Stanford Energy Seminar

Stanford University, April 18, 2016

Physics of Next Generation Batteries

Martin Z. Bazant

Chemical Engineering & Mathematics, MIT

Materials Science and Engineering & SUNCAT Center, Stanford (2015-16)

Mesoscale Battery Physics

Example of “The Middle Way”
R. B. Laughlin et al, PNAS (1999)

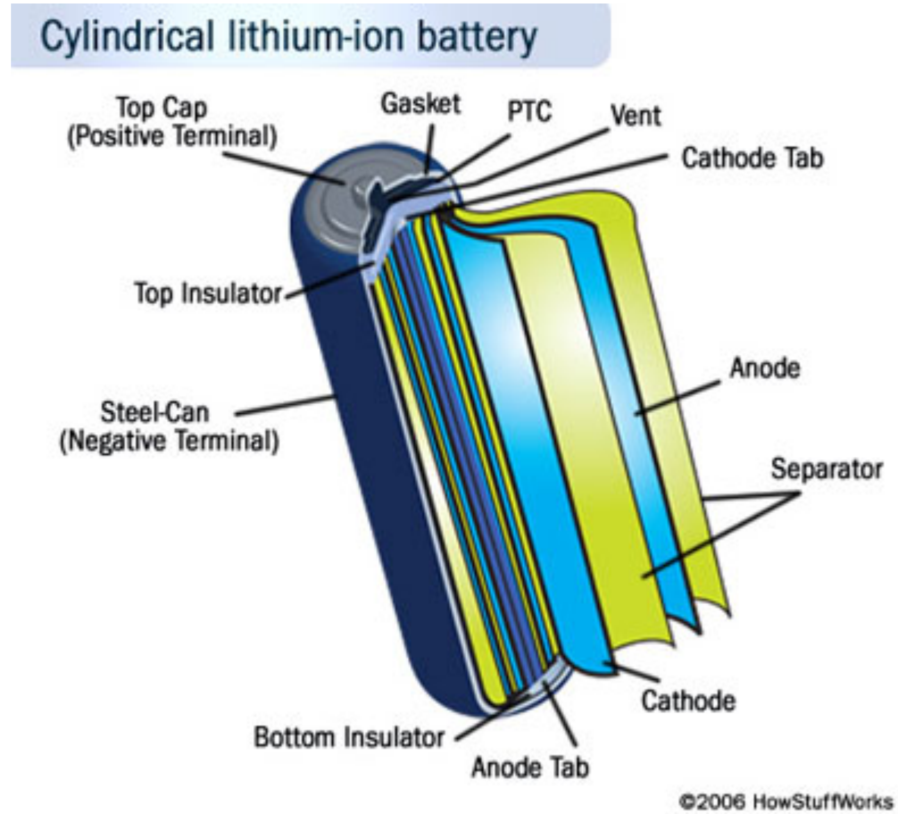
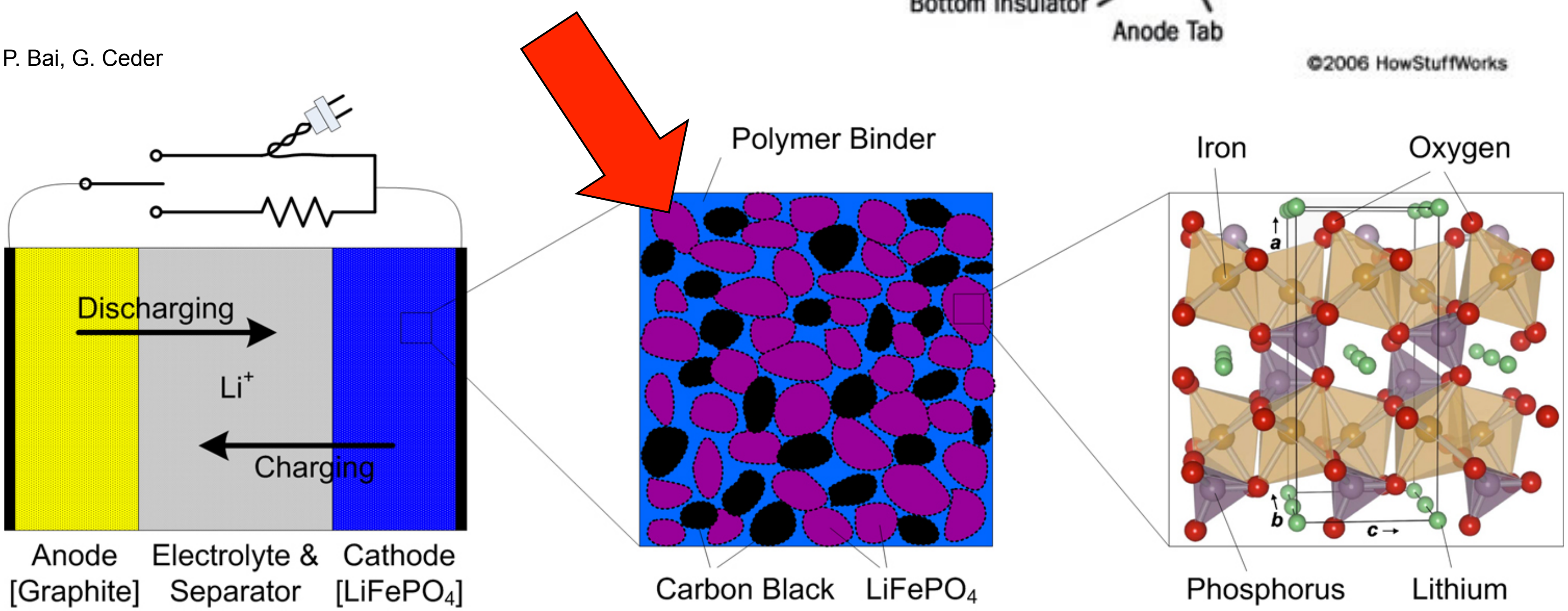
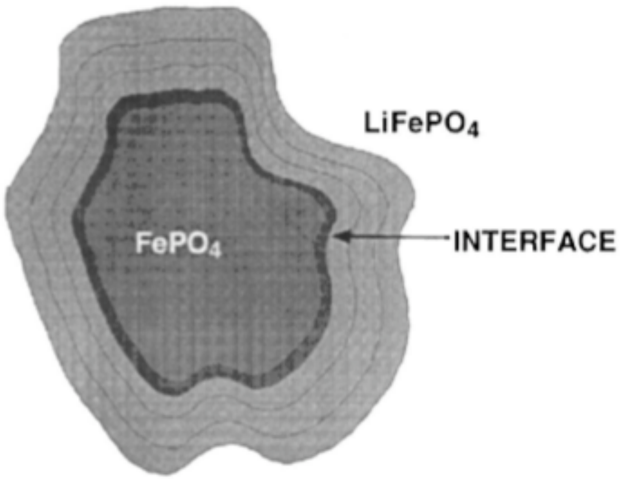


Image: P. Bai, G. Ceder

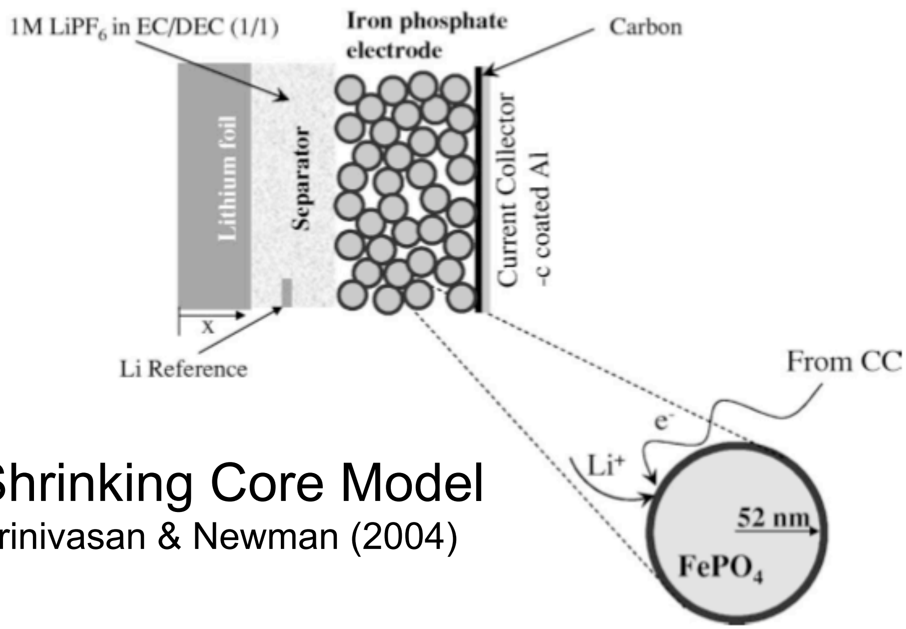


1. Phase Separation in Li-ion Batteries

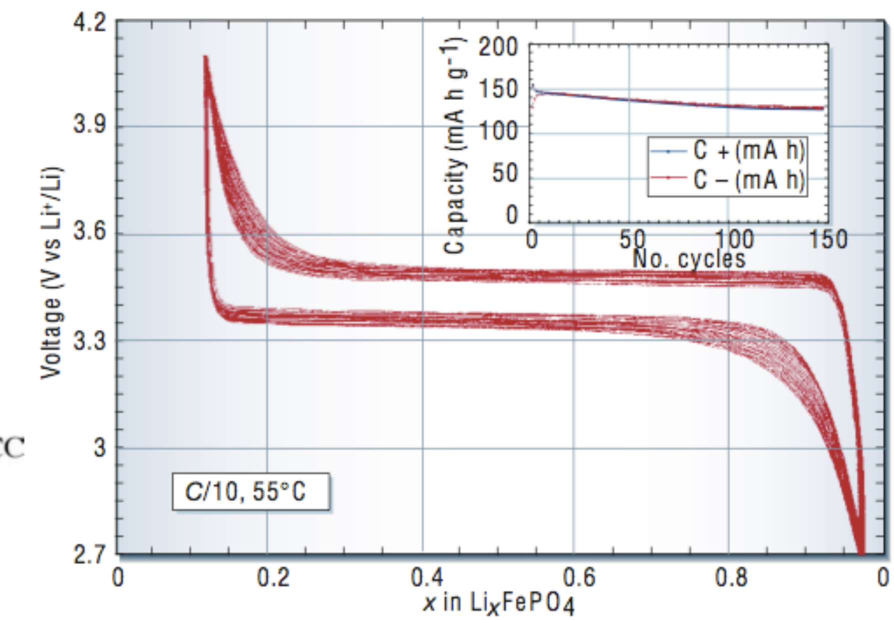
Lithium Iron Phosphate



"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)

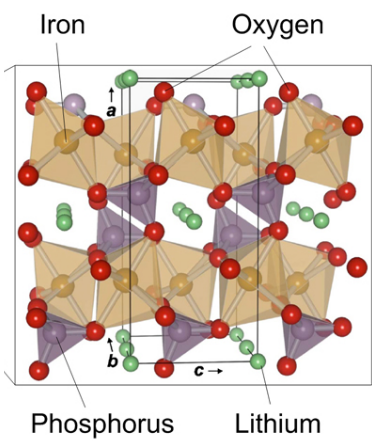


Tarascon et al (2001)

An Incredible Reversal of Fortune

- 1997: “Low power” Li_xFePO_4
- 2009: “Ultrafast” 10 sec. discharge

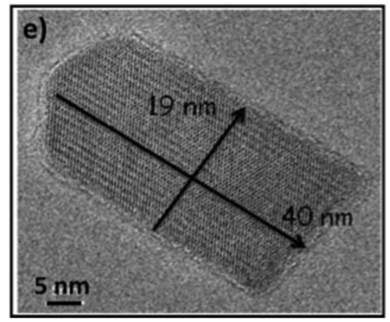
Kang & Ceder, Nature (2009)



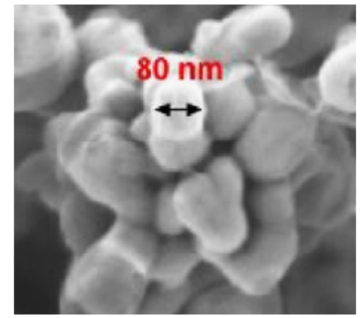
Ideal crystal:
Fast 1D diffusion

Morgan, van der Ven, Ceder (2004)

Why is nano so different?

