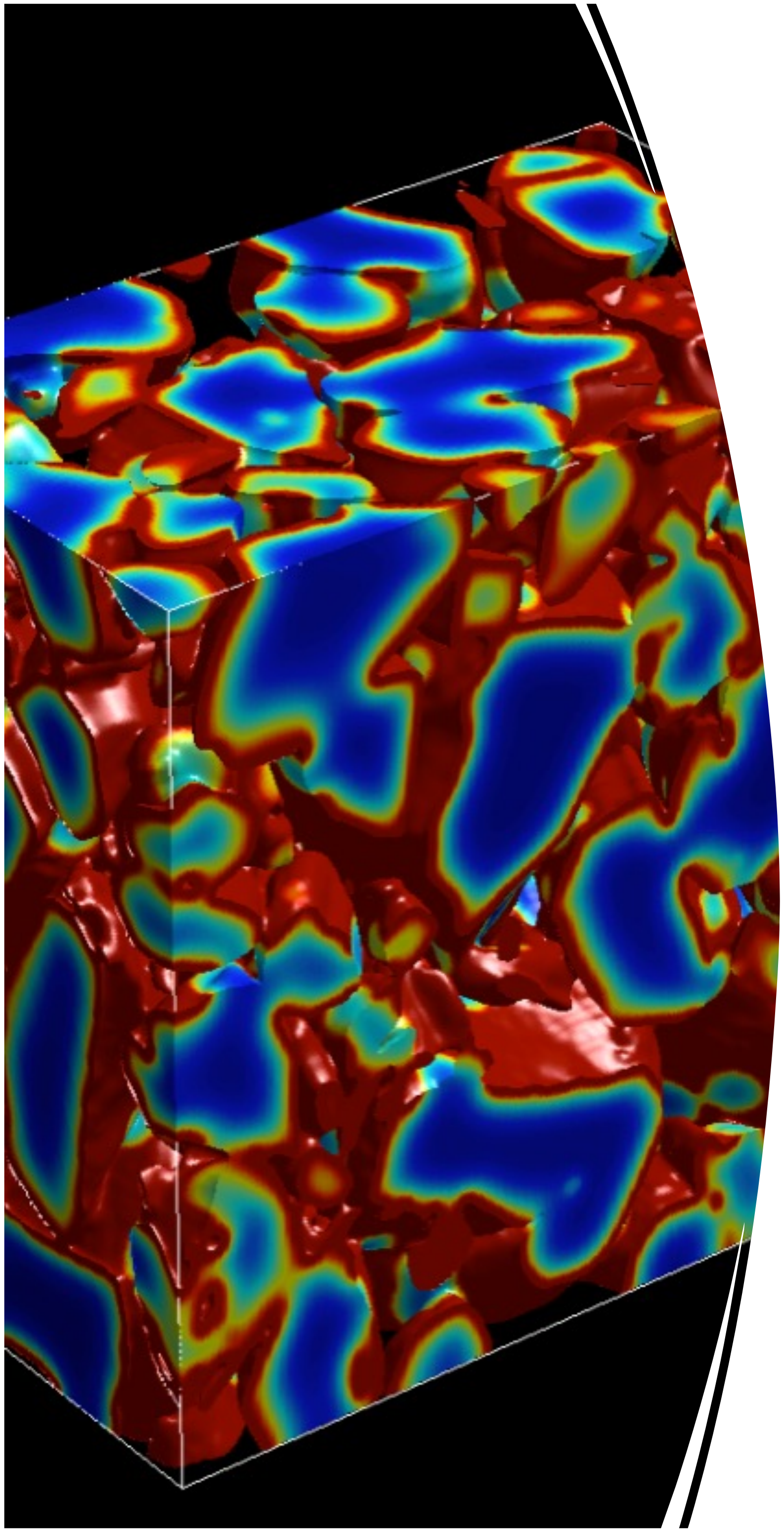


IPAM Tutorial:
The Role of Materials and Microstructures in Electrochemical Energy Storage
Part 1

Katsuyo Thornton
Dept. of Materials Science & Eng.
University of Michigan
kthorn@umich.edu

The Role of Materials and Microstructures in Electrochemical Energy Storage

Lesson Plans

Part 1: Electrochemical Dynamics in Batteries

- General intro
- How batteries work
- Different components of batteries
- Governing equation for electrochemical dynamics
- Key material properties & how they are measured/calculated
- How microstructure affects electrochemical dynamics

Part 2: Electrochemical Dynamics in Batteries

- Additional highlights from simulation results
- Examples of stochasticity

Hands-On Session (next Tuesday)

The Role of Materials and Microstructures in Electrochemical Energy Storage

Lesson Plans

Part 1: Electrochemical Dynamics in Batteries

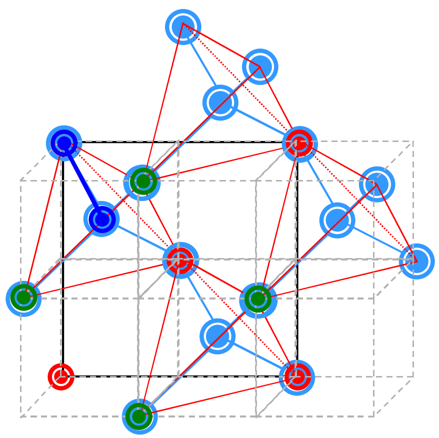
- **How batteries work**
- **Different components of batteries**
- **Governing equation for electrochemical dynamics**
- **Key material properties**
- **How microstructure affects electrochemical dynamics**

Part 2: Electrochemical Dynamics in Batteries

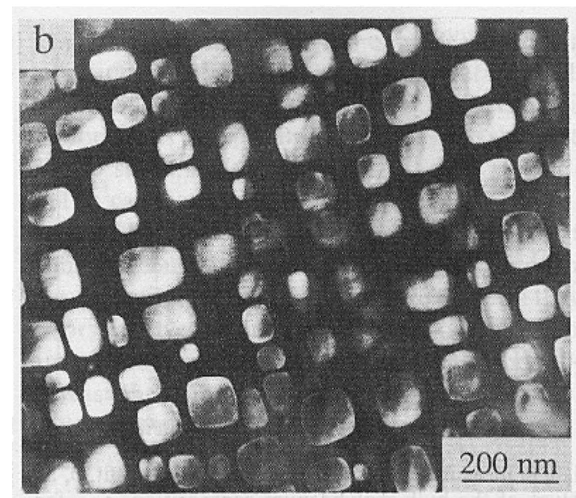
- Additional highlights from simulation results
- Examples of stochasticity

Hands-On Session (next Tuesday)

Materials Science Paradigm



Processing



Fahrmann, et al., Acta Met. 45,1007 (1995)

Structure

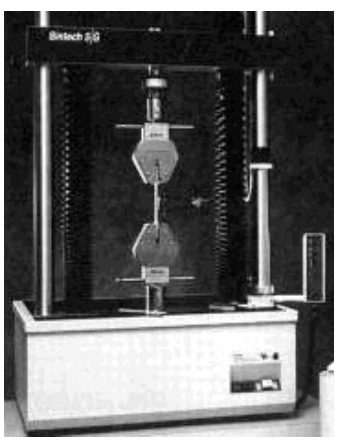
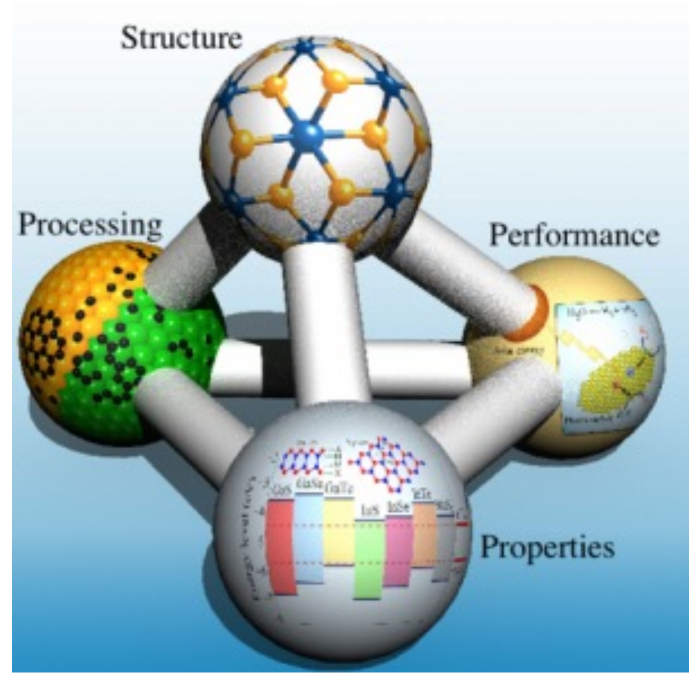


