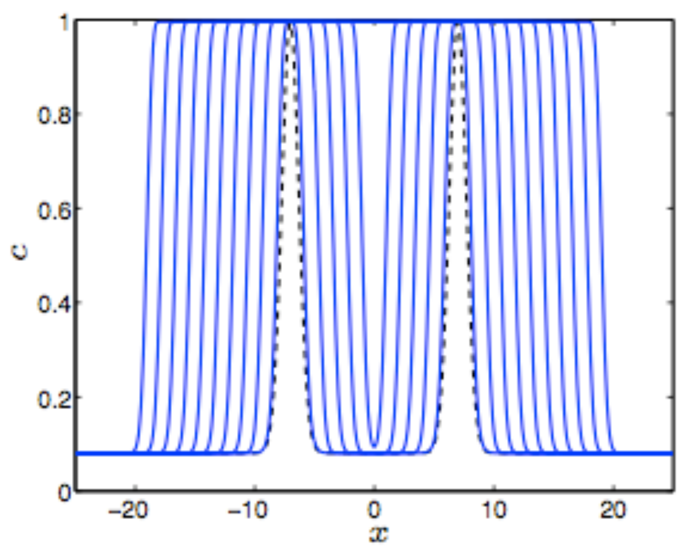
Wave nucleation and annihilation

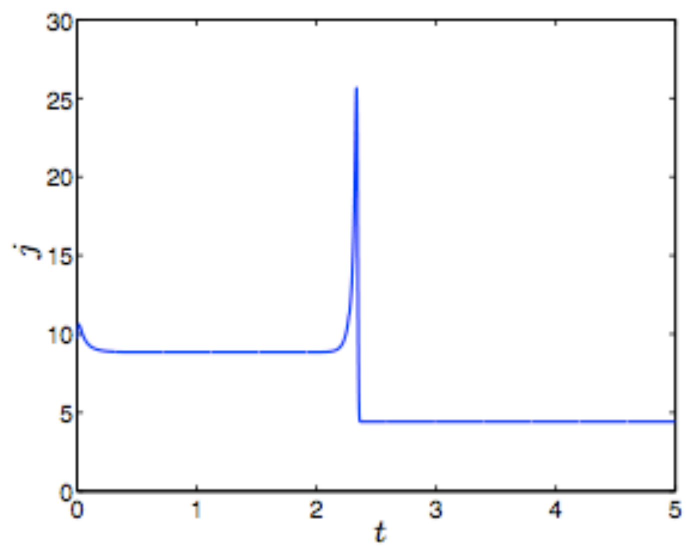


failed insertion



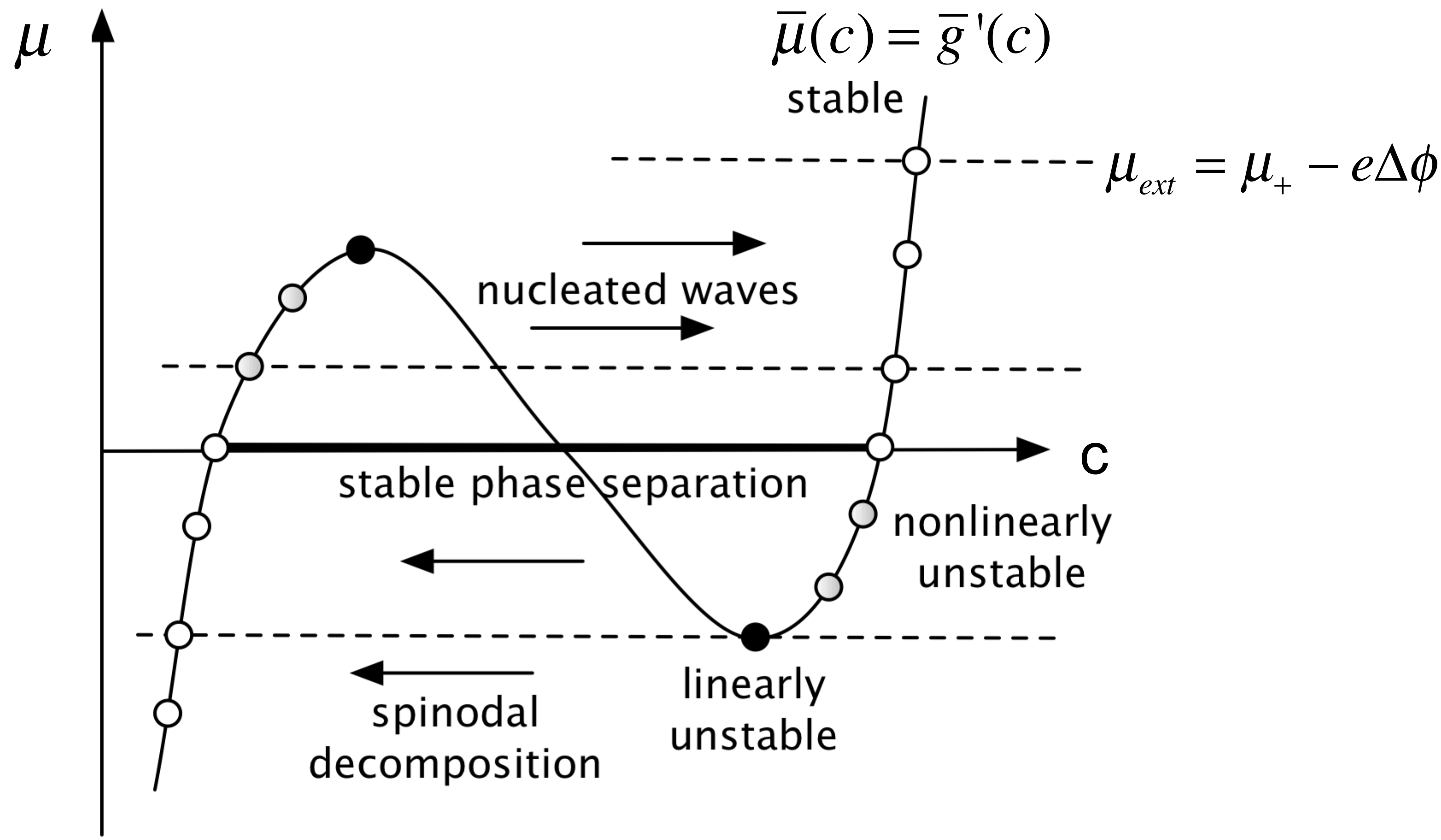
failed extraction



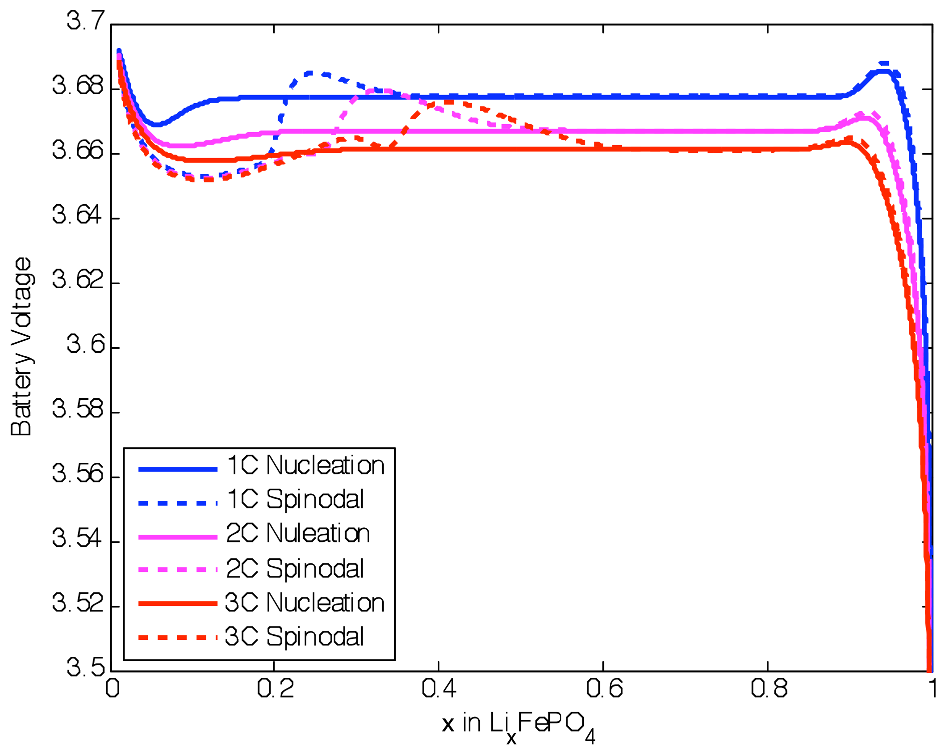


Waves collide at constant voltage …and produce a current spike + step

Theory of intercalation phase transformations at constant voltage



Prediction: Overshoot of the voltage plateau at constant current



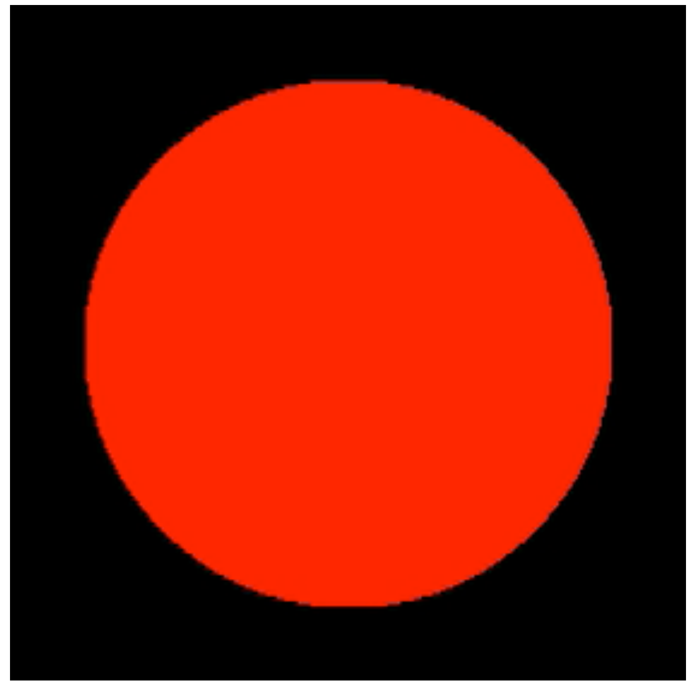
by Peng Bai

- Defects or facet edges can act as nucleation sites for waves