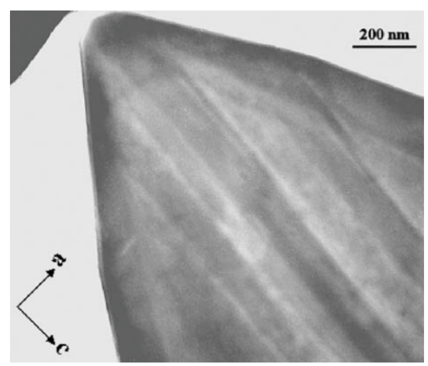


Badi et al, JMC (2011)

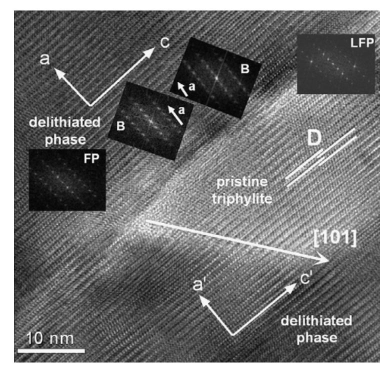


Ramana et al, JPS (2009)

What shrinking core?



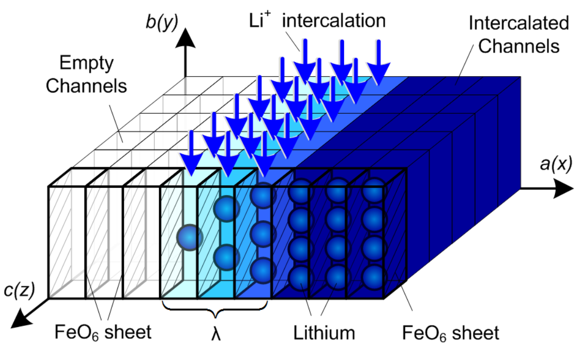
Chen & Richardson EESL (2006)

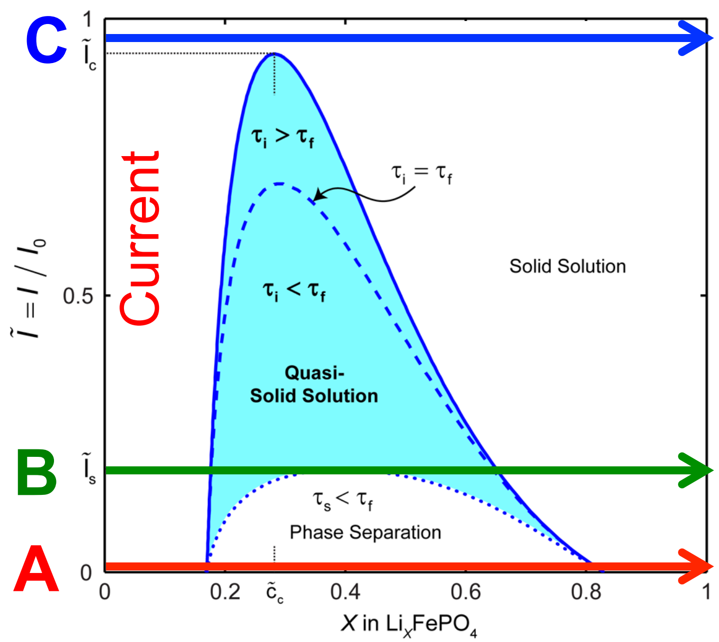


Ramana et al, JPS (2009)

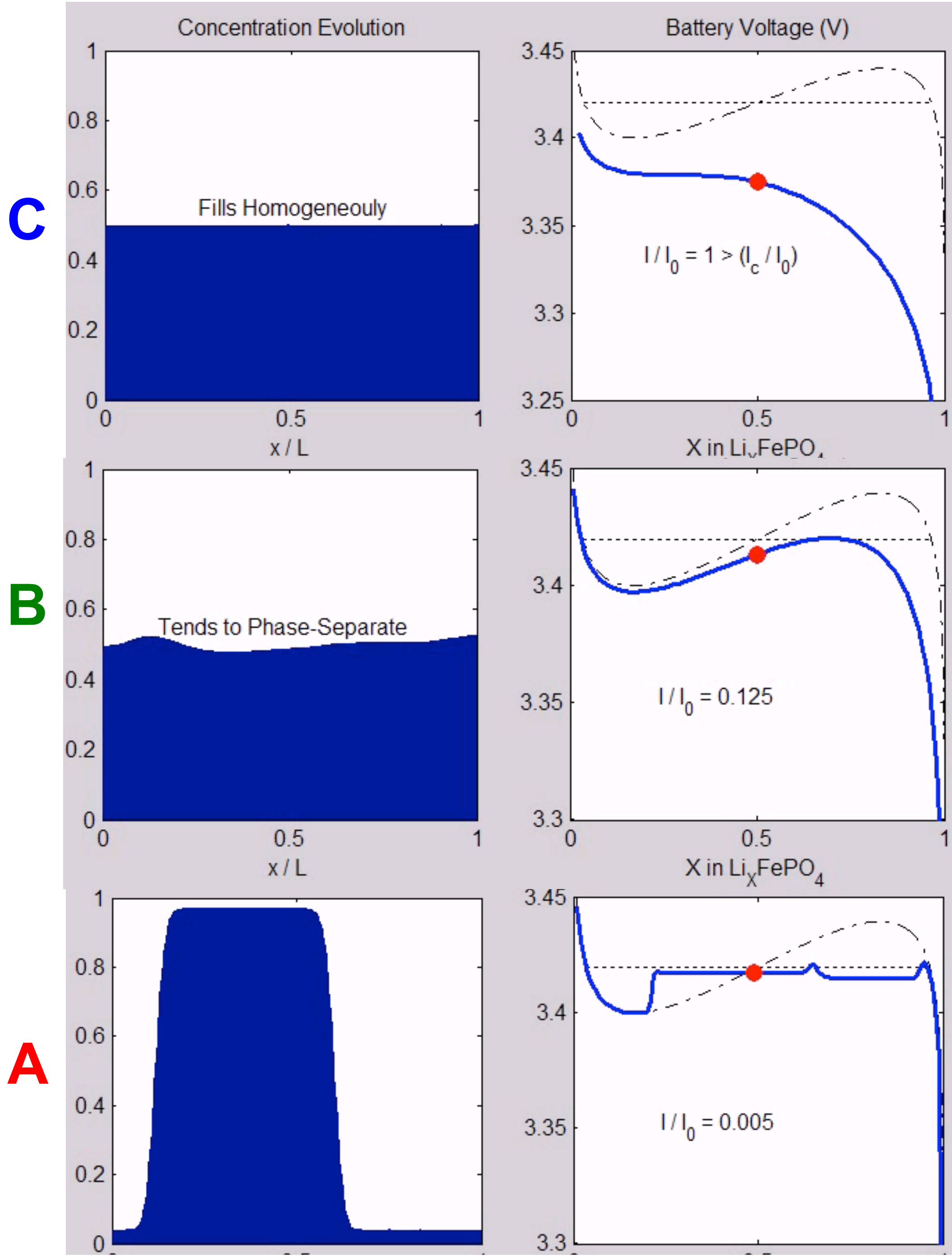
Suppression of Phase Separation at High Discharge Rates

P. Bai, D. A. Cogswell & MZB, *Nano Letters* (2011)





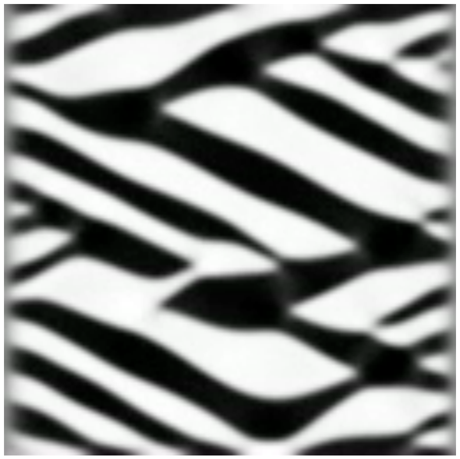
Theory: Linear stability of uniform insertion



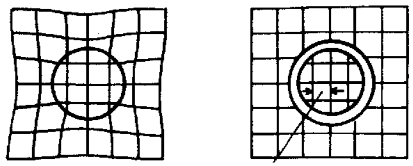
Coherent Phase Separation

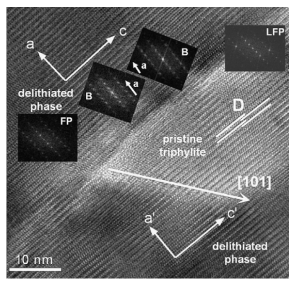
Cogswell & Bazant, *ACS Nano* (2012)

Coherent phase separation



coherent incoherent





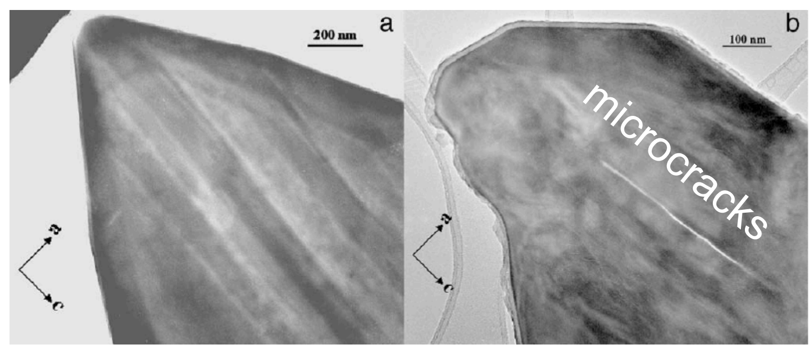
Ramana et al,
ESSL (2009)
L ~ 80nm

Loss of c-axis coherency

Suppression of phase separation
at high discharge rates

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

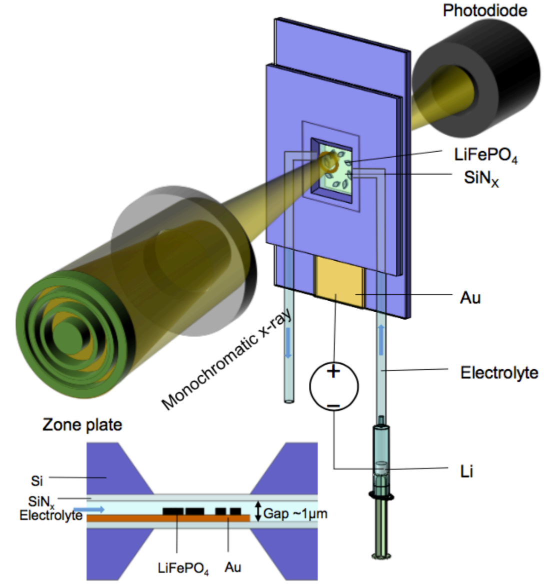
Fast discharge
I/I_0=.3~7C



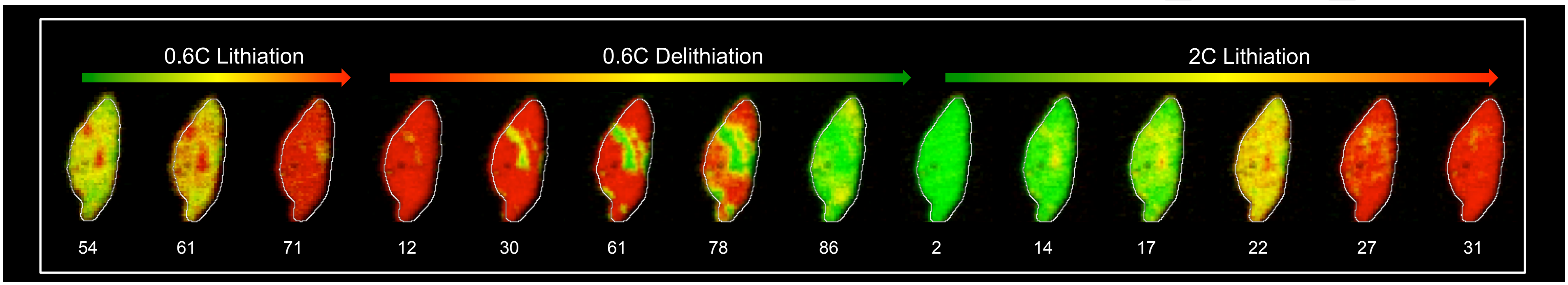
Chen, Song,
Richardson,
JPS (2006)
L ~ 2 um