Image: P.S. Han, MTS Corporation

Properties

Performance

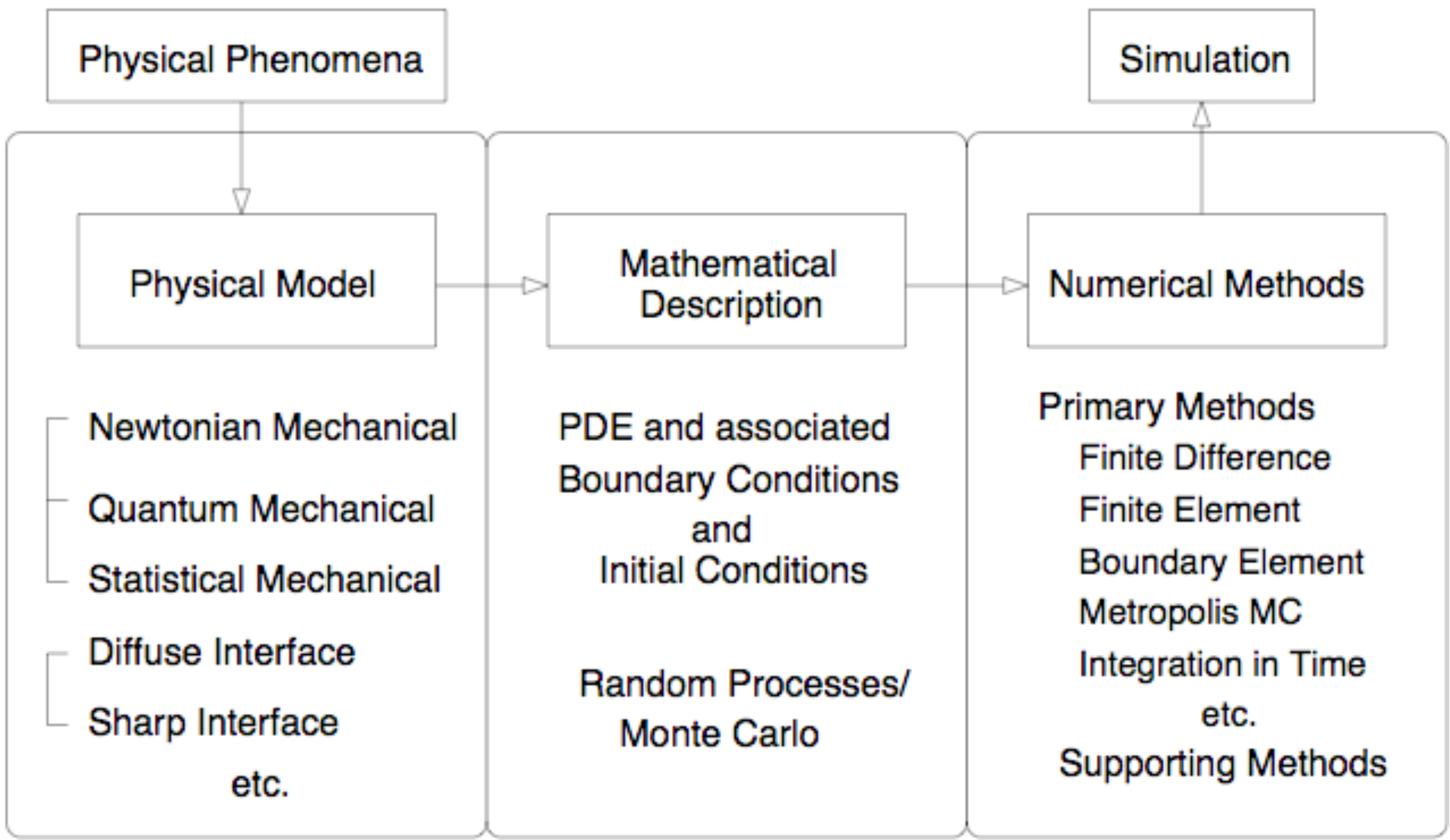
What is Computational MSE?



- MSE: Processing-Structure-Property-Performance
- Materials are governed by their underlying physics
- Their complexity often requires modeling and simulation
  - Modeling: determination of important physics
  - Simulation: prediction based on the model
- Computational MSE: studies of materials by modeling and simulations

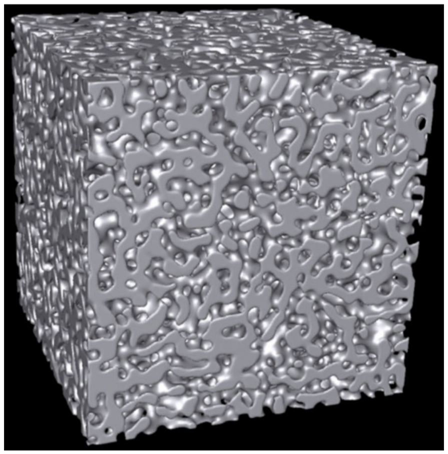
Image: Zhuang & Hennig, *JOM* **66**, 366–374 (2014)

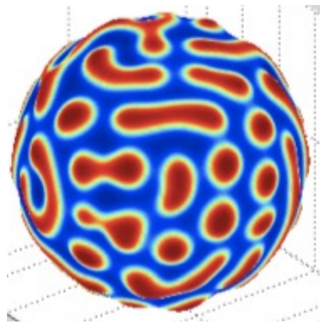
Approaches to Computational Modeling



Thornton’s Research Areas

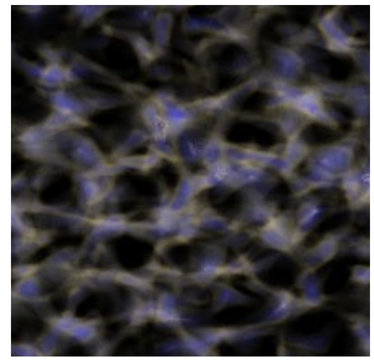
Microstructural Simulations

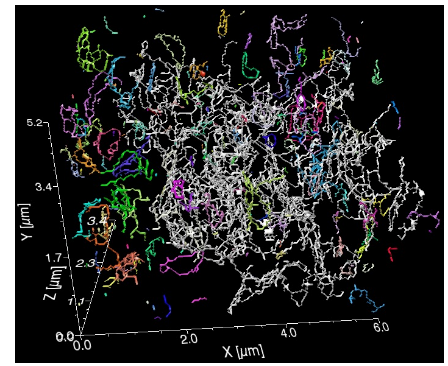




Funkhouser, et al. *J. Chem. Phys.* (2014)

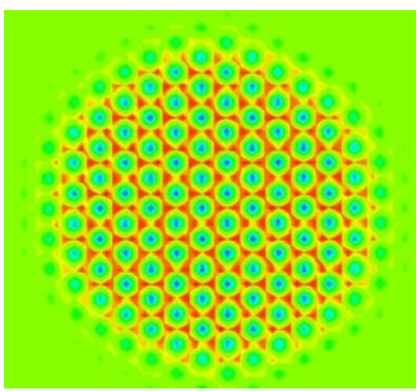
3D Characterization



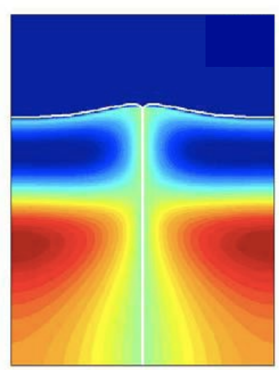


Wilson, James R., et al. *Nature Mat.* (2006)