- In a perfect crystal, phase transformation is triggered by linear instability (like spinodal decomposition, but in an open system)

Simulations of 2D reaction-limited phase transformations at constant current

by Dan Cogswell

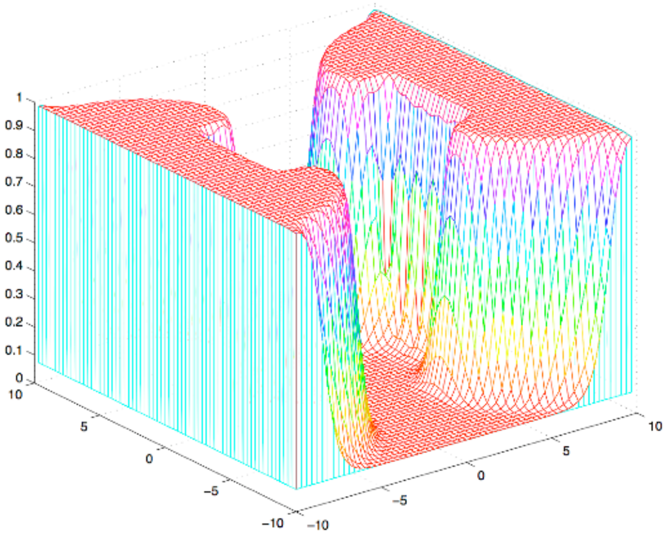
Linear instability
in a perfect crystal

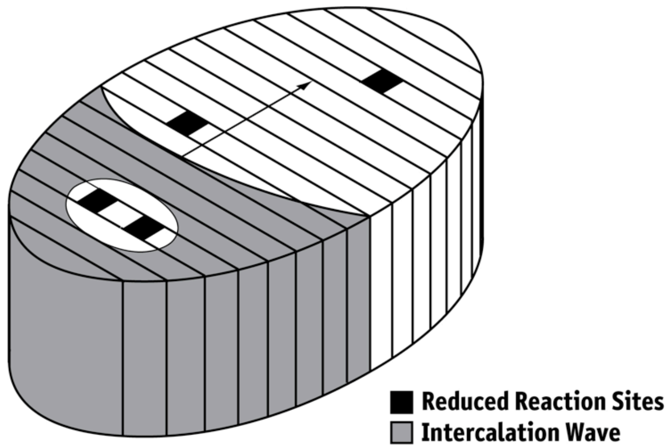


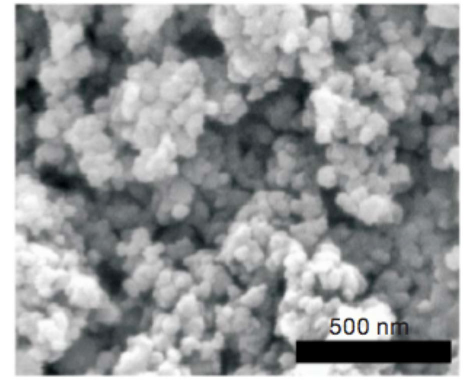
Stochastic nucleation
at the facet edge

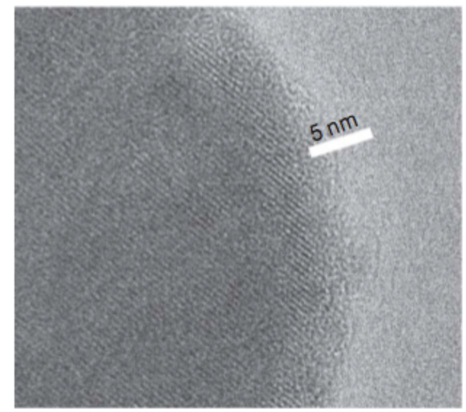
Wave-defect interactions

Burch, Singh, Ceder, Bazant, Solid State Phenomena (2008)