First Direct Evidence from *In Operando* X-ray Imaging

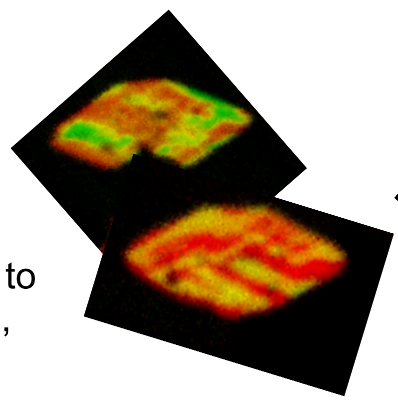
Jongwoo Lim, Yiyang Li,… MZB, William Chueh (Stanford)
submitted (2016)



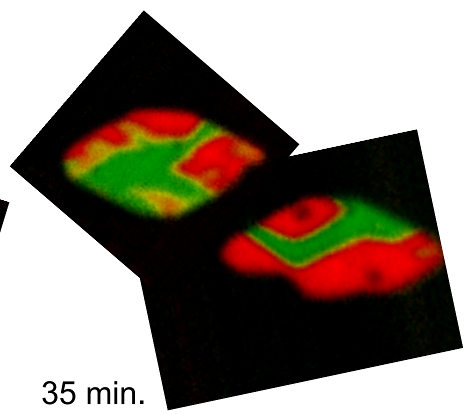
- Reactions suppress phase separation
- Rate-limiting kinetics→ Must engineer *interfaces*



Discharge to 50% at 1C, hold open circuit…

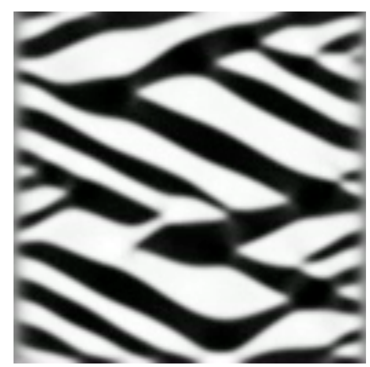


3 min.



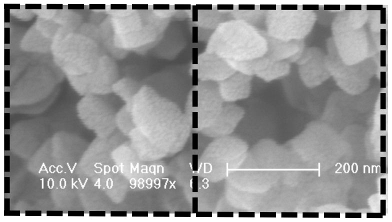
35 min.

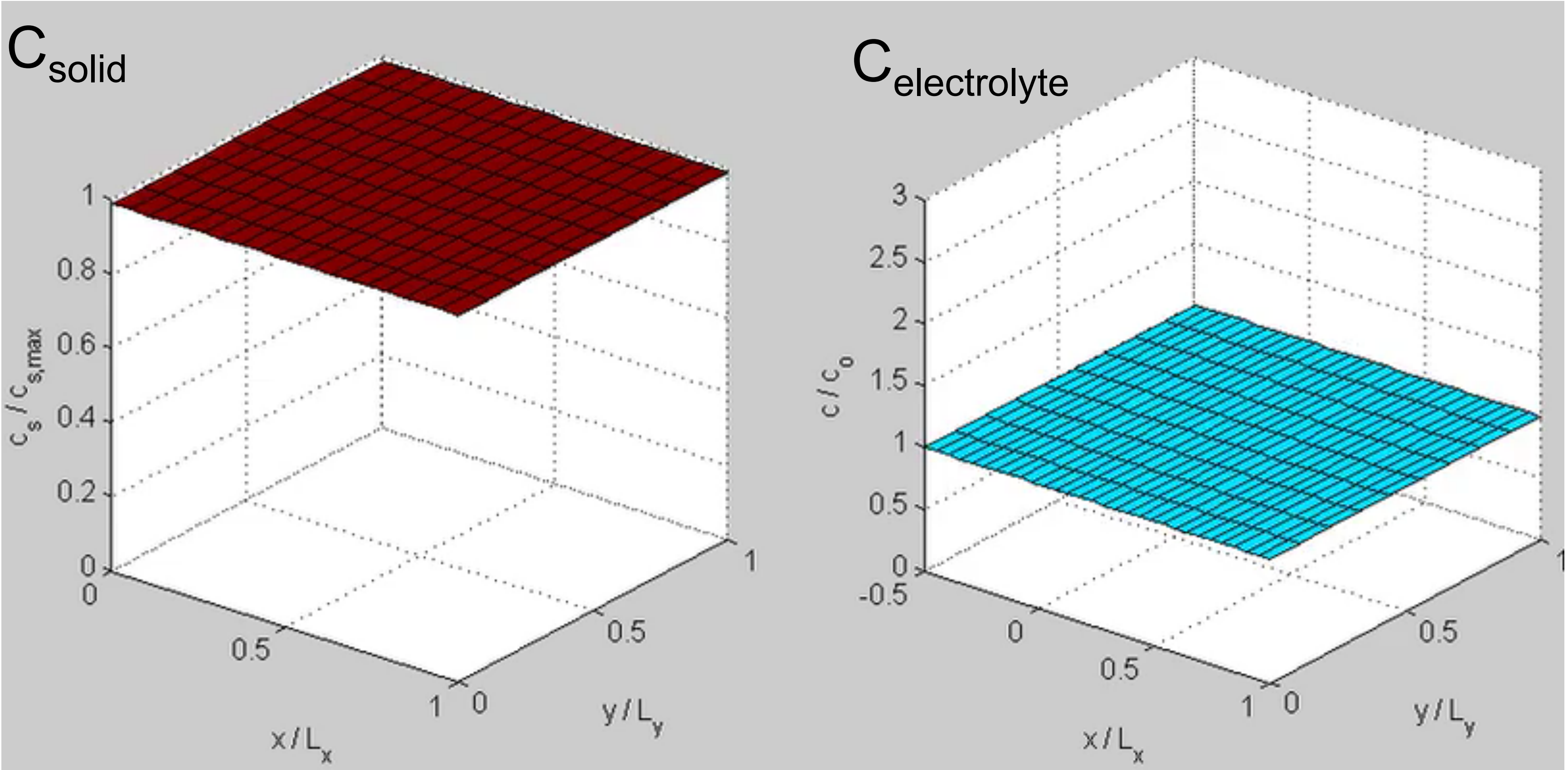
Cogswell, unpublished
L = 2um



Porous Electrode Phase Transformations

TR Ferguson & MZ Bazant
J. Electrochem Soc (2012).
Electrochimica Acta (2014)

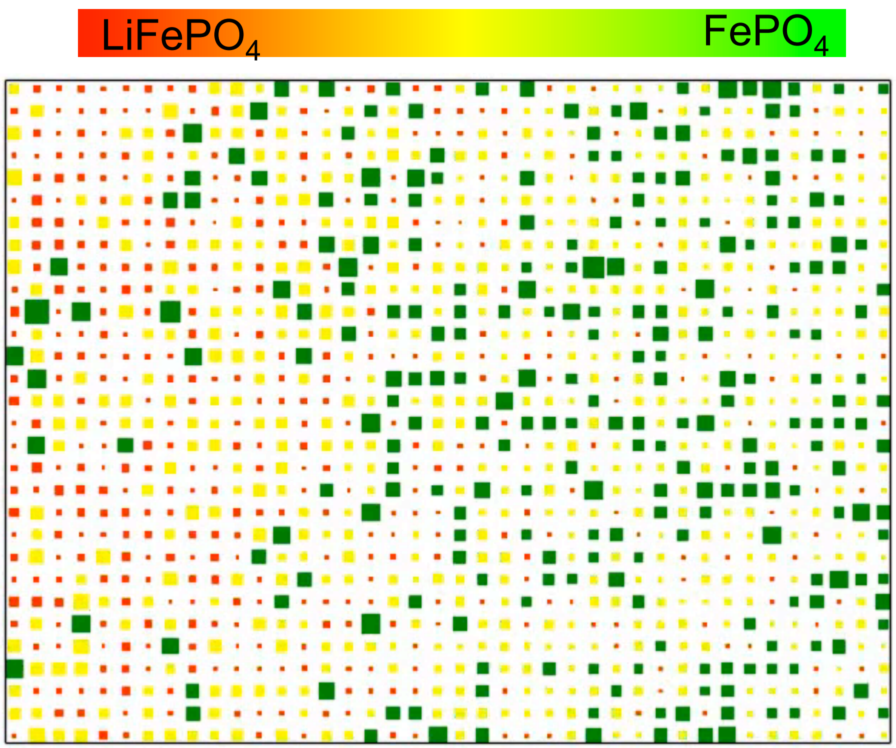




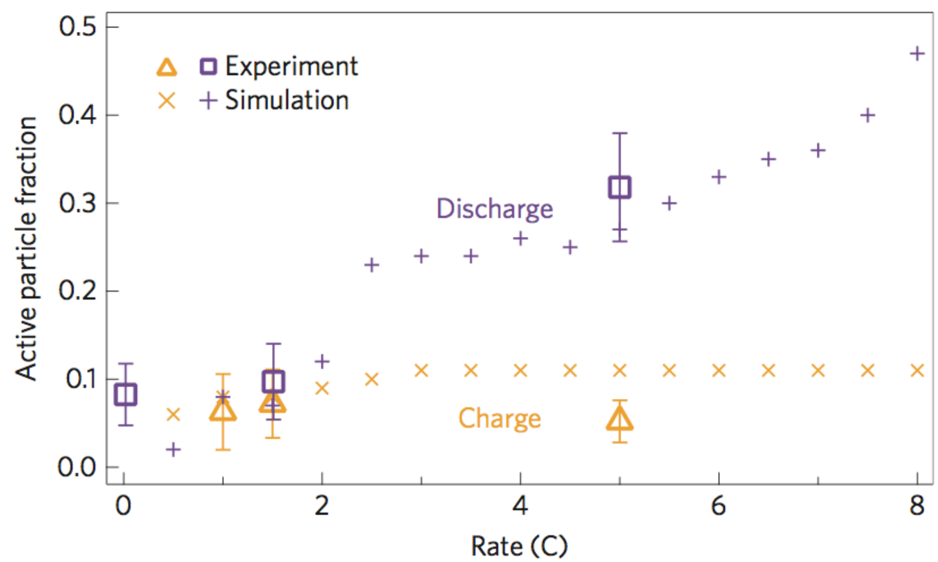
Recharging voltage step, Li extraction from porous cathode

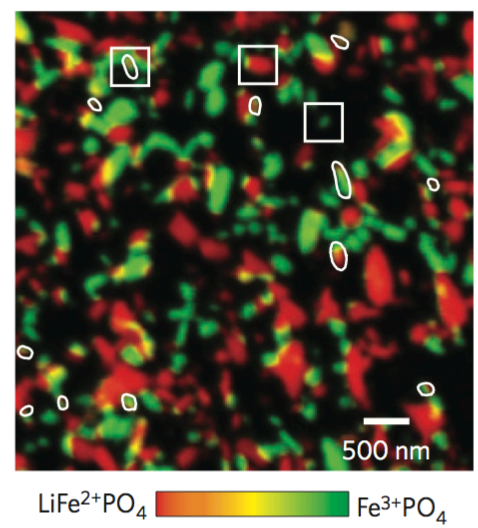
Rate-Dependent Active Population

Yiyang Li, Ray Smith, MZB, William Chueh, *Nature Materials* (2014)