Method Development



Phase field crystal

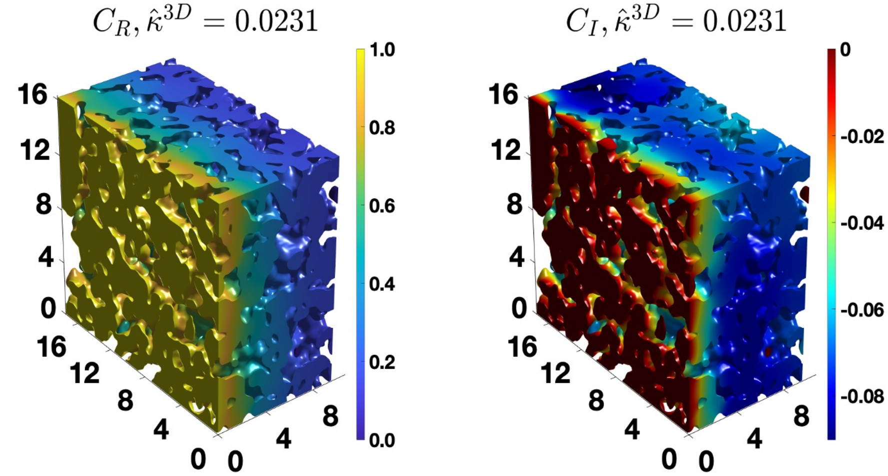


Smoothed boundary

Applications

- Nano/microstructural evolution (including self-assembly)
- Electronic materials
- Structural materials
- Biomaterials
- Energy materials

Electrochemical Phenomena

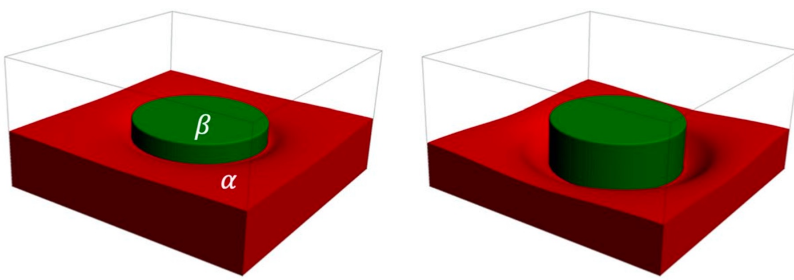


Electrochemical Devices

- Batteries
- Solid-oxide fuel cells/ electrolysis cells

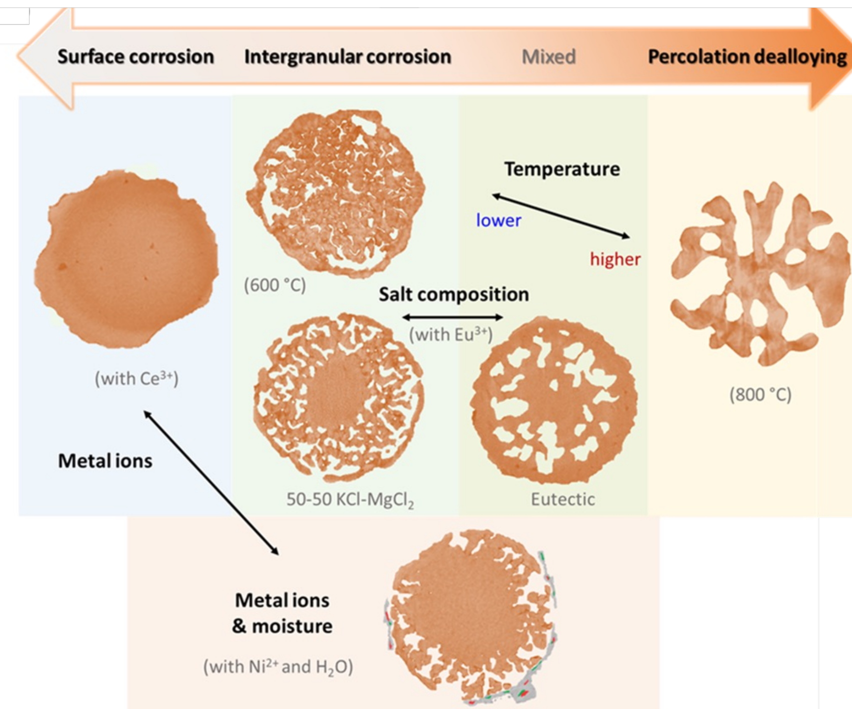
Corrosion

- Corrosion in aqueous solutions
- Corrosion in molten salt



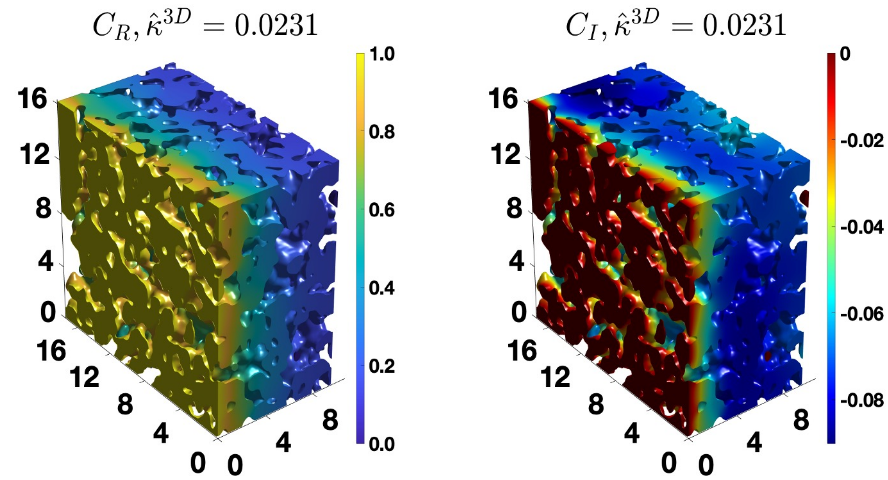
Microgalvanic corrosion

Goel et al. *MRS Communications*, **12**, 1050–1059 (2022)



Liu et al. *ACS Appl. Mater. Interfaces*, **16** (34) 45606–45618 (2024)

Electrochemical Phenomena



Electrochemical Devices

- **Batteries**
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Corrosion

- Corrosion in aqueous solutions
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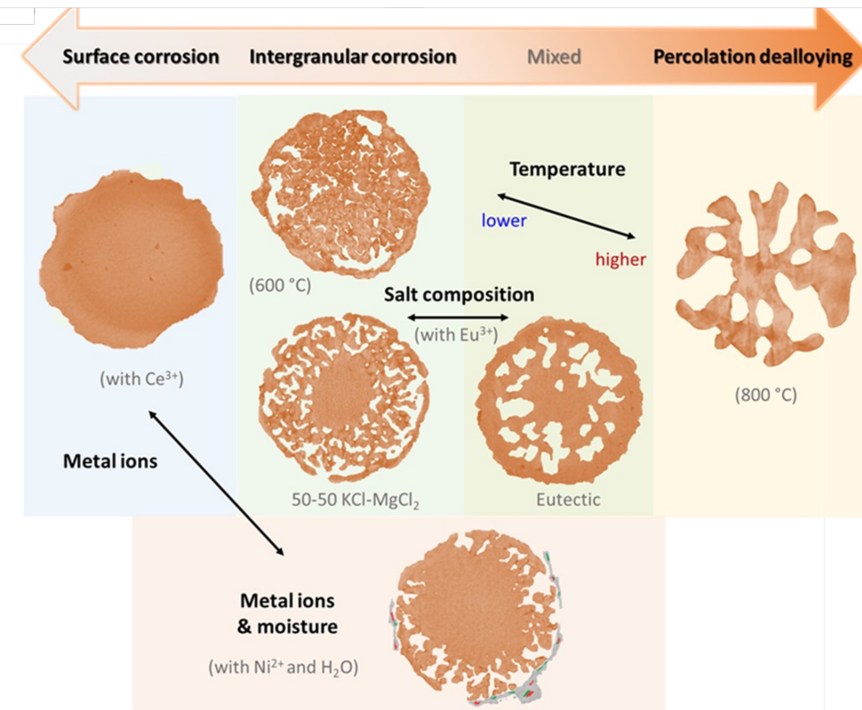

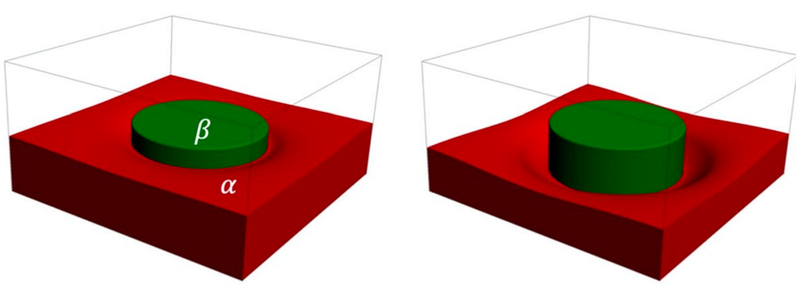

Microgalvanic corrosion

Goel et al. *MRS Communications*, **12**, 1050–1059 (2022)