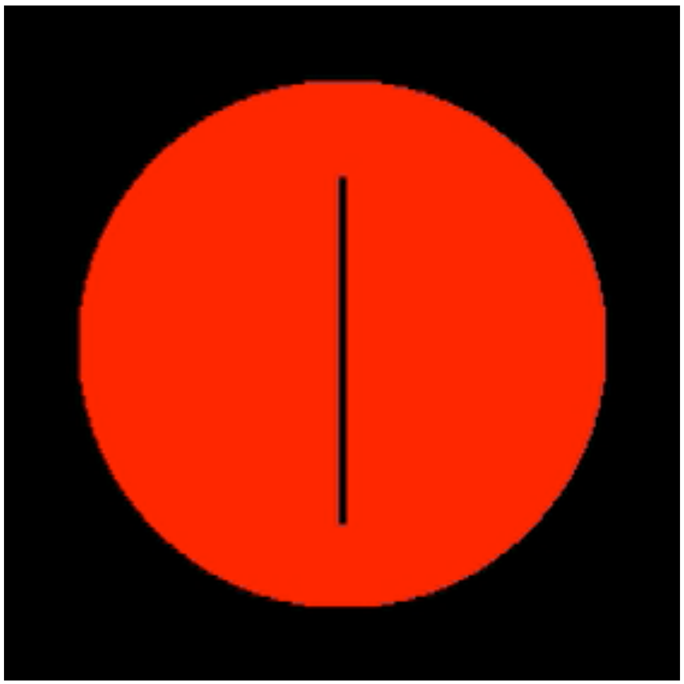


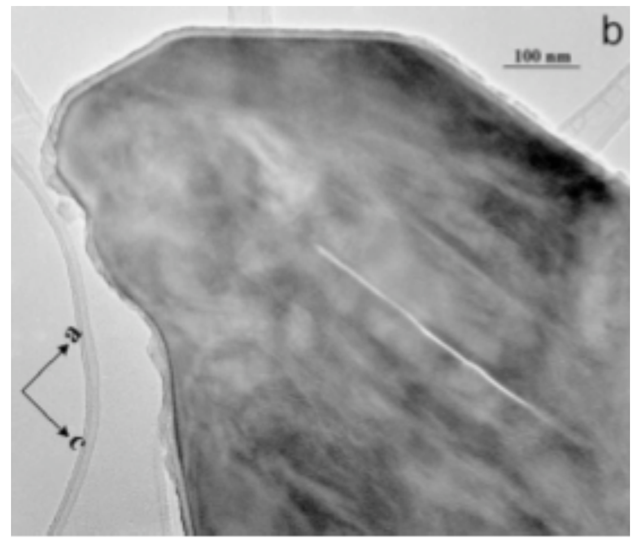


- “kinetic defect” = reduced reaction rate
- inter-phasial tension & elasticity hinder wave motion
- new mechanism for capacity fade & power loss
- may explain ultrafast discharging due to 5nm phosphate glass flim on LiFePO4 nanoparticles (Kang & Ceder 2009)

Intercalation at constant current in the presence of a crack

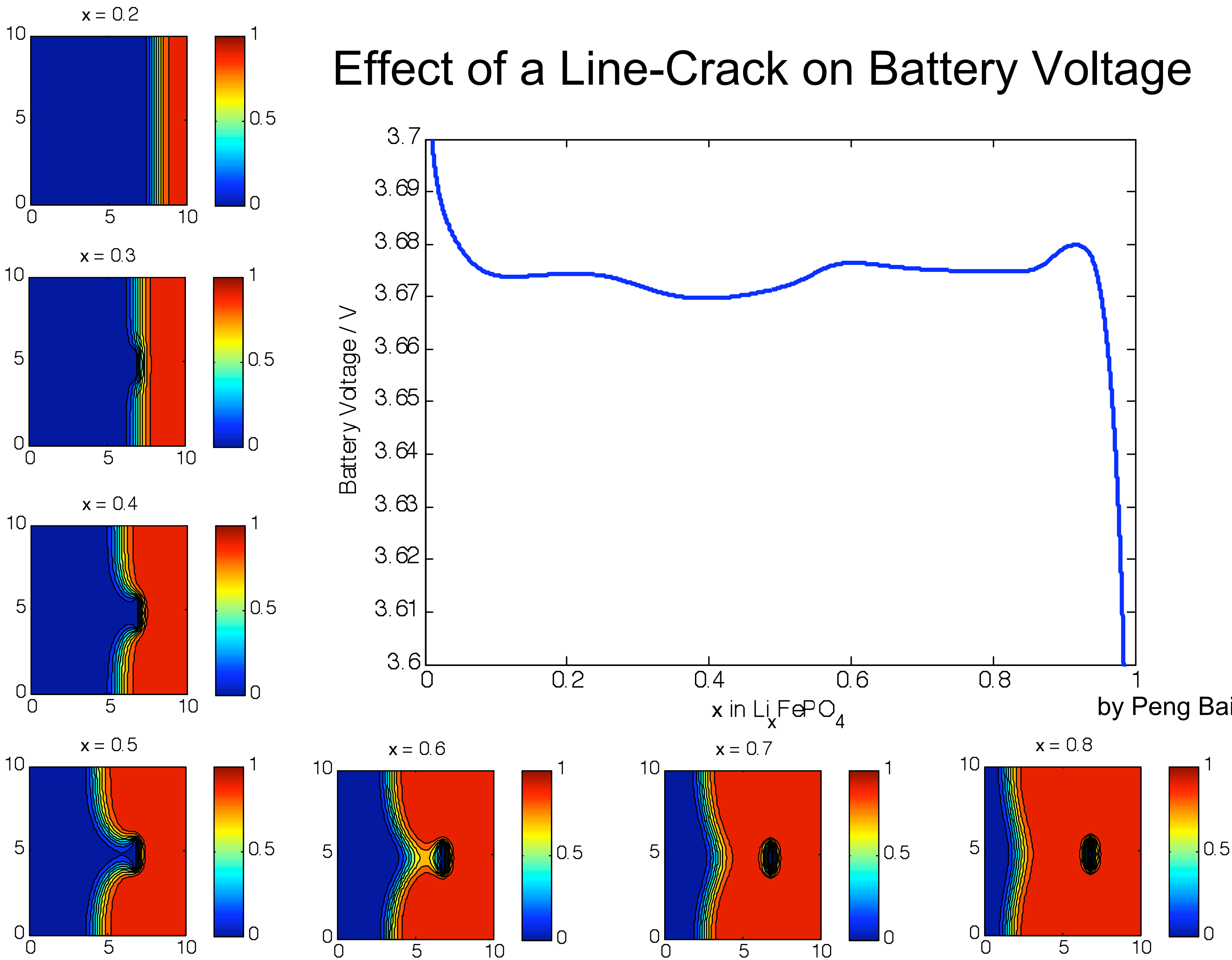
by Dan Cogswell





Chen, Song & Richardson,
Electrochem. Sol. State Lett. (2006)