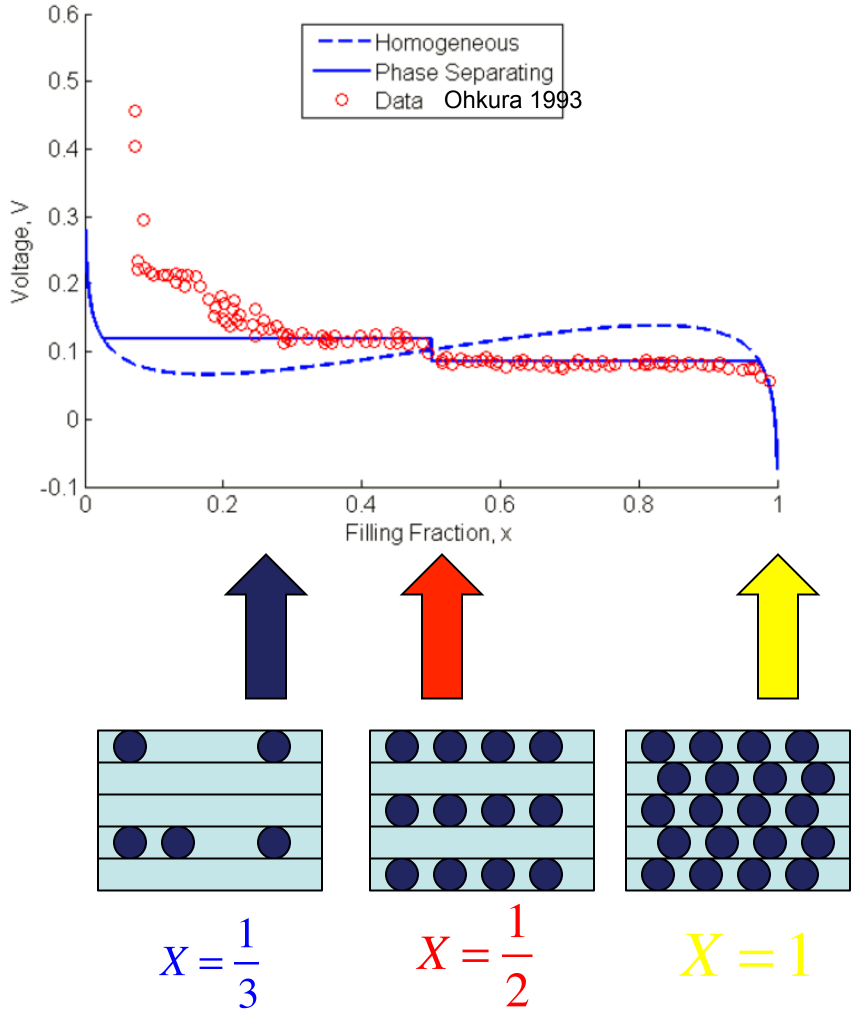


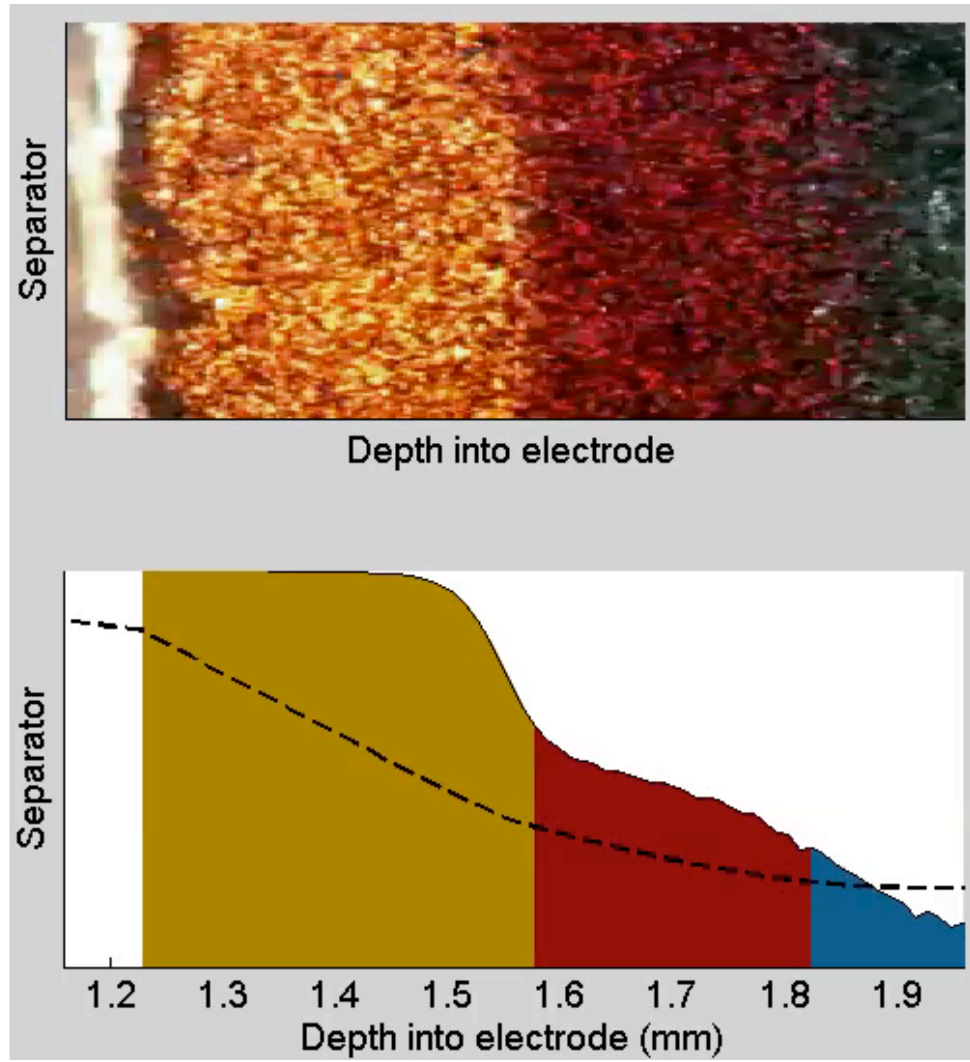
"Mosaic Instability"





Three+ Phases: Li_xC_6 (Graphite Anode)

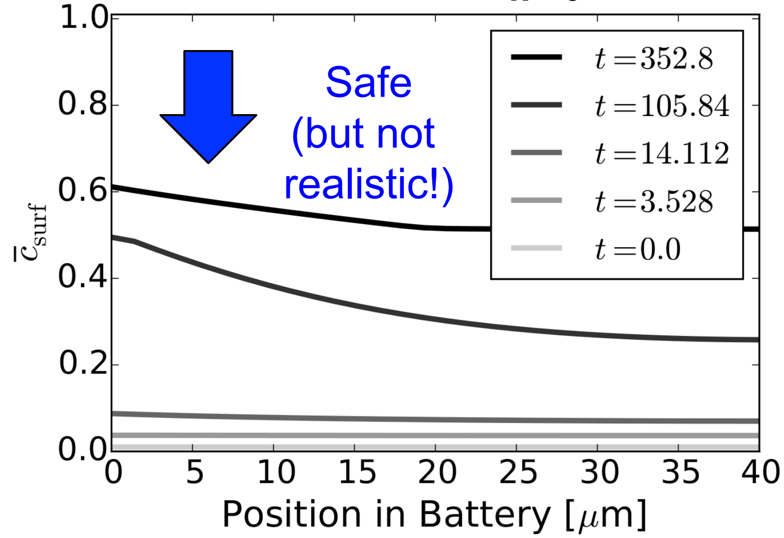




EXPERIMENT: SJ Harris et al, JPCL (2010)
THEORY: Ferguson & Bazant, Elec. Acta (2014)

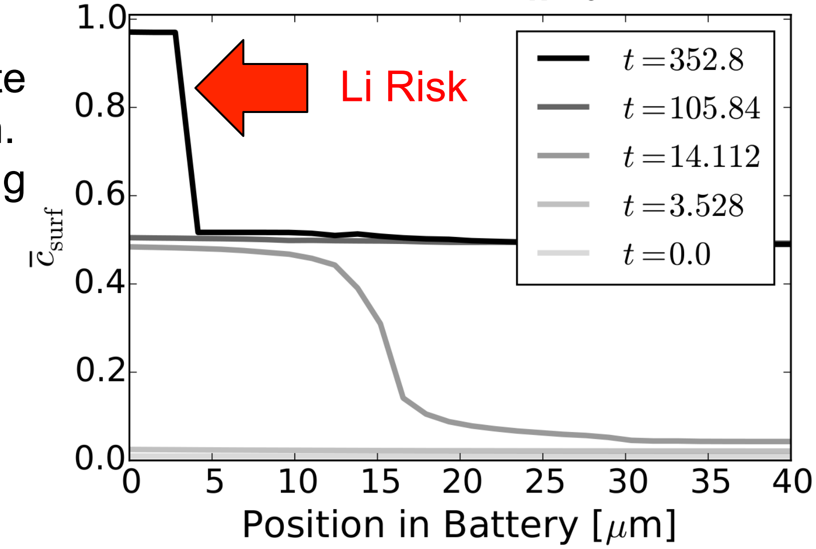
Recharging Rate Limit for Li-ion Batteries

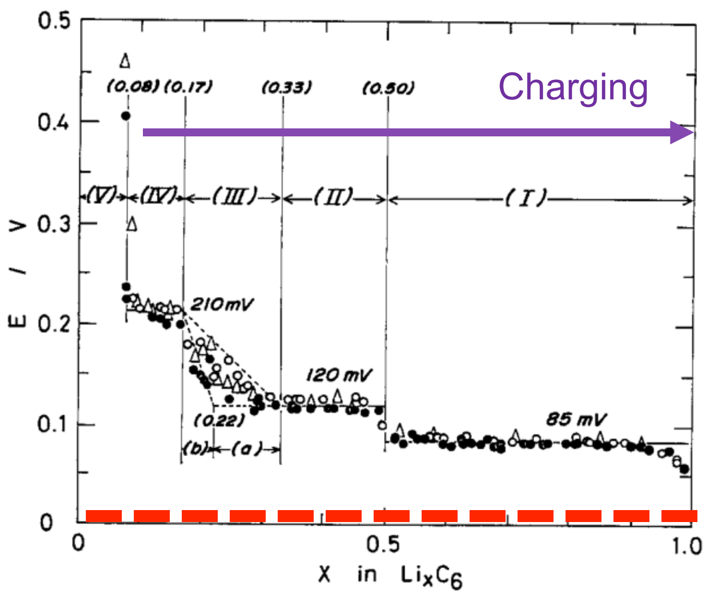
Solid solution "Li_xC_6" particles



10C rate
= 6 min.
charging

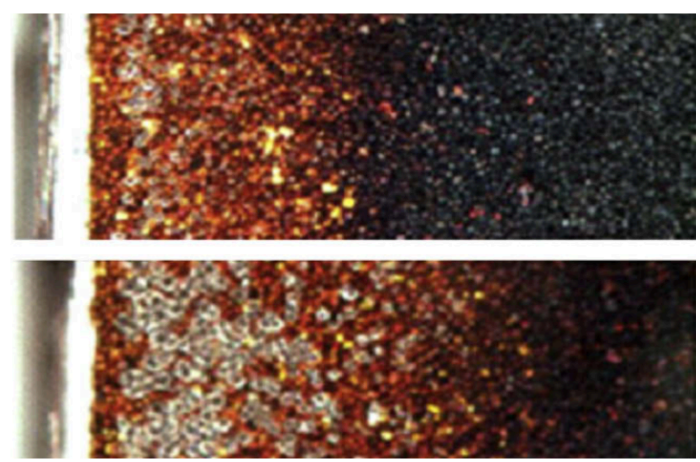
Phase separating Li_xC_6 particles





Li plating risk
(electrodeposition)