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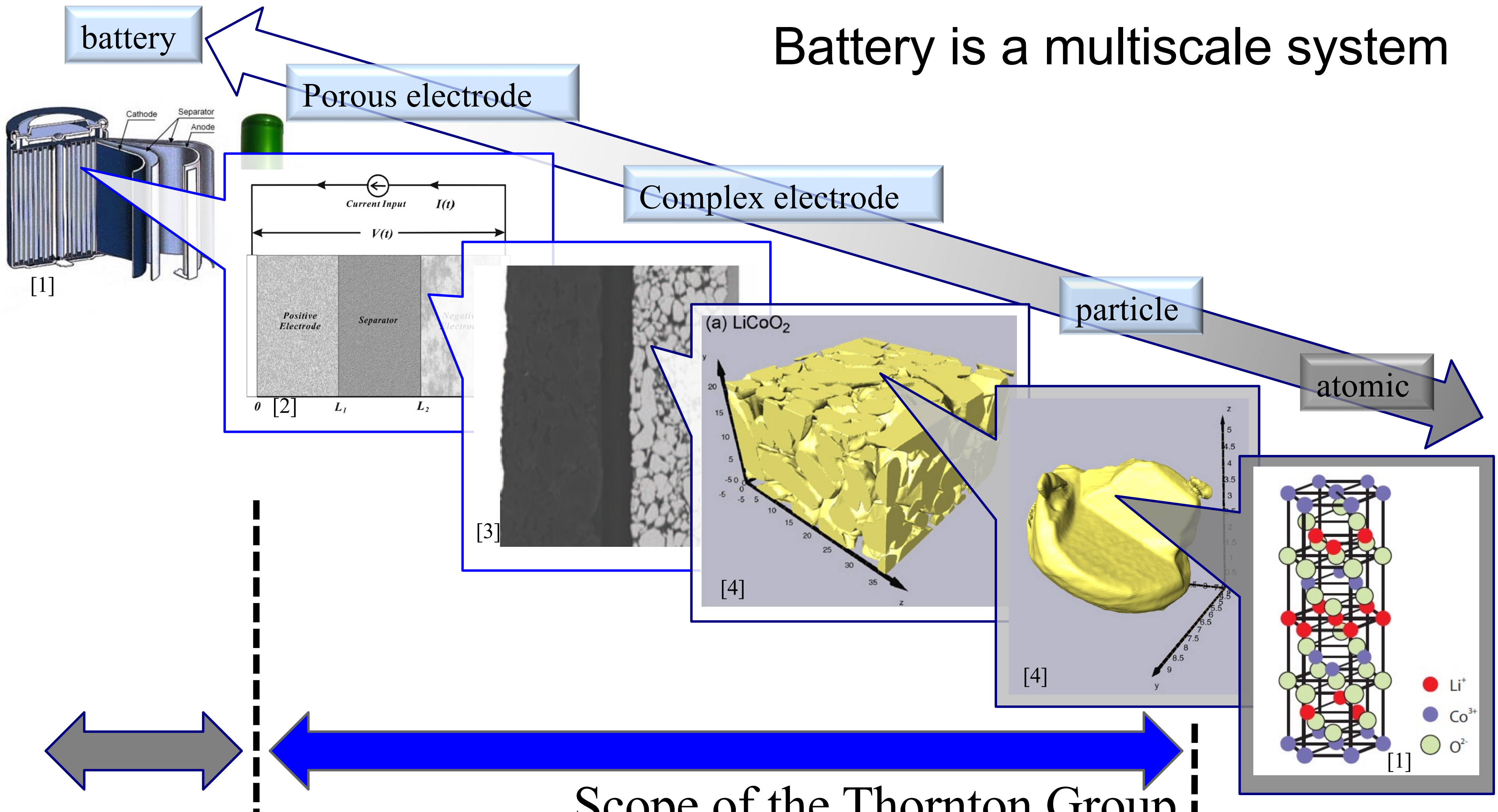
Electrochemical Simulations



Scope of the Thornton Group Research

[1] http://www.azonano.com
[2] Z. Shen *et al.*, *Dyn Sys Meas Cont* (2013)
[3] M. Smith *et al.*, *J Electrochem Soc* (2009)
[4] J. Wilson *et al.*, *J Power Source* (2011)

Background & Terminologies: Electrodes

- **Oxidation or reduction** half-reactions occur at appropriate electrode surfaces
- **Electrodes** can be a cathode or an anode, depending on the type of reaction. They are often a composite of **active electrode particles**, **electrolyte**, and **electronic conductor,** mixed with a binder.
- **Cathode**: electrode at which reduction occurs (electrons are gained by a species).
- **Anode**: electrode at which oxidation occurs (as electrons are lost by some species).
- **Electrolyte**: transports ions, but not electrons – **ionic conductor**. They are typically liquid (solvent and supporting ions), but solid-electrolyte-based batteries are under development.
- **Separator**: is an electrolyte and separates the anode and the cathode to avoid short-circuiting.

Simple batteries

What is a battery? Generally, it is a **device that can store electrical energy** in the form of **chemical energy**.

Anode (negative electrode): $Zn \rightarrow Zn^{2+} + 2e^{-}$ (oxidation)
Cathode (positive electrode): $2H^{+} + 2e^{-} \rightarrow H_2$ (reduction)
Electrolyte/separator

Anode (-) Cathode (+)

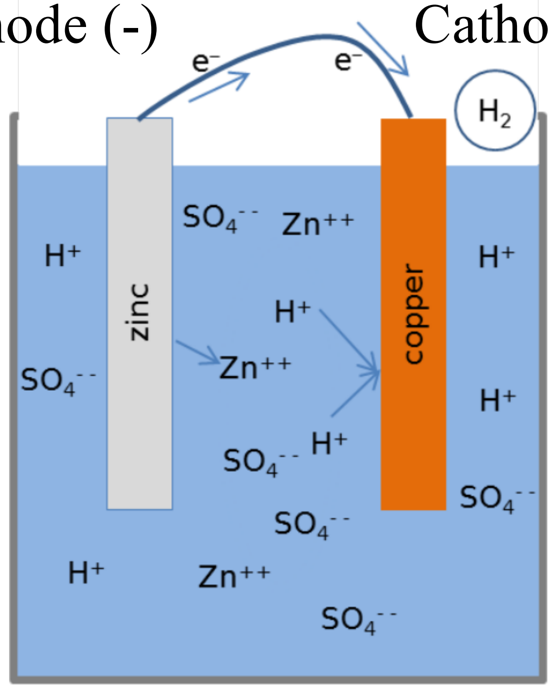
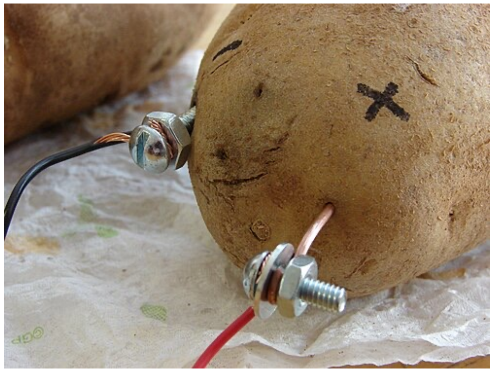
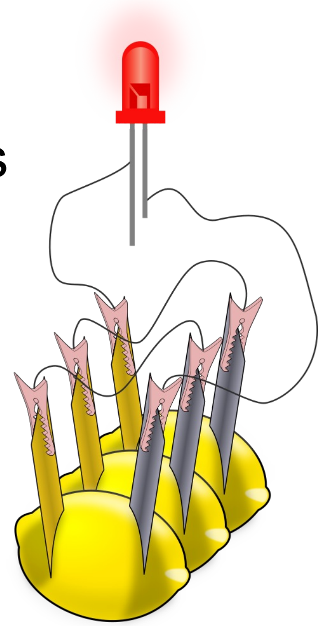