Effect of a Line-Crack on Battery Voltage

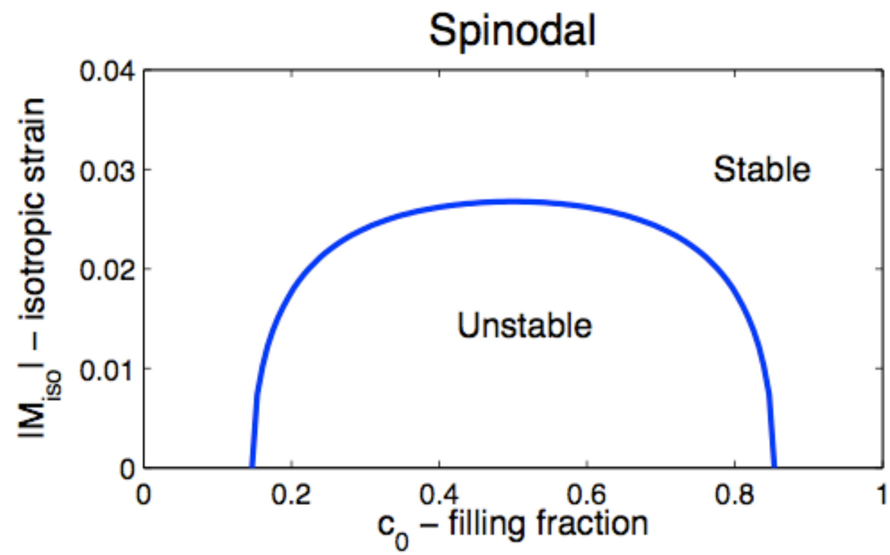


by Peng Bai

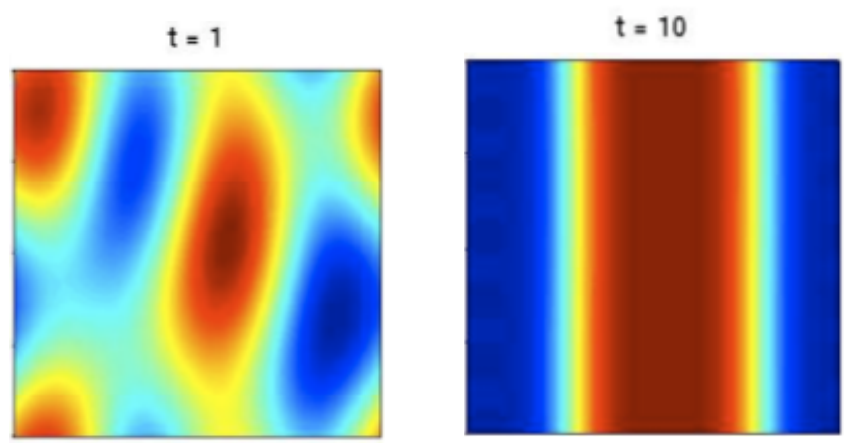
Elastic strain effects

by Liam Stanton

- Elastic energy from lattice mismatch strain suppresses phase separation



- Phase boundary aligns with most rigid planes (softest crystal axis, maximum strain)



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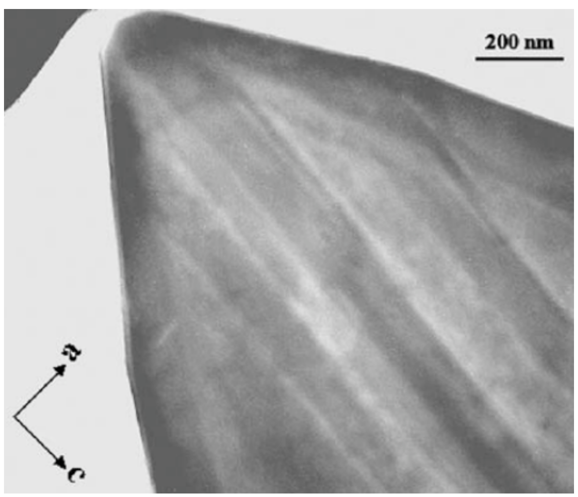
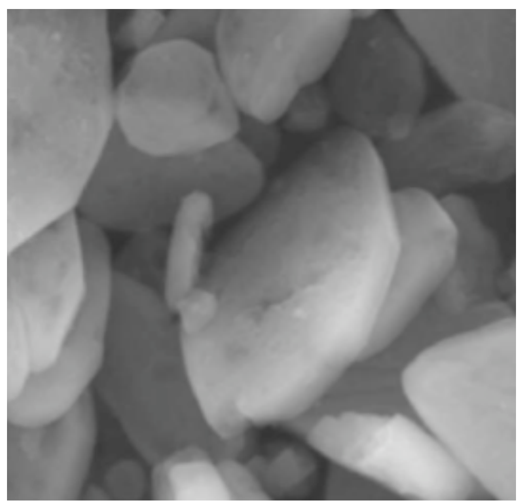
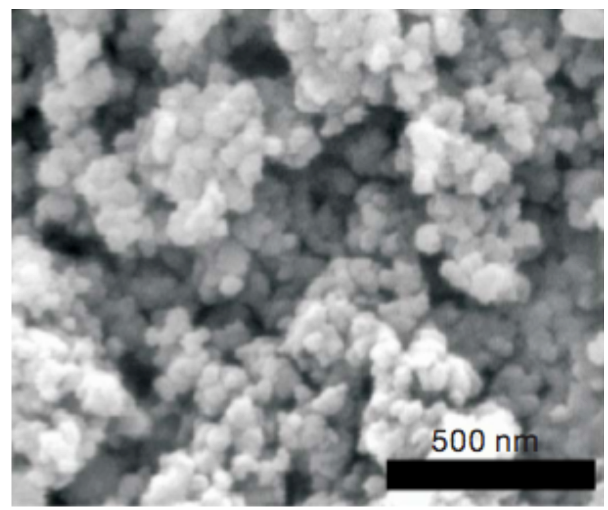




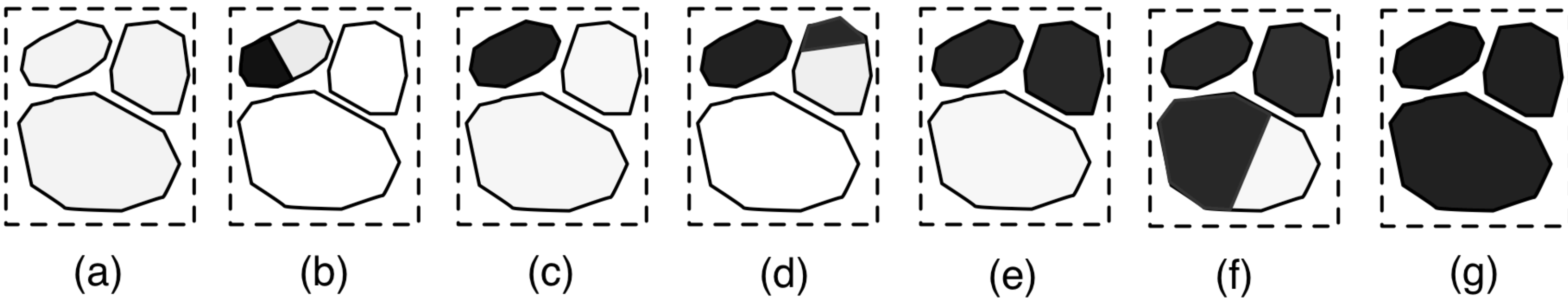
Chen, Song & Richardson, *Electrochem. Sol. State Lett.* (2006)