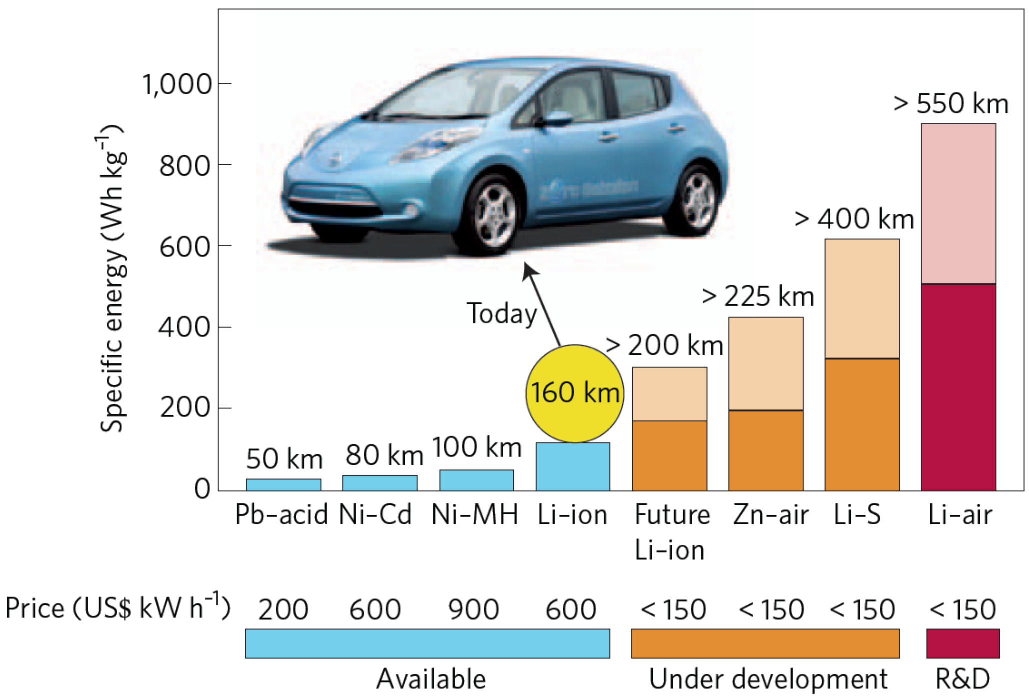
THEORY: R. Smith, K. Thomas-Alyea & MZB, in prep.
EXPERIMENT: Harris et al. (2010)



2. Pattern Formation in Metal Batteries

Metal anodes for Transportation

Bruce et al., Nature Materials (2012)



metal anodes

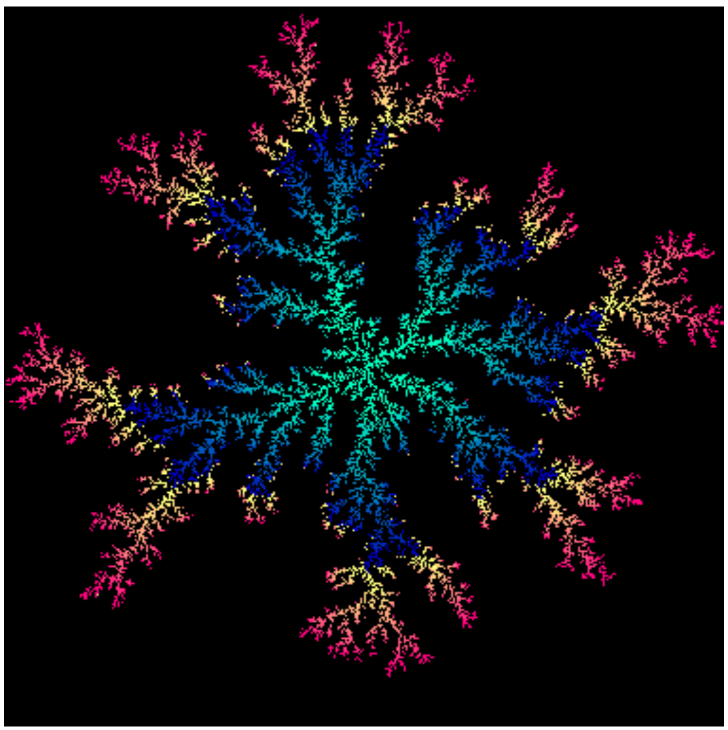
Dendrites can also cause shorts in Li-ion batteries if Li plating occurs…

"Li metal is itself one of the most challenging components of the Li/air cell, as it tends to roughen and develop dendrites with cycling."

J. Christensen et al., JES (2012)

Transport Limited Growth

Diffusion Limited Aggregation (DLA)

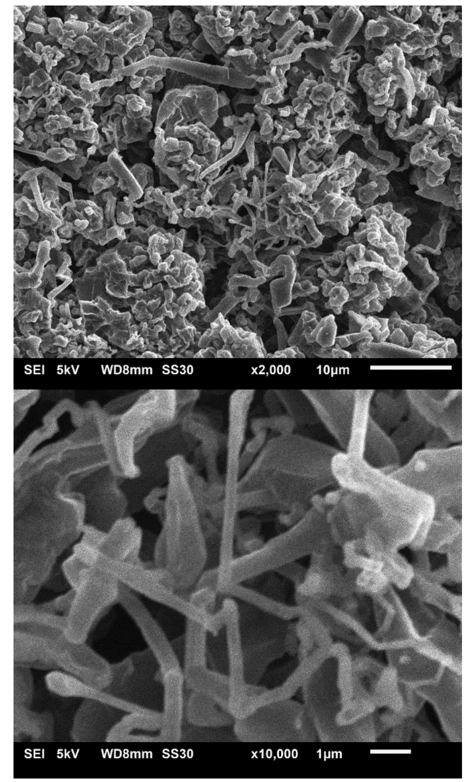


Witten & Sander, PRL (1981).
(image: S. Havlin)

Copper Dendrites

Brady & Ball, PRL (1984).
(image: K. Johnnson, wikipedia)

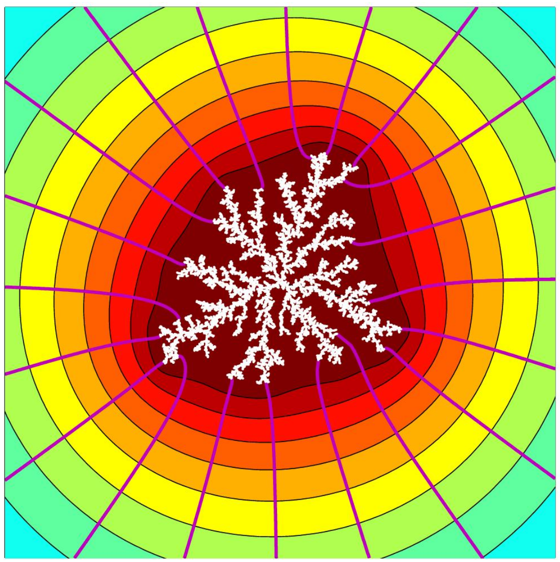
Lithium "Dendrites"(?)



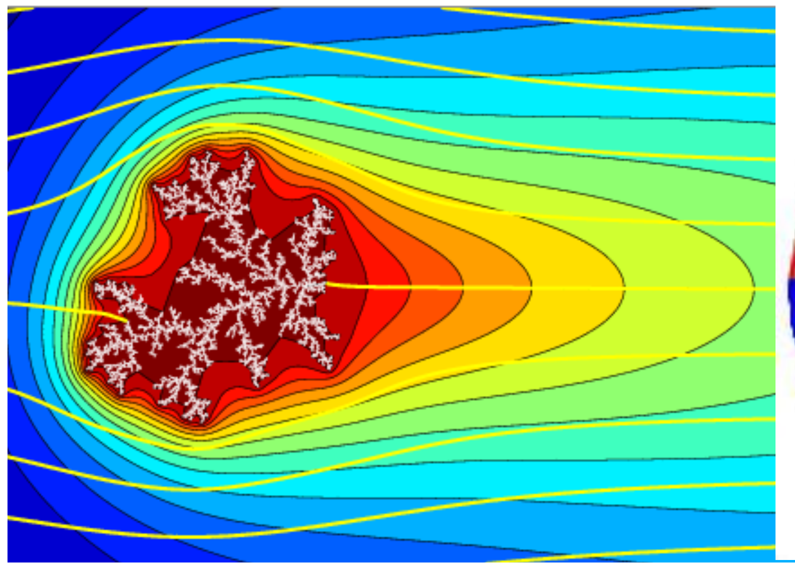
Bai, Brushett, Li, Bazant,
submitted (2016)

Theorem: All transport-limited growth is unstable to dendrites (2d, quasi-steady)

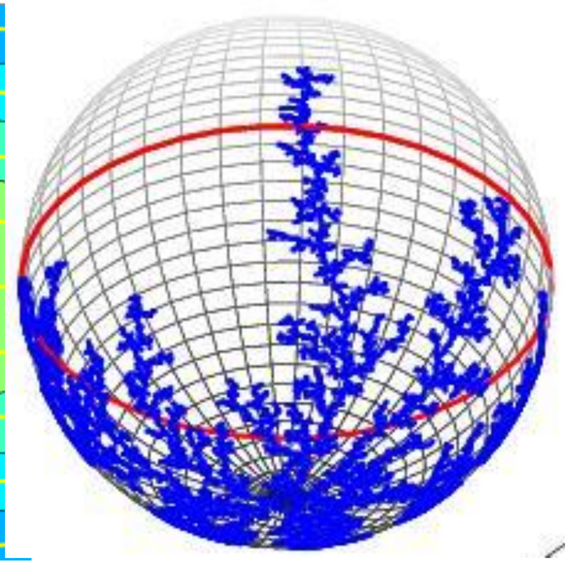
Proof: conformal map dynamics → DLA universality class
M. Z. Bazant, J. Choi, B. Davidovitch, PRL (2003).
M. Z. Bazant, Proc. Roy. Soc. A (2004).



DLA



DLA in a Fluid Flow

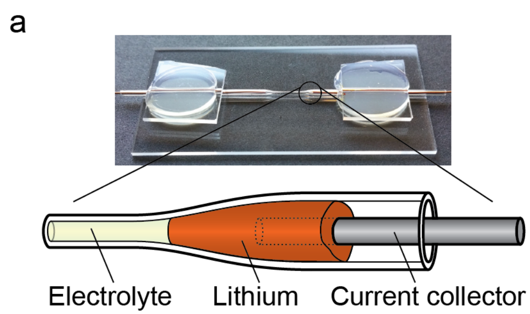


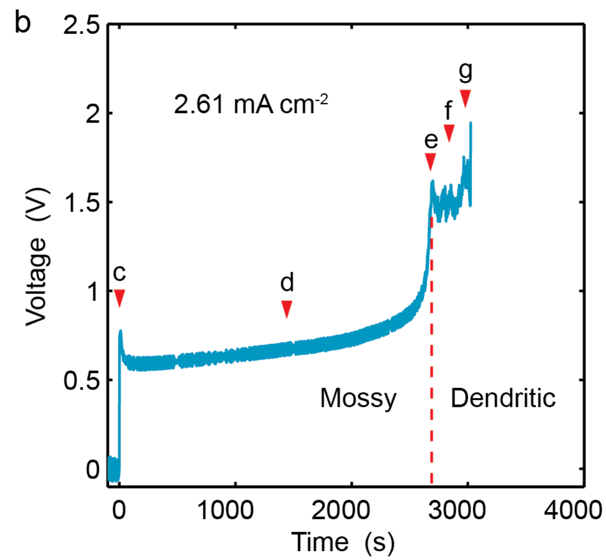
DLA on
Curved Surfaces

Relevant for lithium metal anodes?