Figure credits: Wikipedia

Potato & lemon batteries

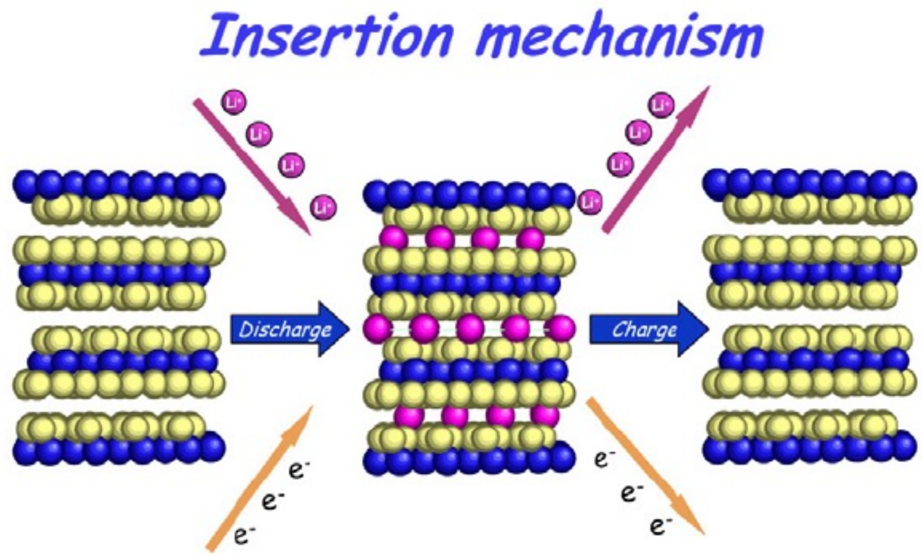




Traditional batteries can only discharge

Innovation: Li Intercalation Compounds

- The host structure remains intact during intercalation and de-intercalation.



Rozier et al. *Israel Journal of Chemistry* 48, 235 (2008)

- Avoids degradation over many, many cycles!
  - Coulombic efficiency (per cycle): the charge extracted to the charge put in.
  - Must be very close to 1. Even at 0.999, $(0.999)^{1000}$ <40%.

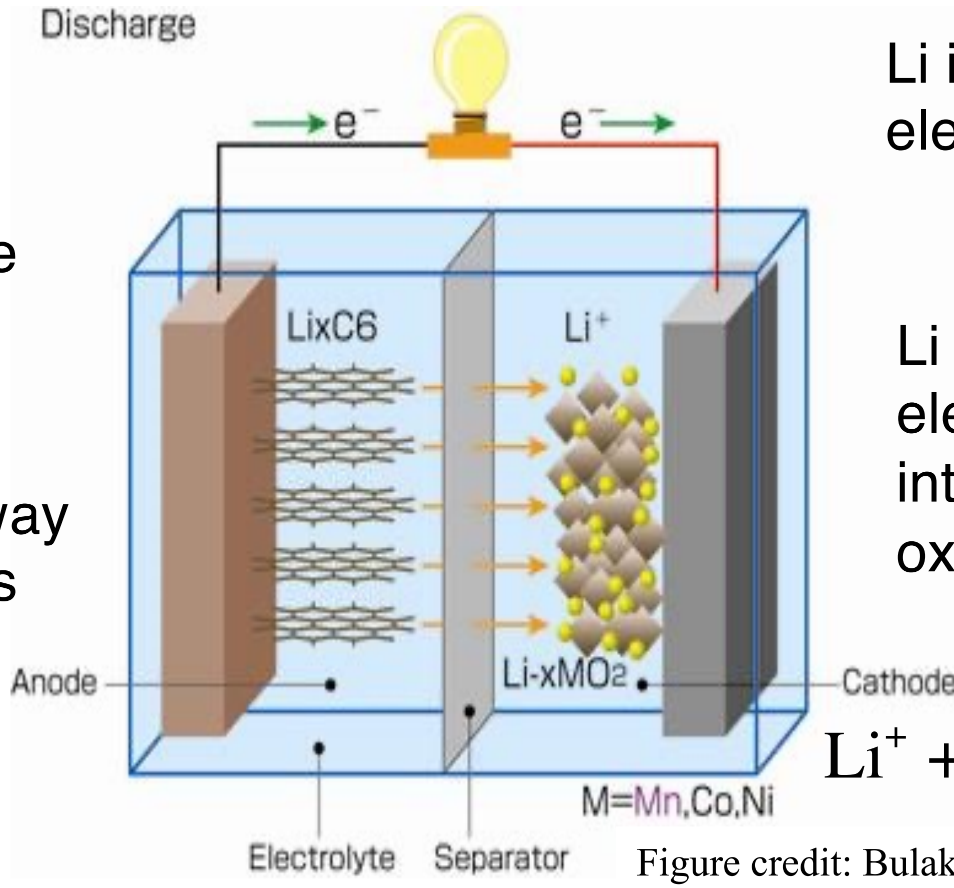
Innovation: Rechargeable Li-ion batteries

Li ions are shuffled back and forth between anode and cathode, making it possible to recharge the batteries

Electrons travel through the outside circuit

Metallic Li gives away electrons and forms Li ion at anode

$$Li \rightarrow Li^{+} + e^{-}$$



Li ions diffuse through electrolyte

Li ions react with electrons and insert into transition metal oxide cathode crystal

$$Li^{+} + e^{-} + MO_2 \rightarrow LiMO_2$$

Figure credit: Bulakhe, et al. (2021).
DOI: 10.1007/978-3-030-68462-4_16

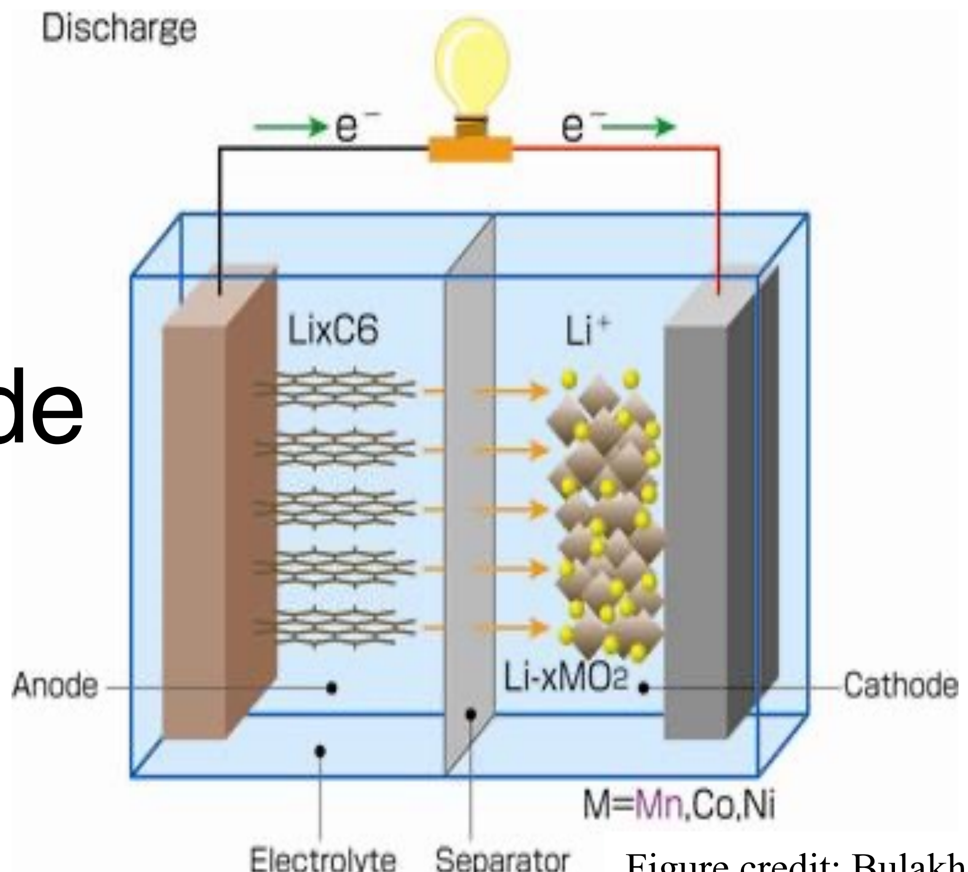
The anode/cathode term is based on the discharge process.

Why does this happen?