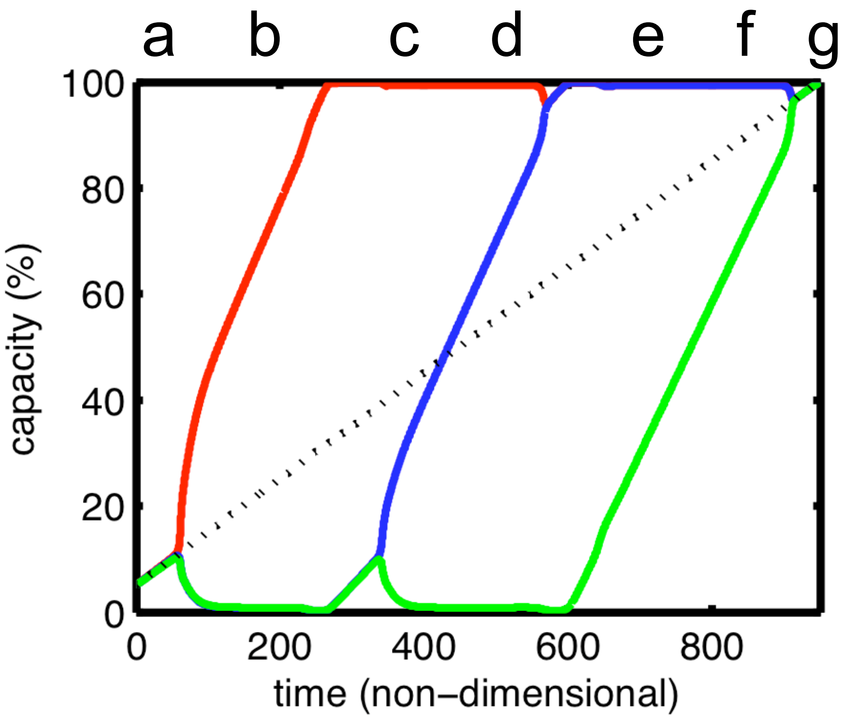


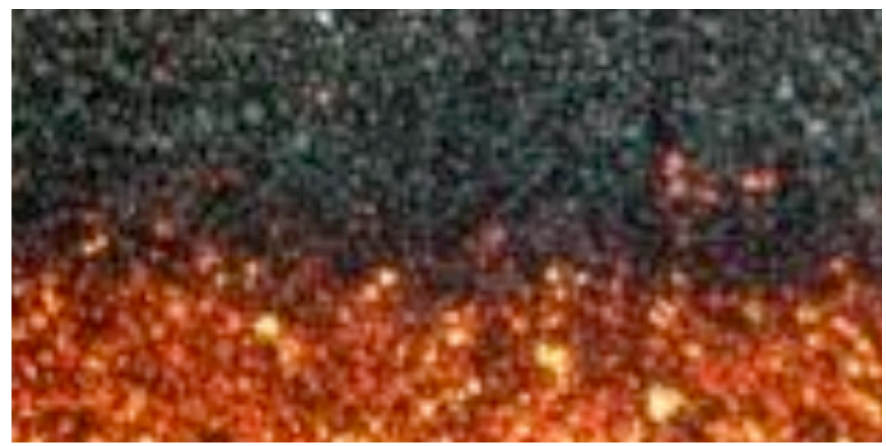
Kang & Ceder, *Nature Materials* (2009)

“Mosaic Instability”

Burch, Ceder, Bazant, in preparation



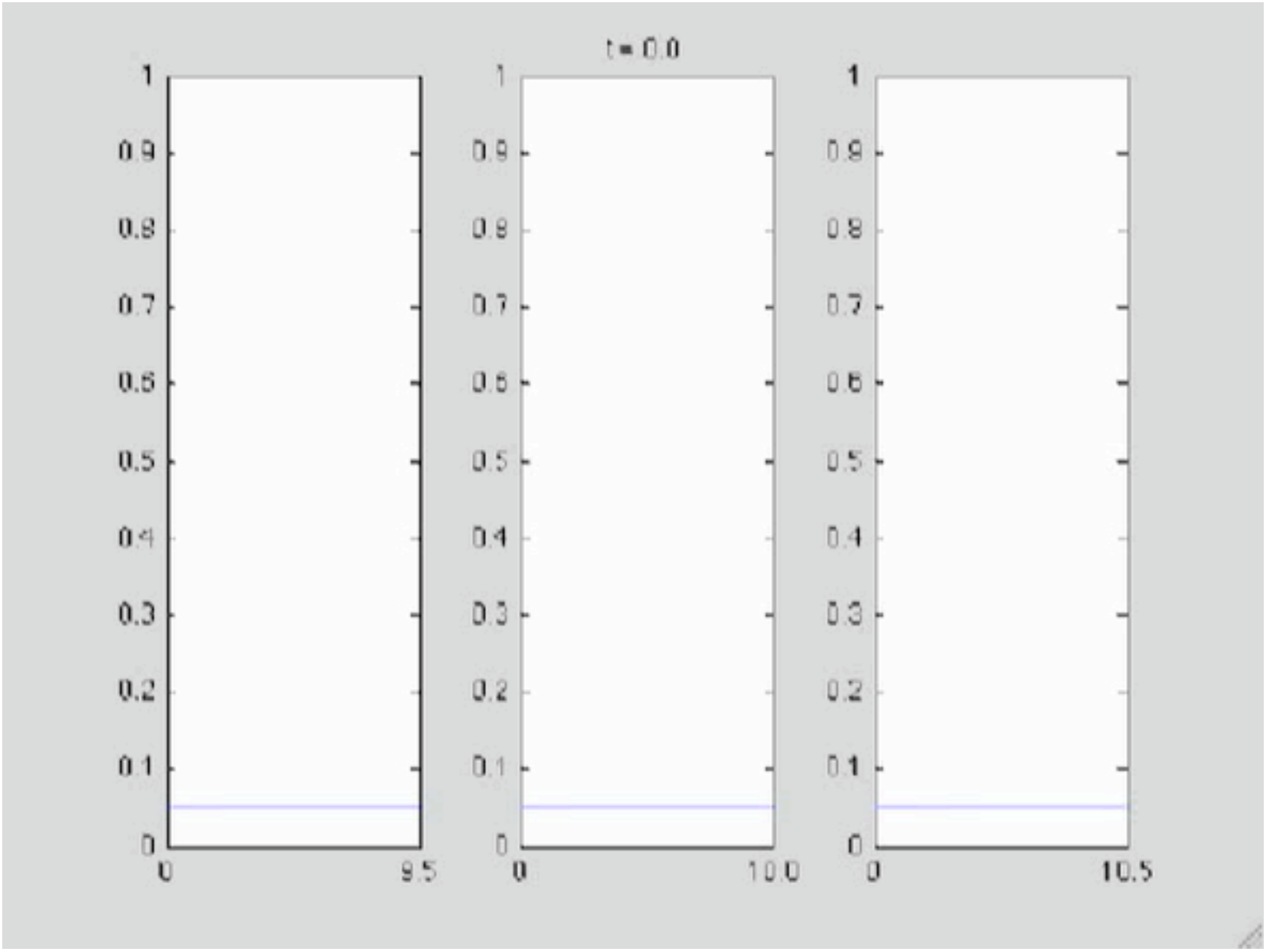




Experimental observation in graphite (S. Harris, GM)

Chem. Phys. Lett. (2010)

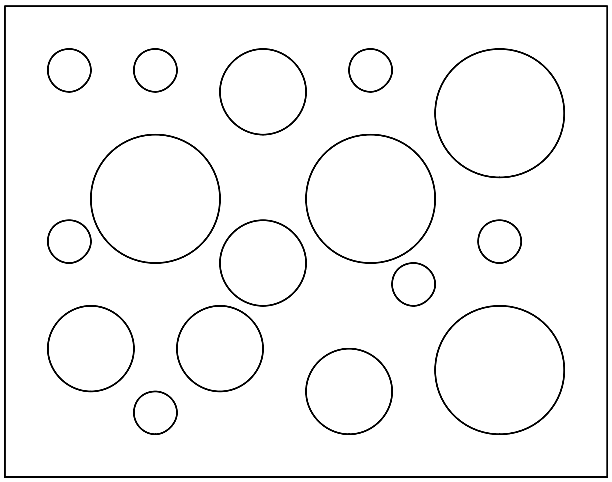
Mosaic Instability



Concentration profiles of intercalated Li in three particles at constant total current (D. Burch)

Effect of particle size distribution

analysis by Matthew Pinson



Assume each particle intercalates at constant voltage (due to phase separation) until it is full.

At constant total current, as the number of active particles decreases, the cell voltage decreases – analogous to the fiber bundle model for mechanical failure.