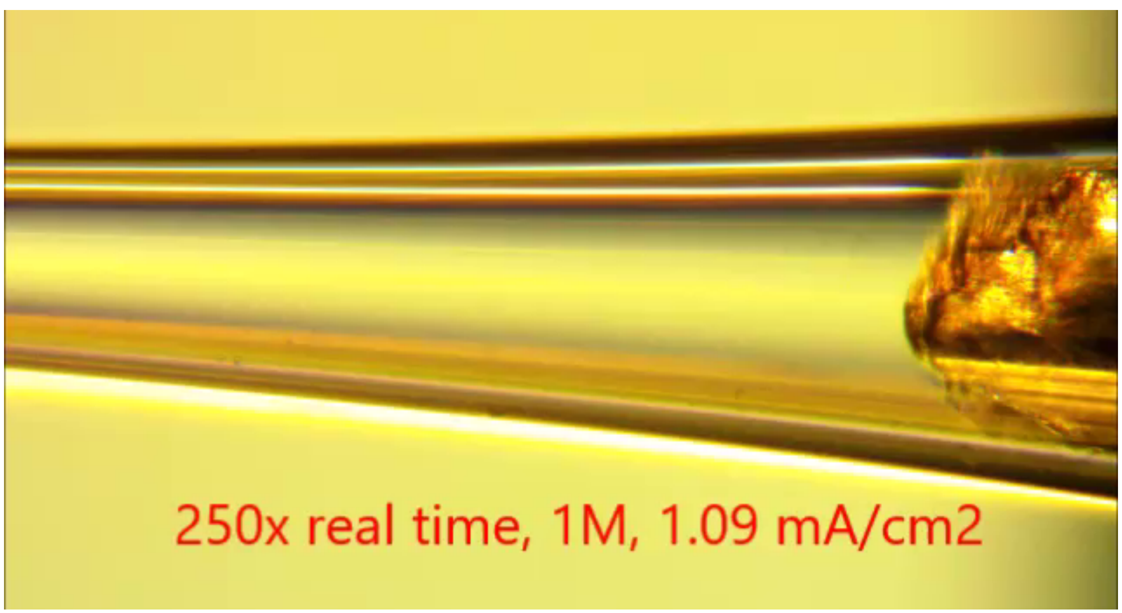
Capillary Cell Experiments

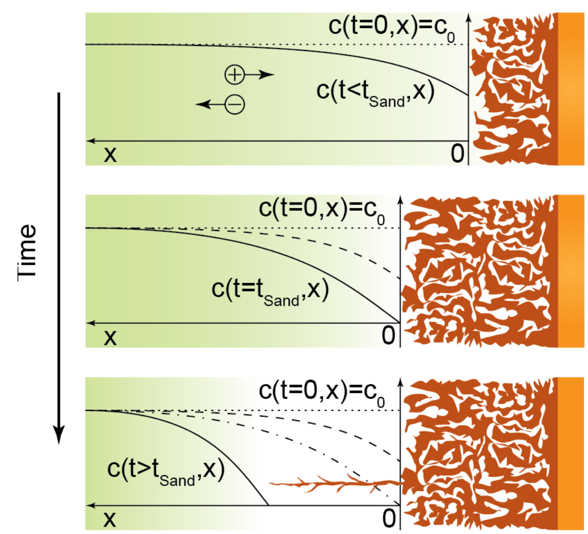
Peng Bai, F. R. Brushett, J. Li, M. Z. Bazant, submitted (2016)





Diffusion limitation:
“Mossy” lithium → Fractal “dendrites”



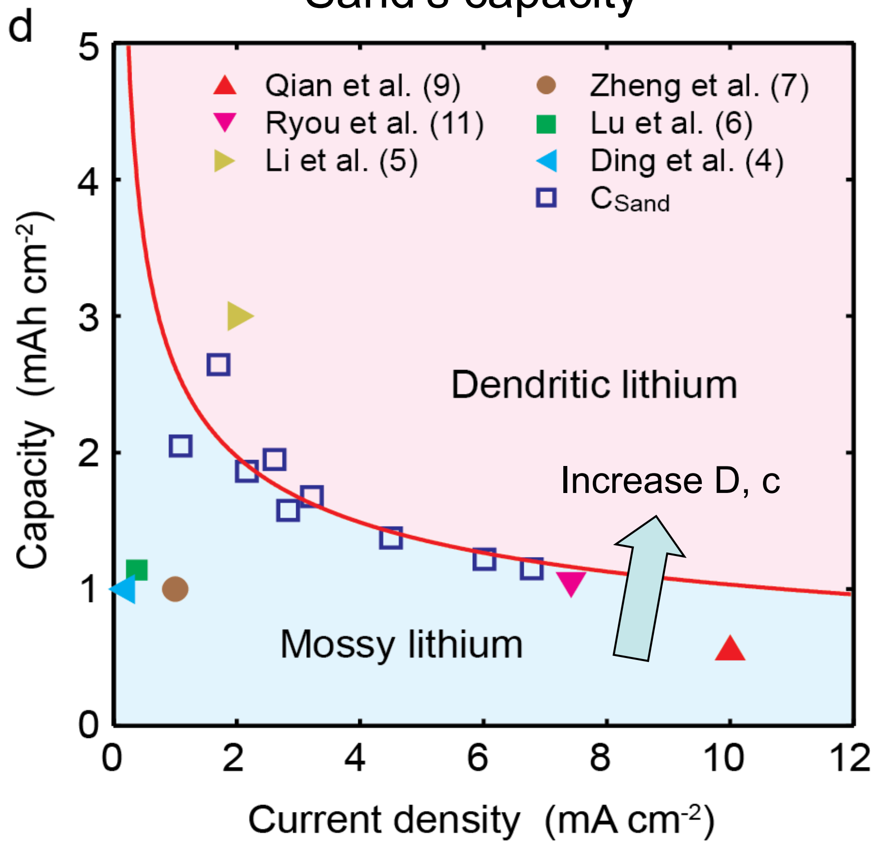


Sand’s Time

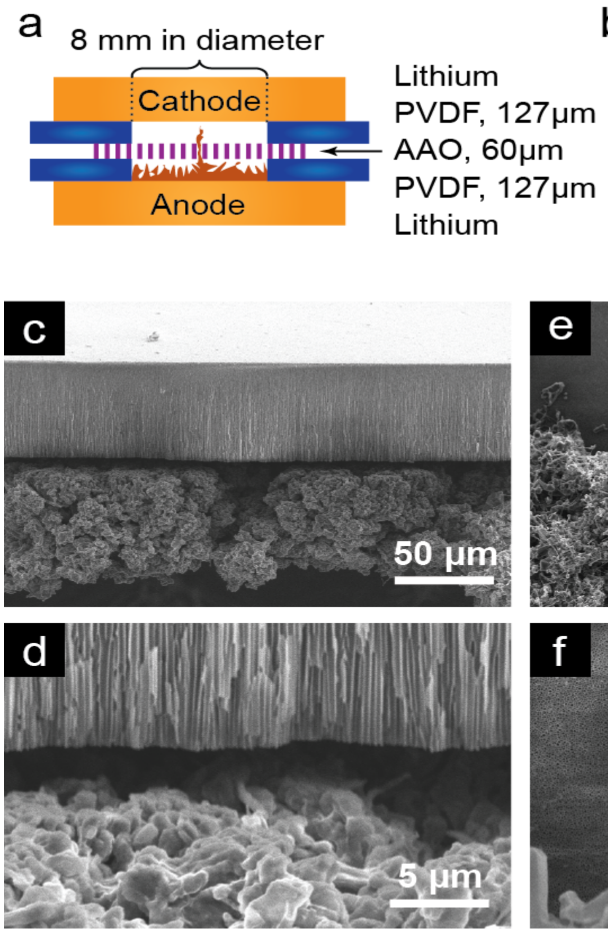
Dendrite-Free Recharging

Bai, Brushett, Li, Bazant, submitted (2016)

"Sand's capacity"



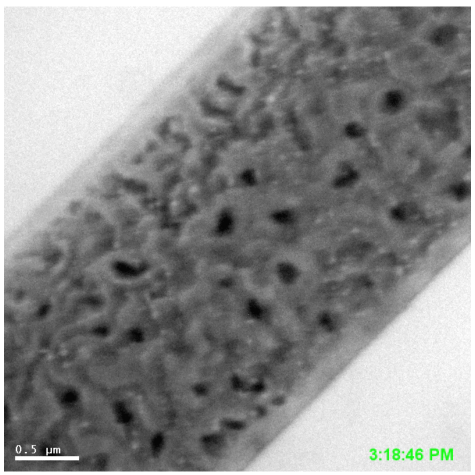
$$C_{Sand} = \frac{\pi F^2 Dc^2}{4t_-^2 I}$$

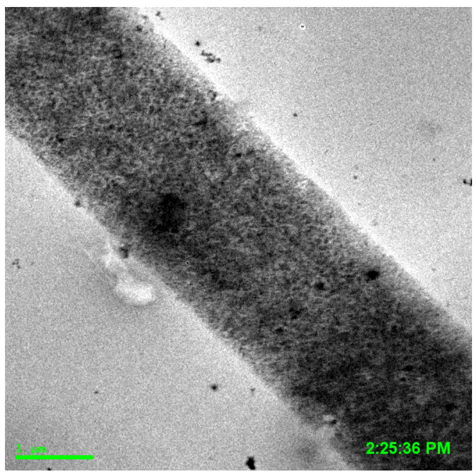


Mossy lithium can be blocked with nanoporous ceramic separators (AAO)

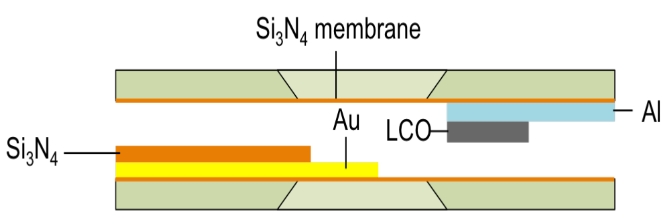
Mossy Lithium: *Two*-Reaction-Limited Growth (SEI + Li)

Akihiro Kushima,… MZB, Ju Li (MIT)
submitted (2016)

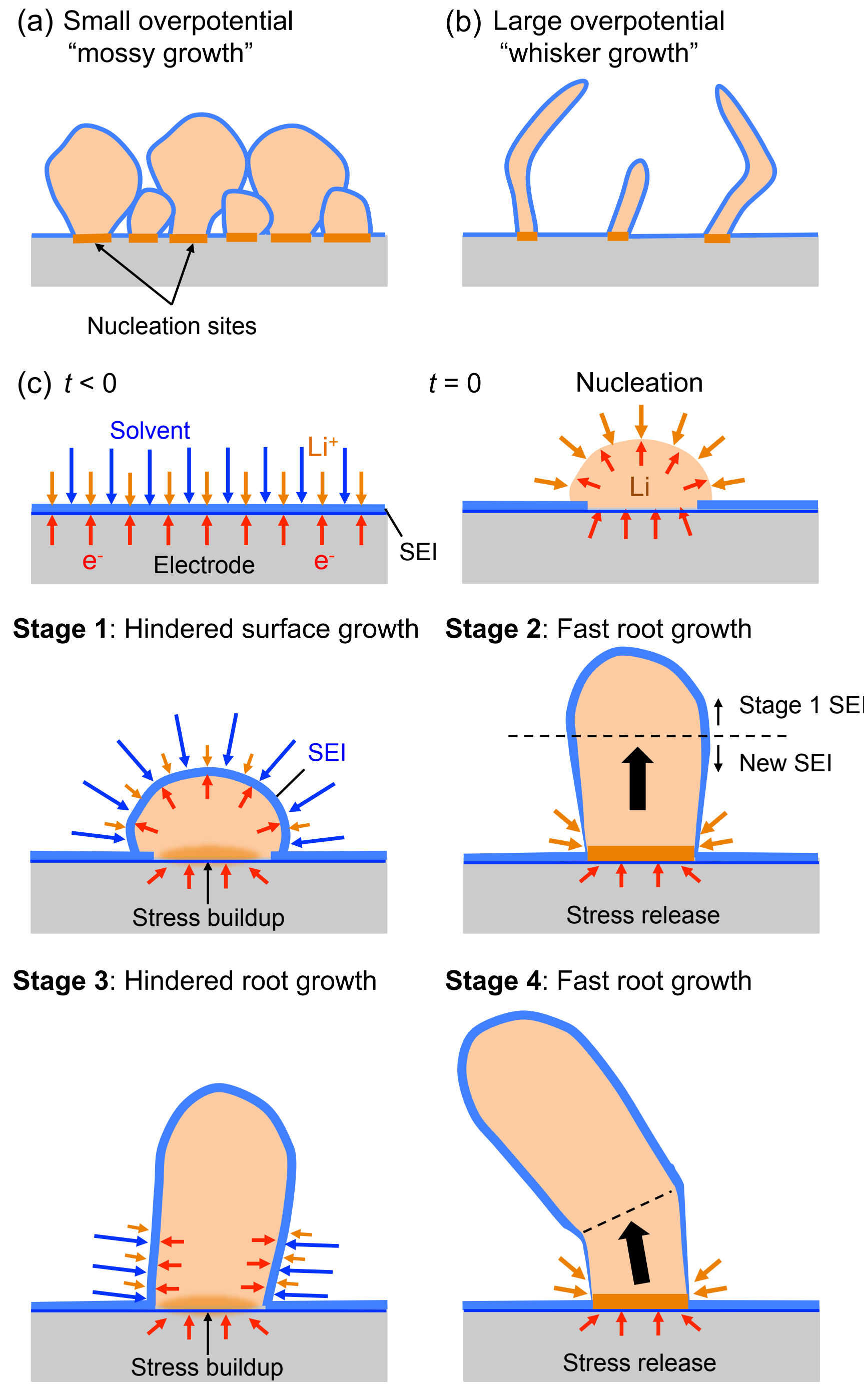




(c)