- Li has a lower *chemical potential* in the cathode than in the anode – that is, Li is thermodynamically more favorable to be in the cathode than in the anode.

Li in anode

(less happy)



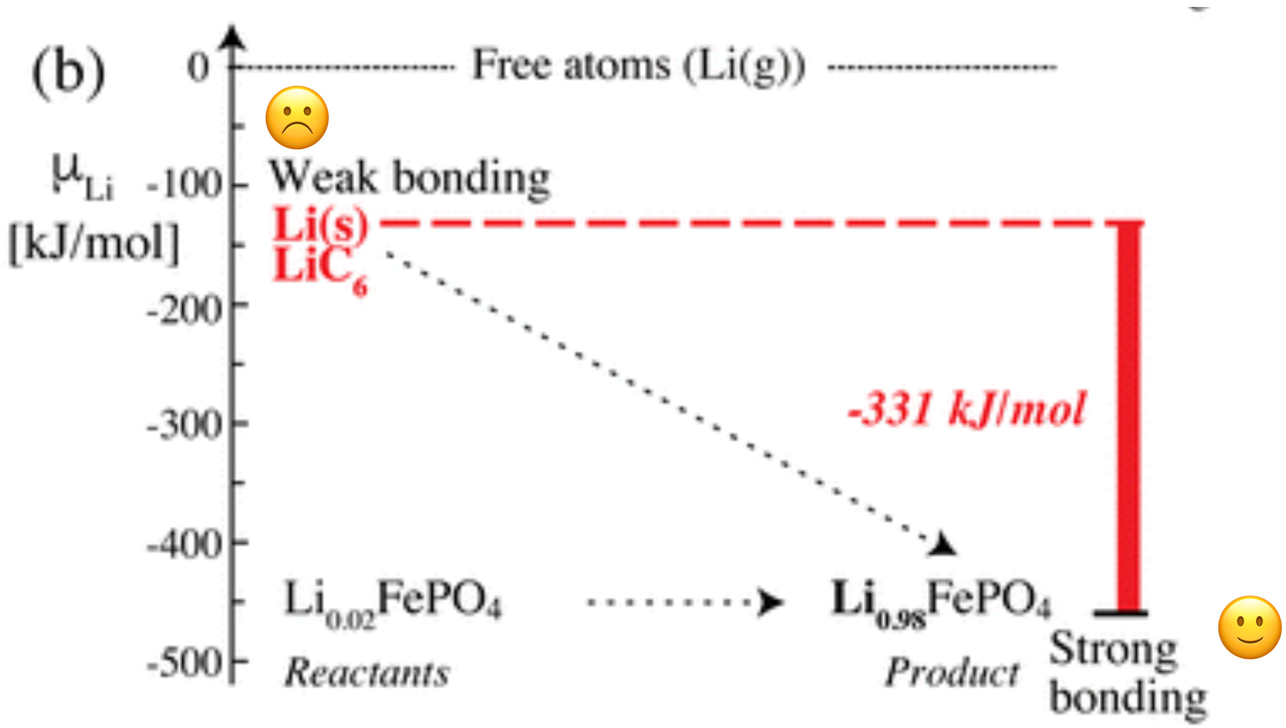
Li in cathode

(happier)

Figure credit: Bulakhe, et al. (2021).
DOI: 10.1007/978-3-030-68462-4_16

We can quantify the driving force

Example: Lithium iron phosphate (cathode material) vs. graphite

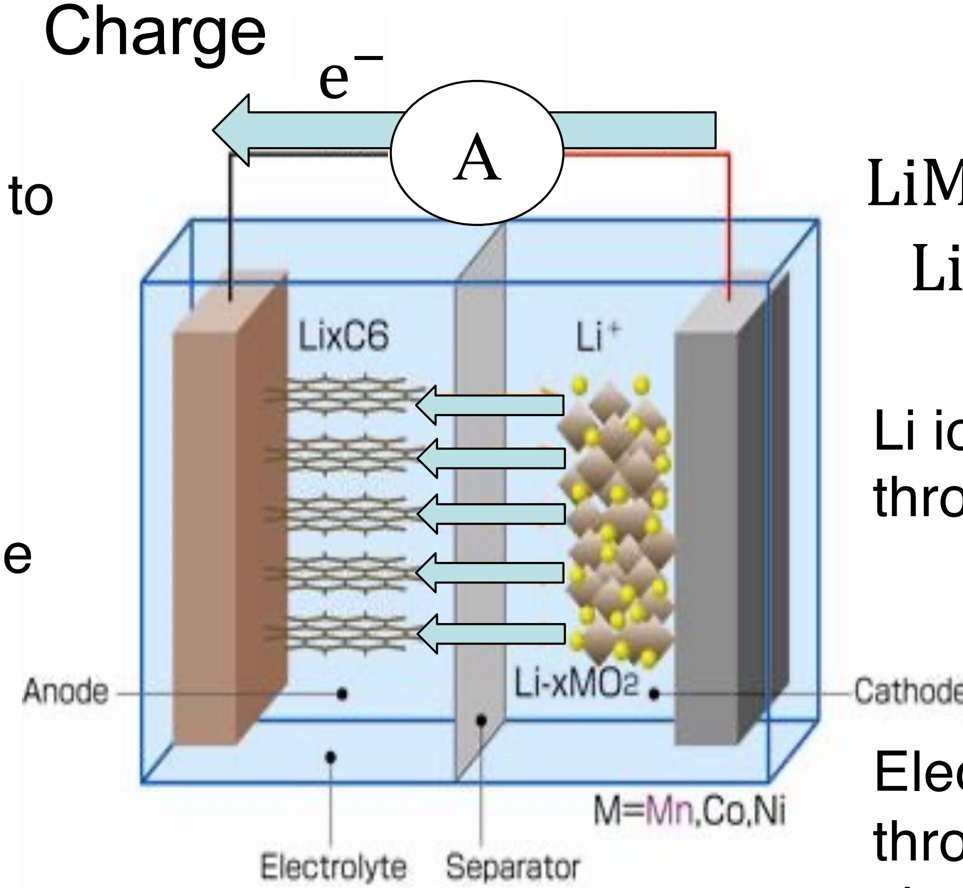


Finkelstein et al., *Phys. Chem. Chem. Phys.*, 2024, 26, 24157-24171

The charging process

Applied potential (to deliver a set current) reverses the direction of the electron and Li^+ flow such that Li^+ is extracted from the cathode and is intercalated into the anode.

Charge



Voltage is applied to attract Li^+ and e^- toward the anode

Li re-intercalates into graphite anode

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

$$LiMO_2 \rightarrow Li^+ + e^- + MO_2$$

Li ions diffuse/migrates through the electrolyte

Electrons move through the external circuit

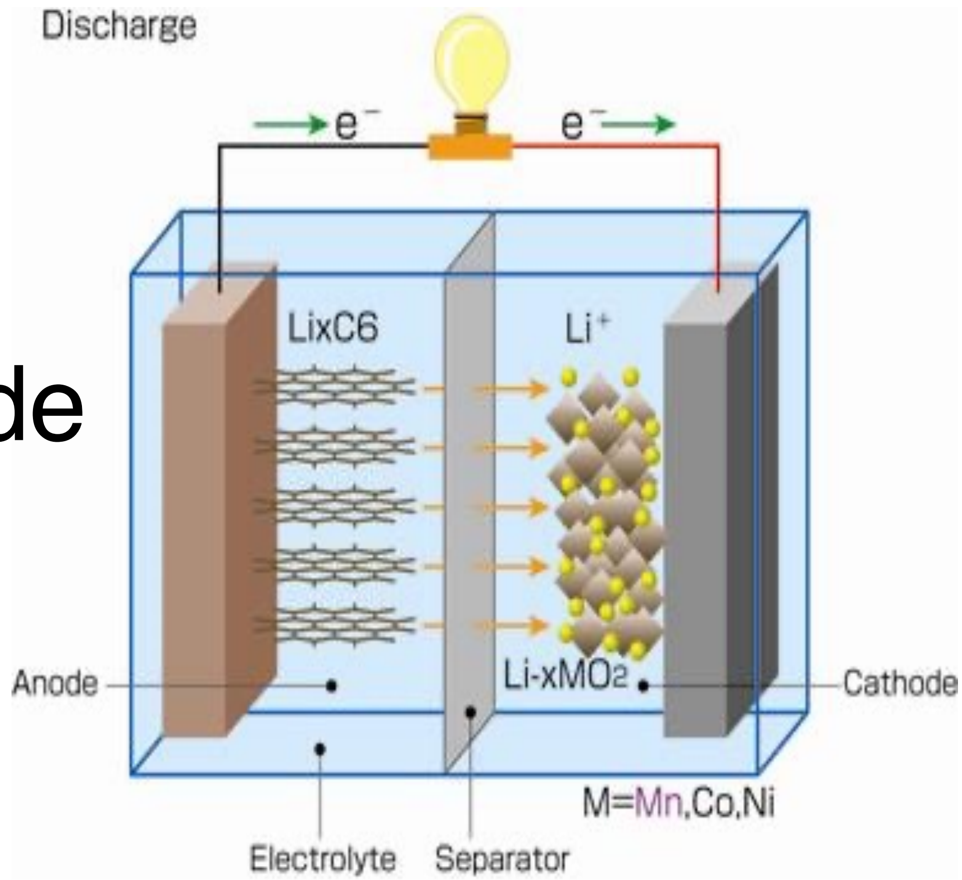
Figure credit: Bulakhe, et al. (2021).
DOI: 10.1007/978-3-030-68462-4_16

Why not 😄 in cathode?