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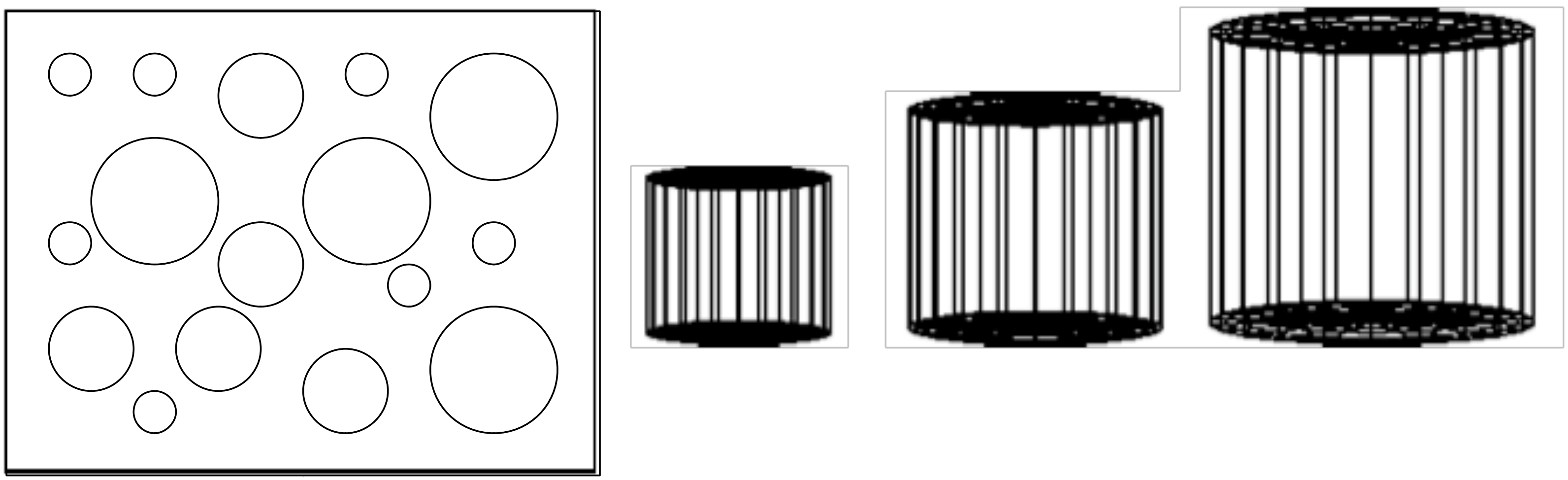

$\Phi_A(r)$

$\boxed{\eta = l/(\sigma_{lm}\Phi_A)}$

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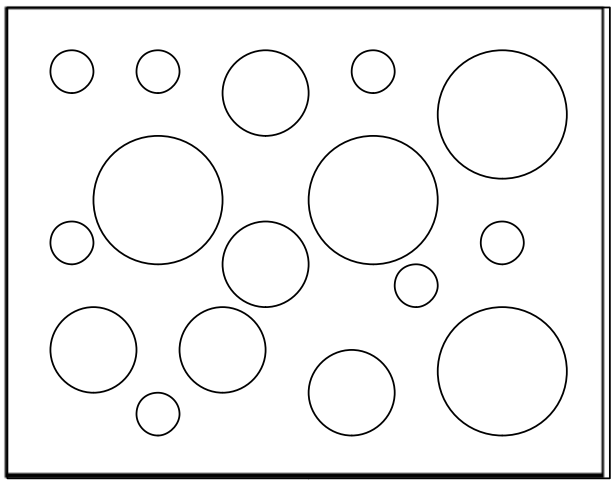

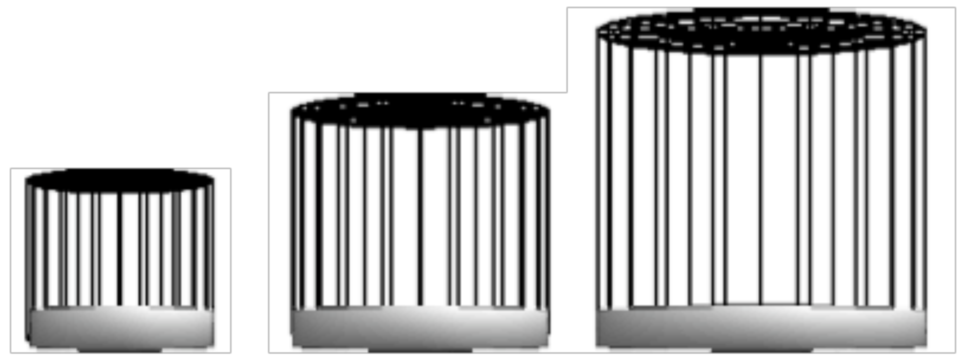

$\Phi_A(r)$

$\boxed{\eta = l/(\sigma_{ln}\Phi_A)}$

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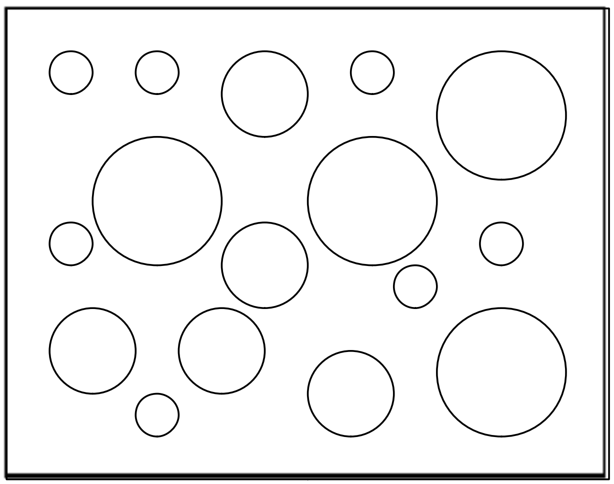