Liquid-cell HR TEM

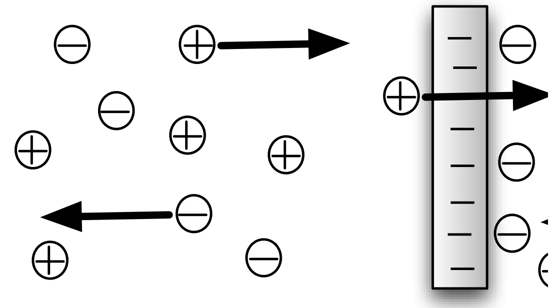


3. Beyond Diffusion Limitation: Shock Electrochemistry

Deionization Shock Waves in Porous Media

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x}\left(\rho_s \frac{I}{\sigma(c)}\right) = D\frac{\partial^2 c}{\partial x^2}$$

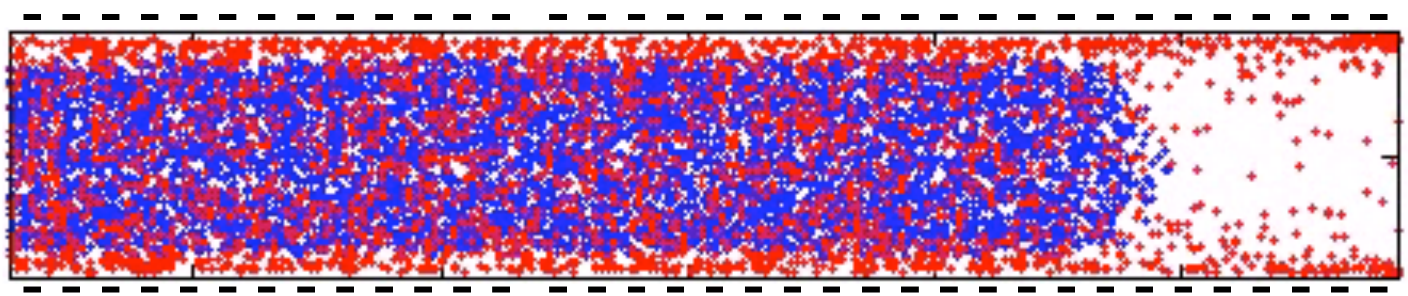
Surface conduction Electrolyte diffusion



Charged microchannel, overlimiting current

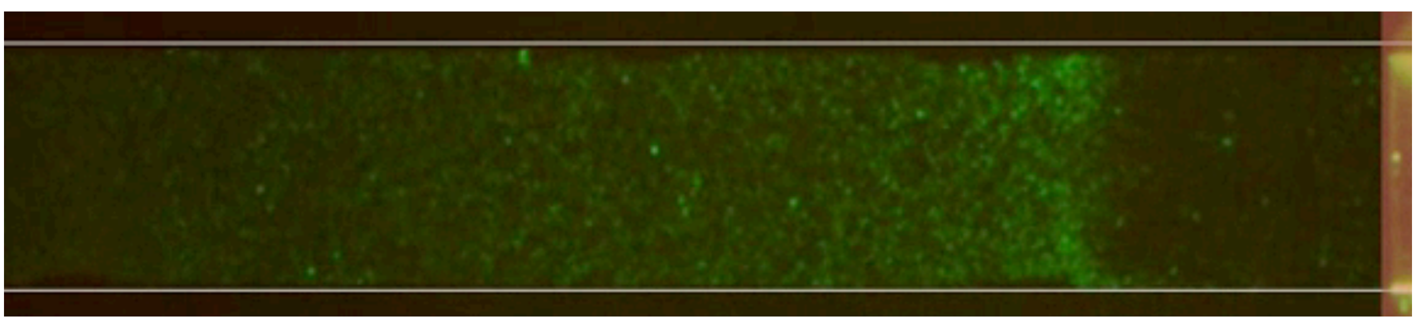
THEORY: Mani & Bazant, Phys. Rev. E (2011); Mani, Zangle, Santiago, Langmuir (2009)

Bulk electrolyte diffusion



Surface conduction

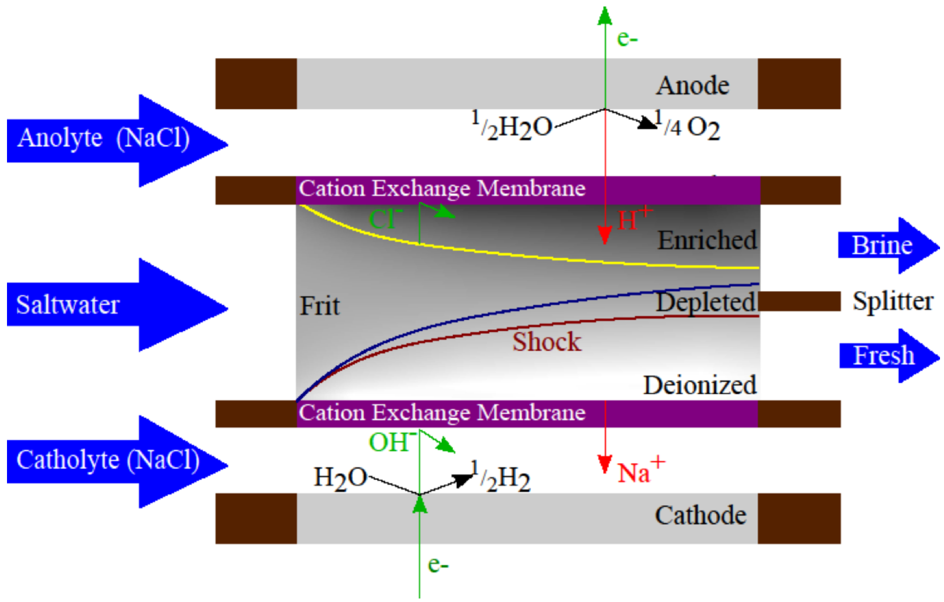
EXPERIMENT: Nam, …, Bazant, Kim, PRL (2015); Zangle, Mani, Santiago (2009)



“Shock Electrochemistry”

1. Shock Electrodialysis

Schlumberger et al, Env. Sci. Tech. Letters (2015)



ACS in the News

ACS Publications
Most Trusted. Most Cited. Most Read.

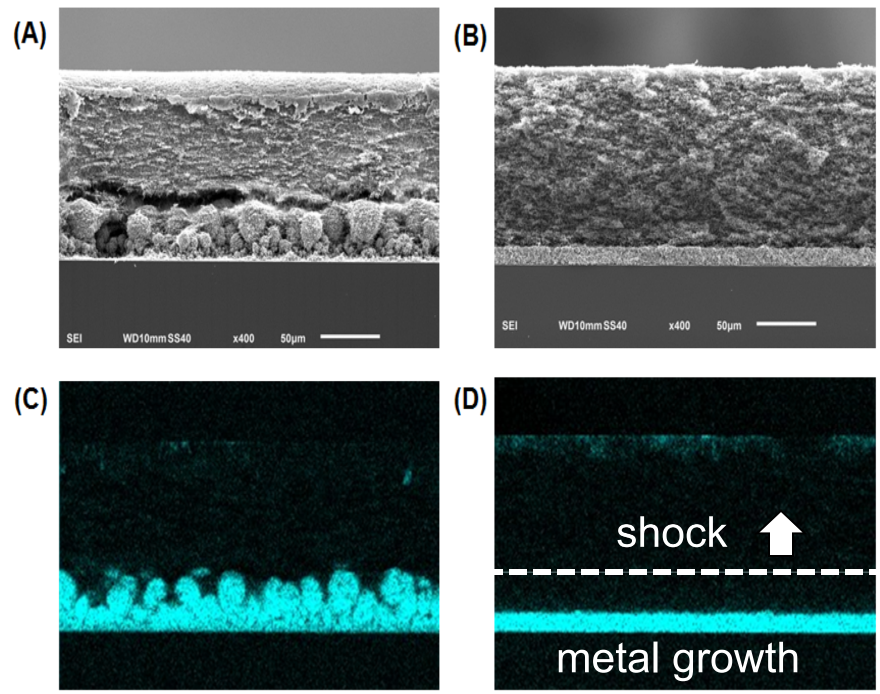
Scientists Turn Salt Water Into Drinking Water By Shocking The Salt Out With Electricity

PROCESSING E-NEWS | WATER & WASTEWATER

SCIENTISTS DEVELOP DESALINATION METHOD THAT ALSO PURIFIES WATER

2. Shock Electrodeposition

Han et al, *Sci. Reports* (2014); submitted (2016)
http://arxiv.org/abs/1505.05604



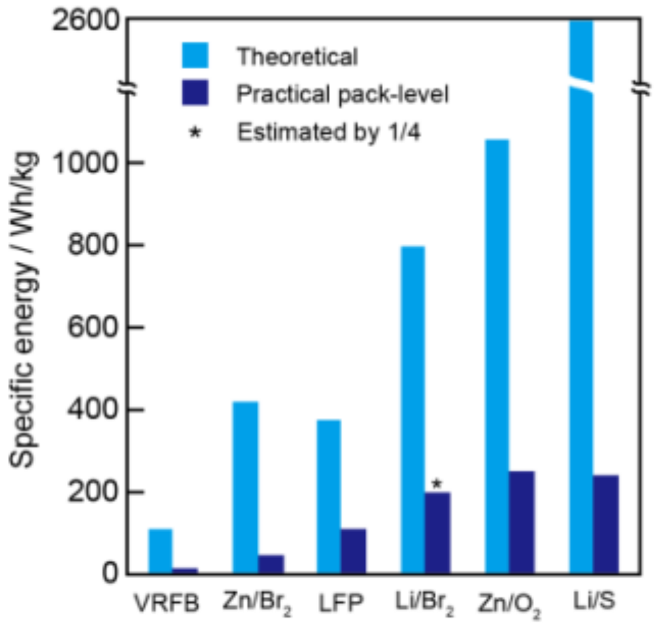
$\rho_s > 0$ $\rho_s < 0$

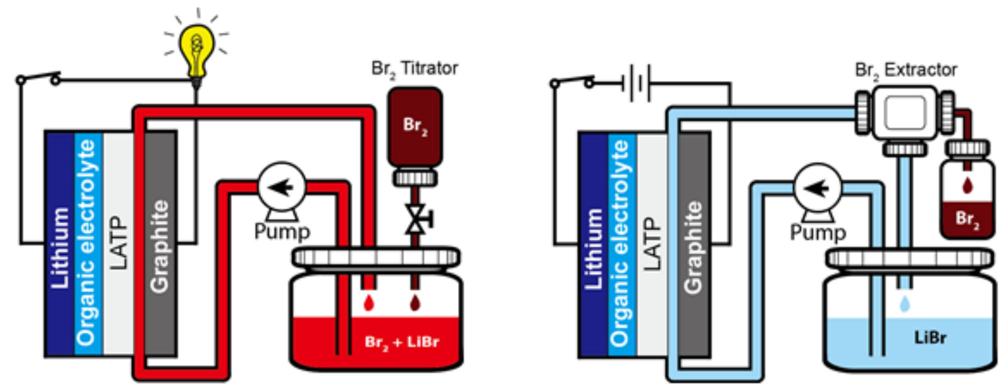
- Suppression of copper dendrites
- Could this work for Li metal?