- Question: Why I note 🙂 (happy) not 😄 (extremely happy)?

Li in anode ☹️

(less happy)



Li in cathode 🙂

(happier)

Figure credit: Bulakhe, et al. (2021).
DOI: 10.1007/978-3-030-68462-4_16

Quick review & question break

- Some general intro
- Terminologies:
  - Reactions: oxidation & reduction
  - Electrodes: anode (-'ve) & cathode (+'ve) – electrochemically active or a composite having active materials
  - Electrolyte: electrochemically inert, transports ion(s) only
- Simple batteries
- Rechargeable batteries:
  - Intercalation compounds
  - Discharge process & driving force
  - Charge process
- Questions?

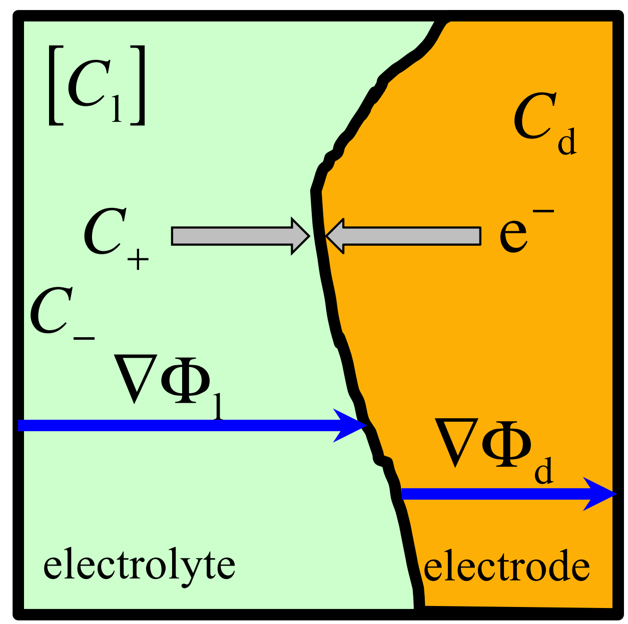
Continuum Modeling: the Big Picture

- The driving force for chemical transport is proportional to the gradient in chemical potential.
- Depending on the cathode materials, the system may remain single phase or phase separate.
- Single-phase intercalation compounds: Diffusion equation
- Multiphase intercalation compounds: Phase field equation
- These equations are coupled to the diffusion equation solved in the electrolyte region through the Butler-Volmer reaction rate.

Example: an electrochemical dynamics model of an electrode (part of a ½ cell)

Five physical processes and associated equations define the electrochemical model in the half cell:

1) Li diffusion/phase transformation in solid
2) Li ion transport in liquid
3) Current continuity in solid
4) Current continuity in electrolyte
5) Reaction at solid-liquid interface



Example: an electrochemical dynamics model of an electrode (part of a ½ cell)

Five equations: 1) diffusion in solid, 2) transport in liquid, 3) current continuity in solid, 4) current continuity in liquid, and 5) reaction at solid-liquid interface

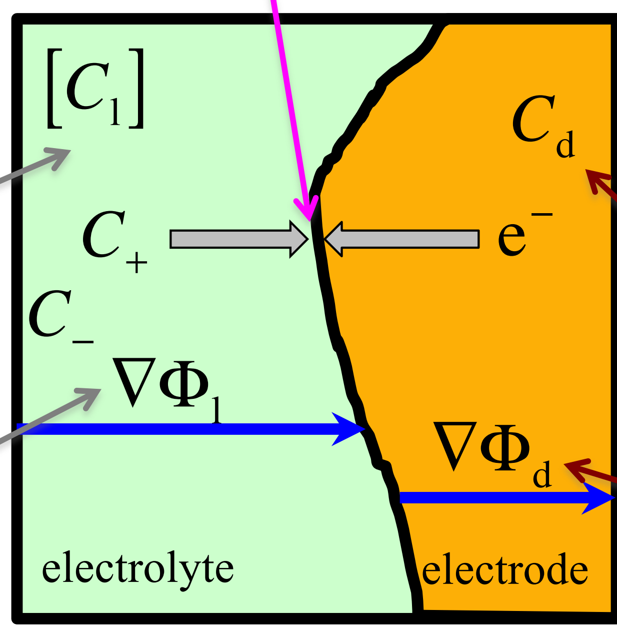
$$C_+ + e^- + X \to C_d X$$

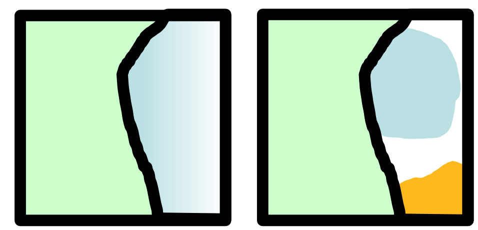
Butler-Volmer

$$R_{rxn} = \mathbf{n}\cdot \frac{\mathbf{i}}{z_+ F} = \frac{i_0\sqrt{a_l}}{F}\left[\exp\left(\frac{-\alpha F}{RT}(\phi_d - \phi_l - \phi_{eq})\right) - \exp\left(\frac{(1-\alpha)F}{RT}(\phi_d - \phi_l - \phi_{eq})\right)\right]$$

$$\frac{\partial C_l}{\partial t} = \nabla\cdot\left(D_l \nabla C_l\right) - \frac{\mathbf{i}\cdot\nabla t_+}{z_+ \nu_+ F}$$

$$F\nabla\cdot\left[\left(z_+u_+ - z_-u_-\right)C_l\nabla\Phi_l\right] = \nabla\cdot\left[\left(D_- - D_+\right)\nabla C_l\right]$$





$$\frac{\partial C_d}{\partial t} = \nabla\cdot\left(D_d \nabla C_d\right)$$

$$\nabla\cdot\left(\kappa_s \nabla\Phi_s\right) = 0$$

John Newman and Karen E. Thomas-Alyea. Electrochemical Systems. Wiley Inter-Science, third edition, 2004.