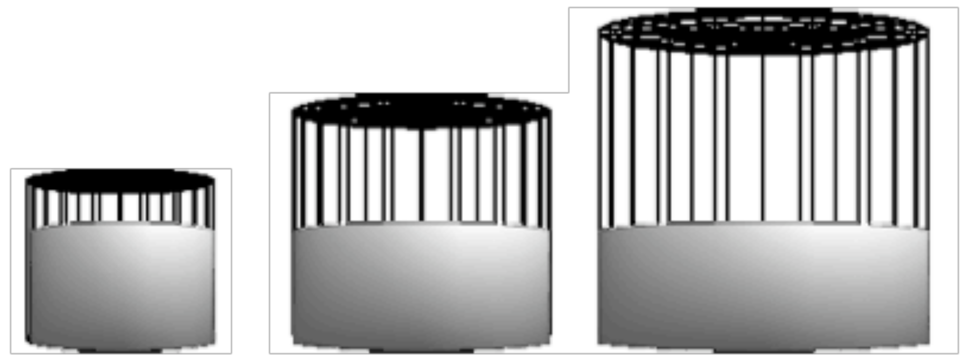

$\Phi_A(r)$ $\boxed{\eta = I/(\sigma_{lin}\Phi_A)}$

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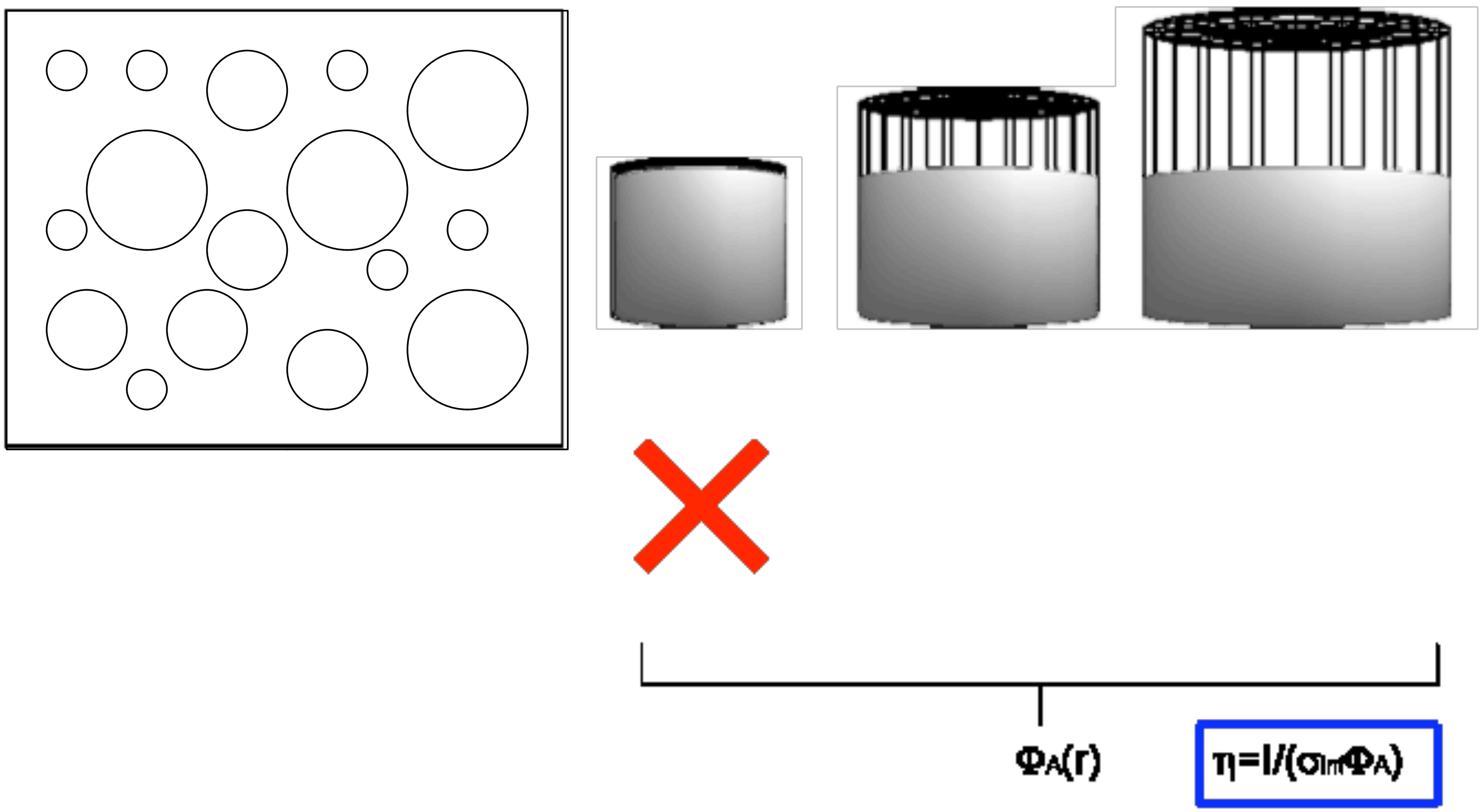

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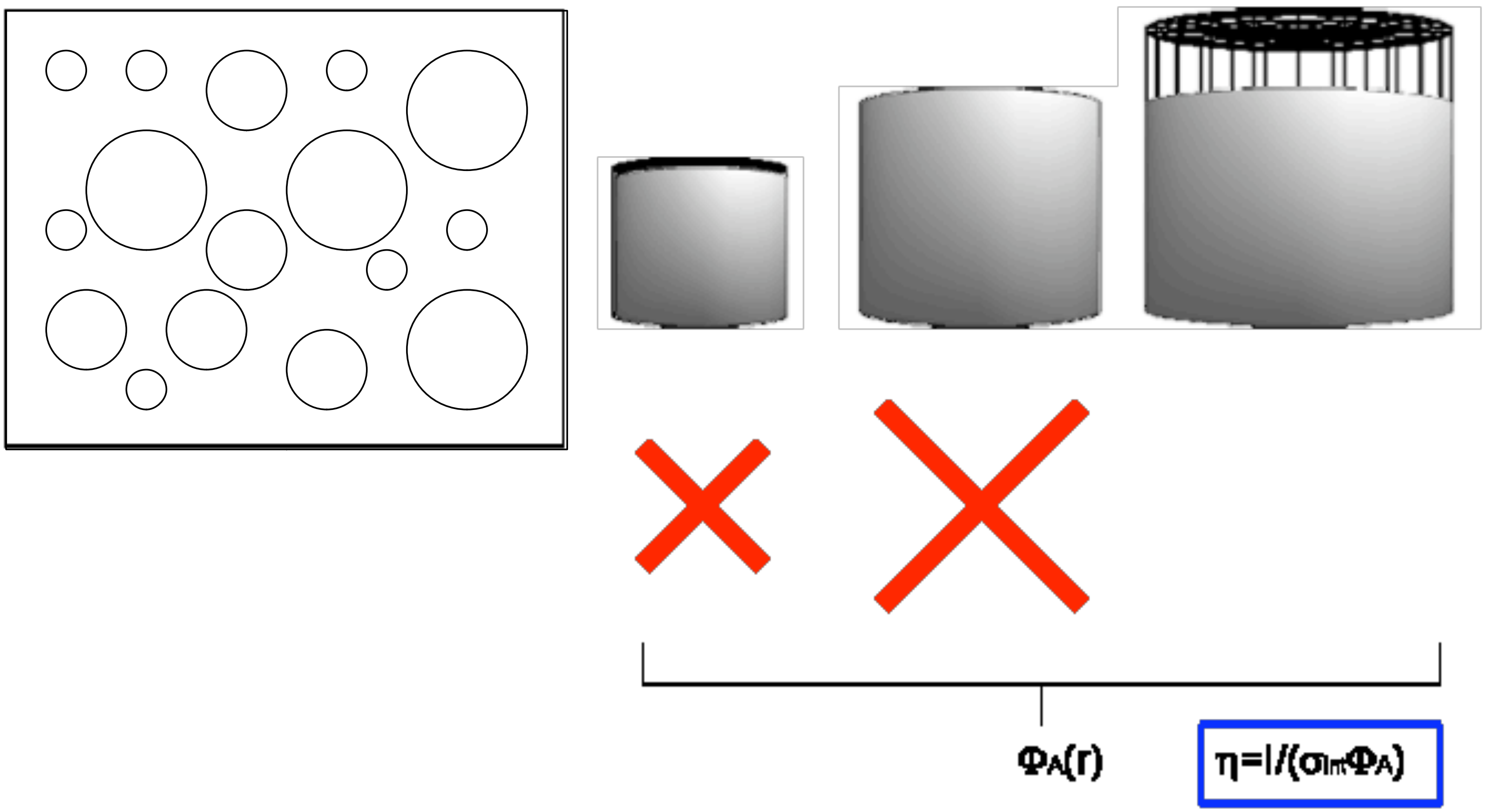