4. “Extreme” Flow Batteries

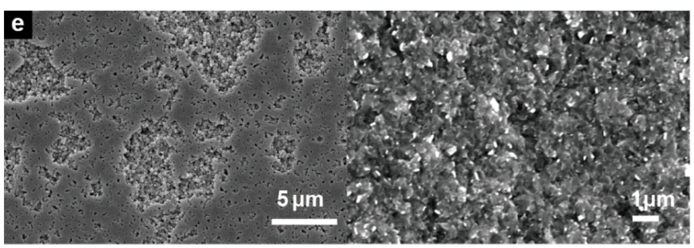
Li-Br_2(-O_2) Flow Battery

Bai & Bazant, *J. Mat Chem. A* (2015); *Electrochimica Acta* (2016)



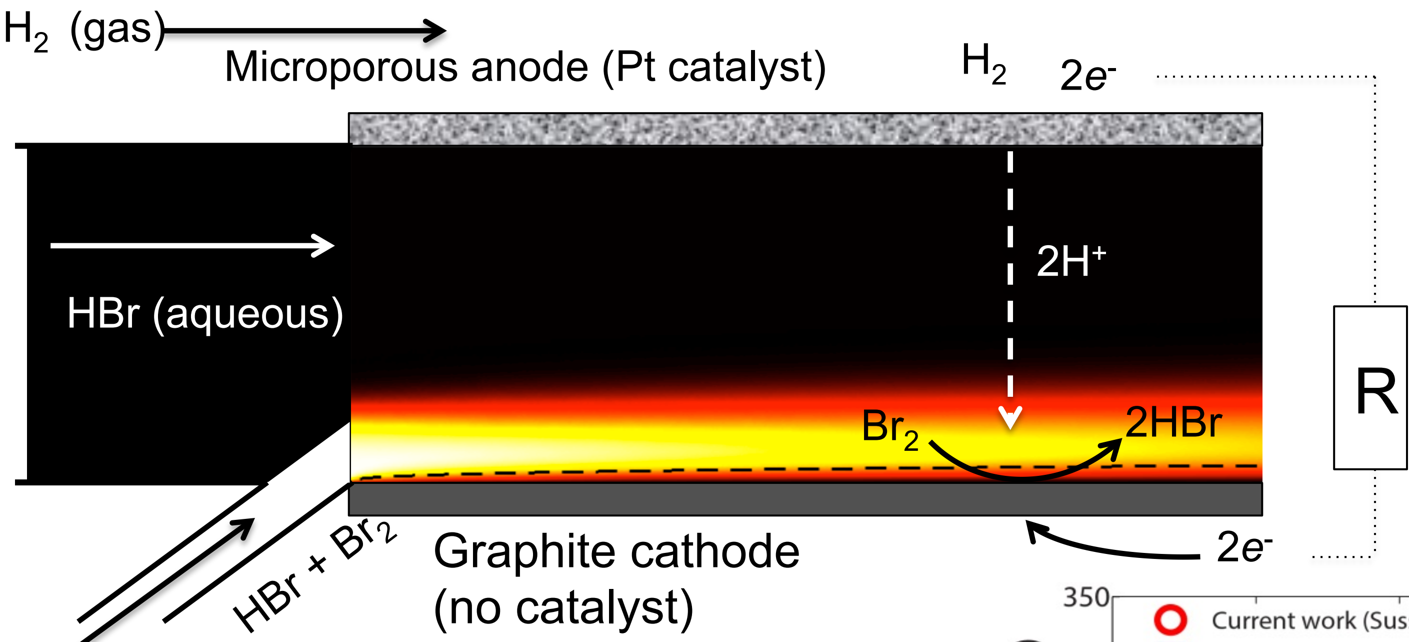


LiBr solubility 11M, 19m; 4.13V
Theoretical capacity 791 Wh/kg



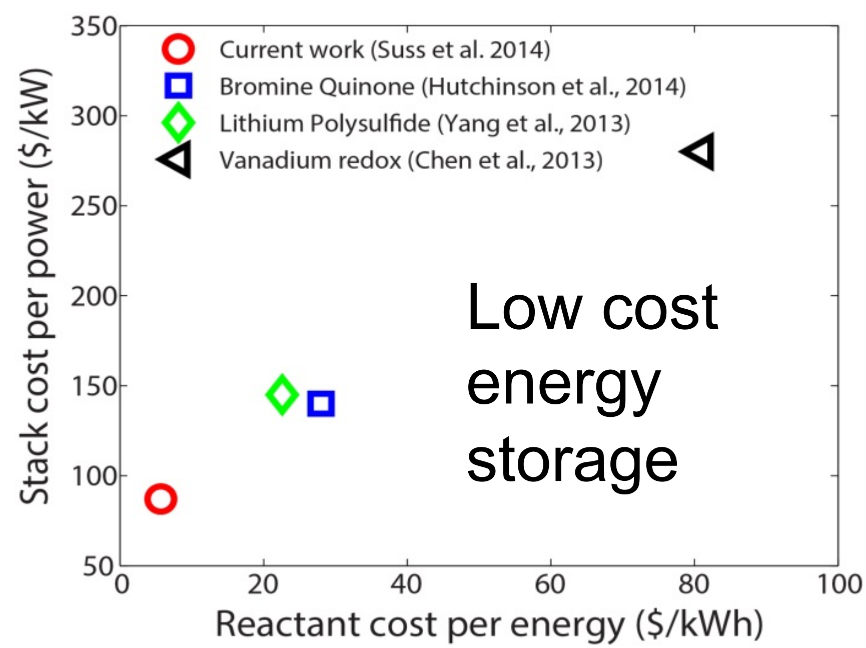
- Demonstrated ~10M LiBr, 5M Br2 ~ 360 Wh/kg (need flow)
- "Recharge" Br_2 externally
- Low power (9 mW/cm^2) & short lifetime due to LATP membrane decay
- Can also run on dissolved oxygen (tap, seawater) at 3 mW/cm^2 ~ state-of-art Li-air batteries!
- Maybe go membraneless?

Membraneless H_2-Br_2 Flow Batteries



Max power = 0.8 W/cm^2

90% efficient @ 0.25 W/cm^2



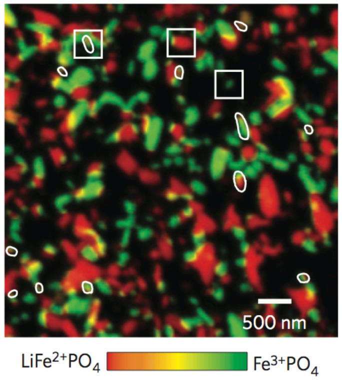
Membraneless Vanadium Redox Fuel Cell: Stroock, Whitesides (2002) (no recharging)

Rechargeable H_2-Br_2 planar cell
W. A. Braff, MZB, C. R. Buie,
Nature Communications (2013);

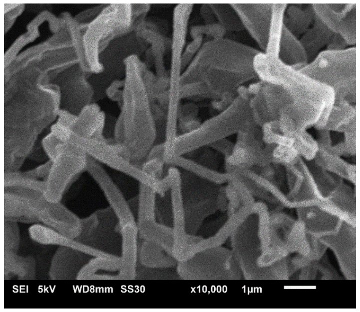
Cycleable H-Br_2 flow-though porous cell
Suss, Braff, Buie, Bazant, submitted (2016).

Conclusions

- Li-ion batteries
  - Nanoparticles: suppressed phase separation
  - Mosaic instability: flat voltage, Li plating risk
  - Paradigm shift: bulk properties → interfaces



- Li-metal batteries
  - Short-causing "dendrites" can be avoided
  - "Mossy" Li from SEI+Li: can block, but → capacity fade
- Flow batteries
  - Low cost energy storage
  - Maybe also for transportation?



Theory of Chemical Kinetics and Charge Transfer Based on Nonequilibrium Thermodynamics

M. Z. Bazant, *Accounts of Chemical Research* (2013)

Free energy functional

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

Diffusional chemical potential and activity

$$\boxed{\mu_i = \frac{\delta G}{\delta c_i} = k_B T \ln a_i} = \mu^{\Theta}{}_i + \bar{g}'(c) - \nabla \cdot K \nabla c + U : \sigma + \ldots$$

Cahn-Hilliard Equation

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

Nernst Equation

$$\Delta\phi_{eq} = \Delta\phi^{\Theta} + \frac{k_B T}{ne} \ln \frac{a_O a_e^n}{a_R} \qquad \hat{n} \cdot eF = I$$

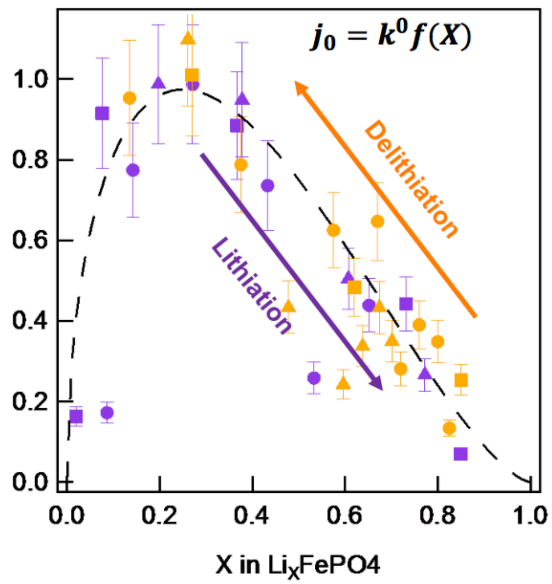
Butler-Volmer Equation

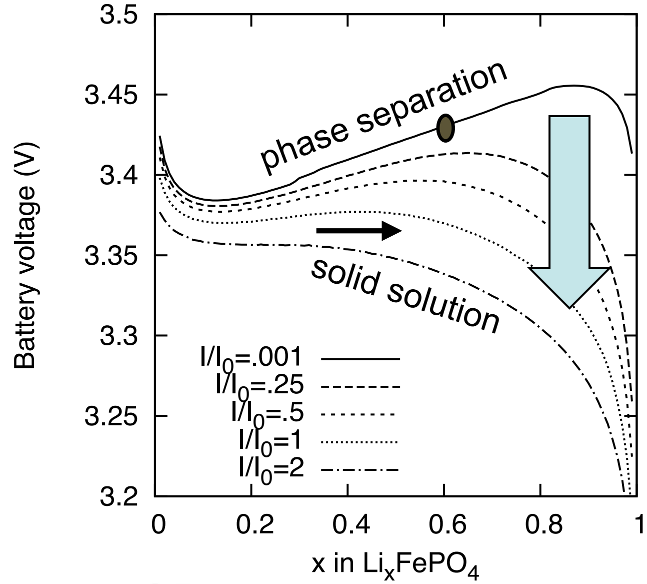
$$\eta = \Delta\phi - \Delta\phi_{eq}$$

$$I = \gamma_{\ddagger}^{-1} a_R{}^{\alpha} \left(a_O a^n{}_e \right)^{1-\alpha} \left(e^{-\alpha_c \tilde{\eta}} - e^{\alpha_a \tilde{\eta}} \right)$$

Solid Solution is Stabilized by *Reactions*

Measured exchange current vs. *local* composition





Activation Overpotential

Theory confirmed:

Skewed $I_0(c)$ required for suppression of phase separation