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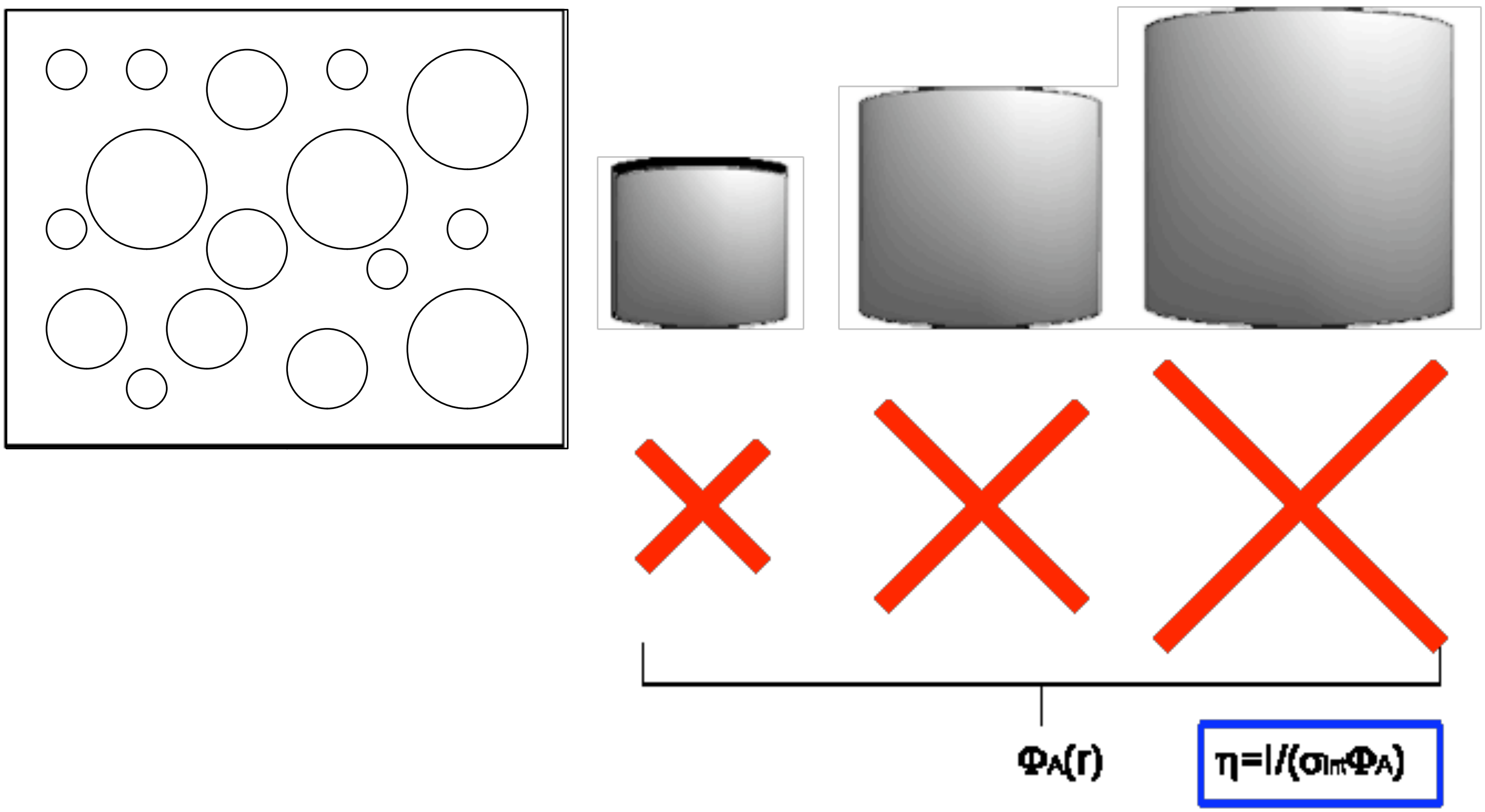
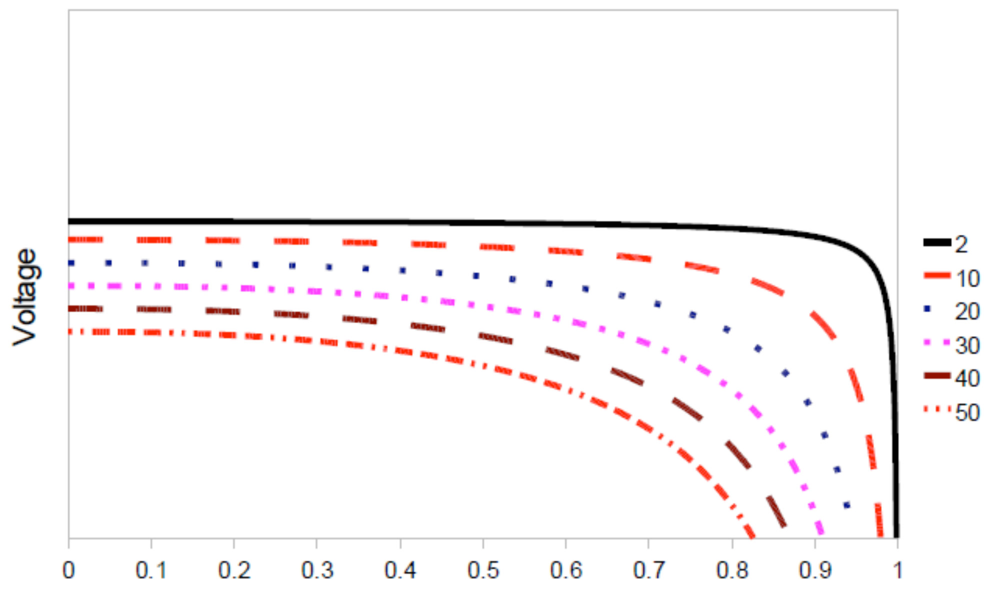
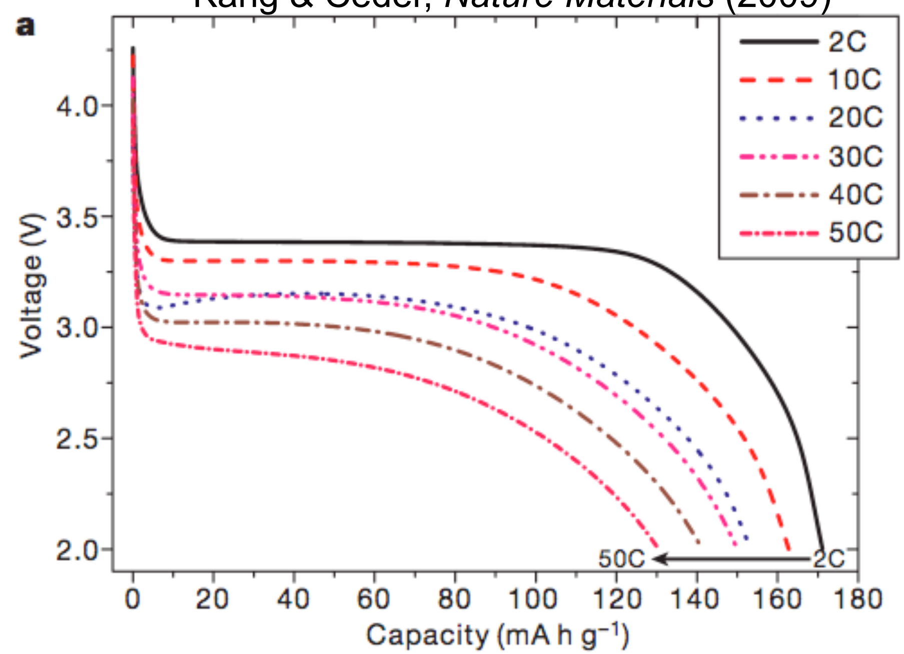


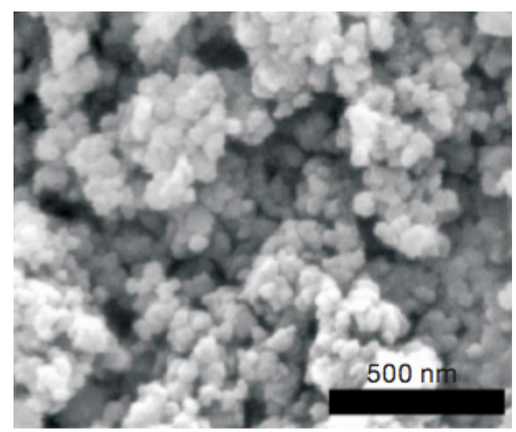
Comparison with experiment



Ultrafast LiFePO4

Kang & Ceder, *Nature Materials* (2009)





Theory with only *one adjustable parameter* (interfacial resistance), and a broad size distribution

Summary

- Nanoscale modeling framework for Li-ion batteries based on non-equilibrium thermodynamics
- Reaction-limited insertion waves
- Mosaic instability
- “Fiber-bundle effect”
- Other work in the group:
  - Modified porous electrode theory, fit to experiments
  - Double layers (Frumkin correction, capacitive charging)
  - Stochastic effects (capacity fade, lifetime)

http://bazantgroup.mit.edu/BMG