Traditional models for batteries

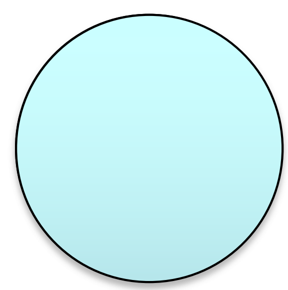
Various levels of assumptions have been made

Assume there is no microstructure

Or assume uniform concentration or analytical solution to 1D diffusion equation in particles

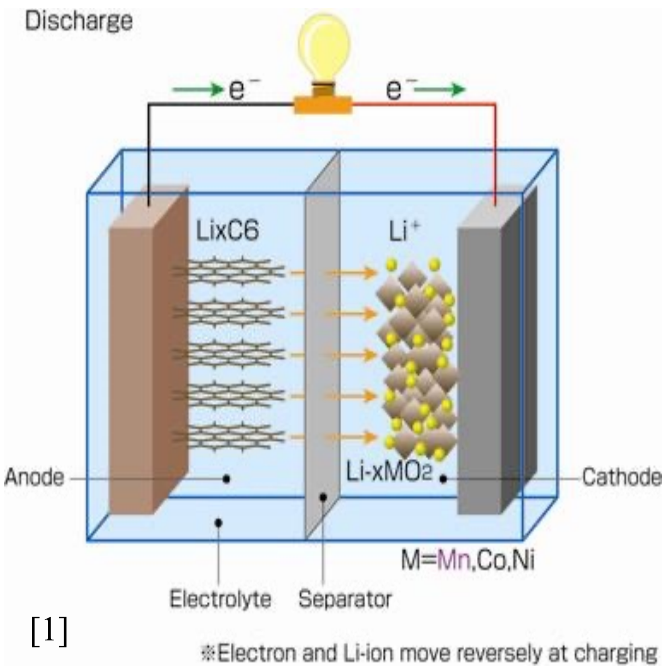
Or assume particles phase transform in a manner that can be described by spherical "shrinking core" model

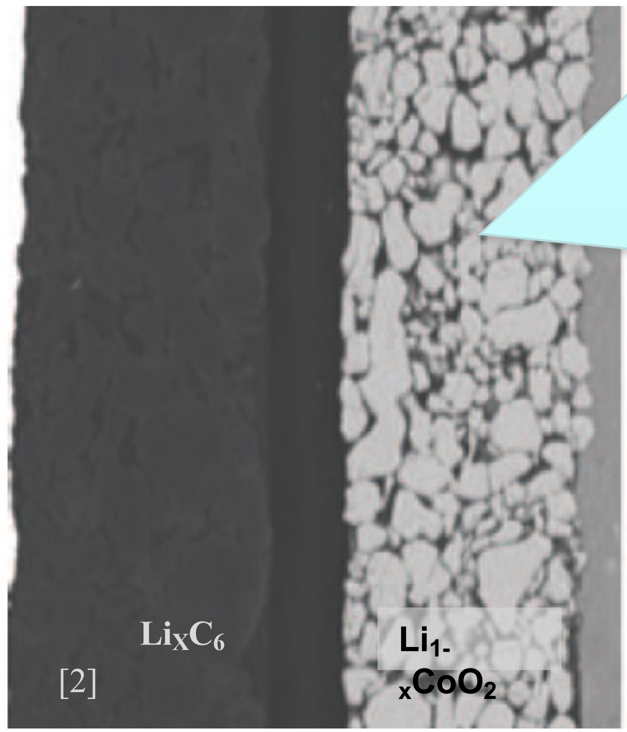
But…..

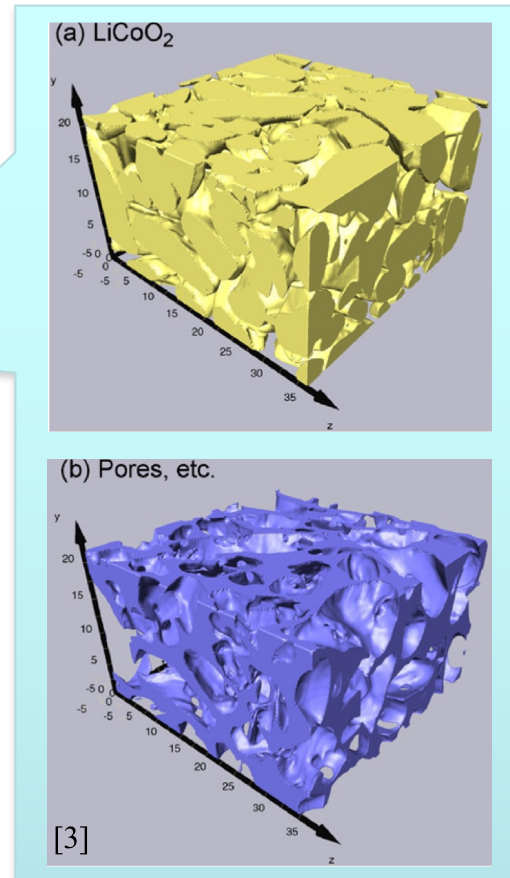


Microstructures in Li-ion batteries are complex!

– Tortuosity of ionic diffusion pathways, surface regions for reaction and percolation of electronic conducting pathways all affect electrochemical processes.







[1] Bulakhe, et al. (2021).
DOI: 10.1007/978-3-030-68462-4_16

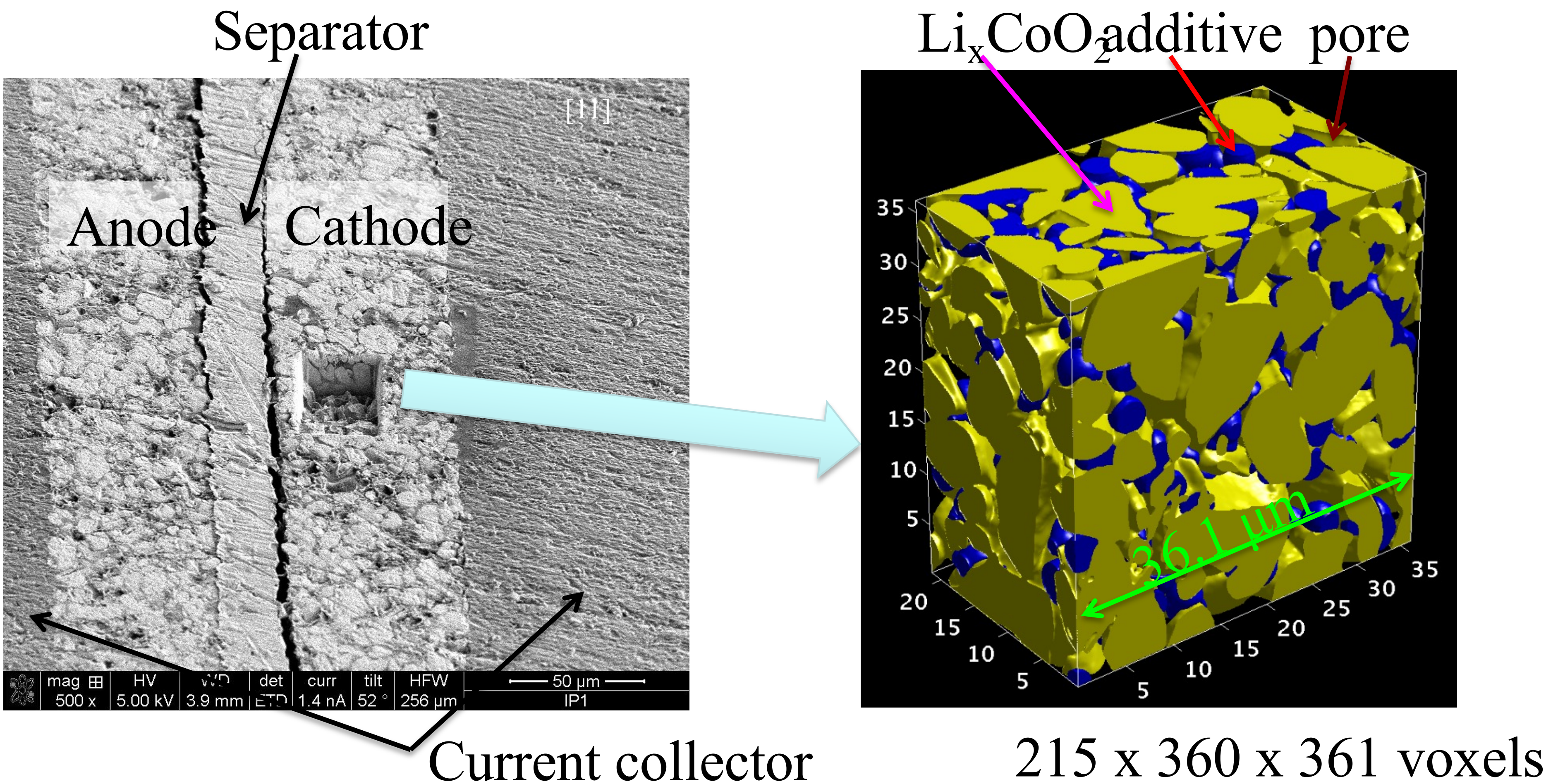
[2] Smith et al, *J Electrochem Soc*, (2009)

[3] Wilson et al, *J Power Source*, (2011)

Complex Microstructure of $LiCoO_2$ Cathode (Scott Barnett, Northwestern)

Wilson et al, *J Power Source*, (2011)

Using FIB-SEM to obtain microstructure (sample from a laptop battery)

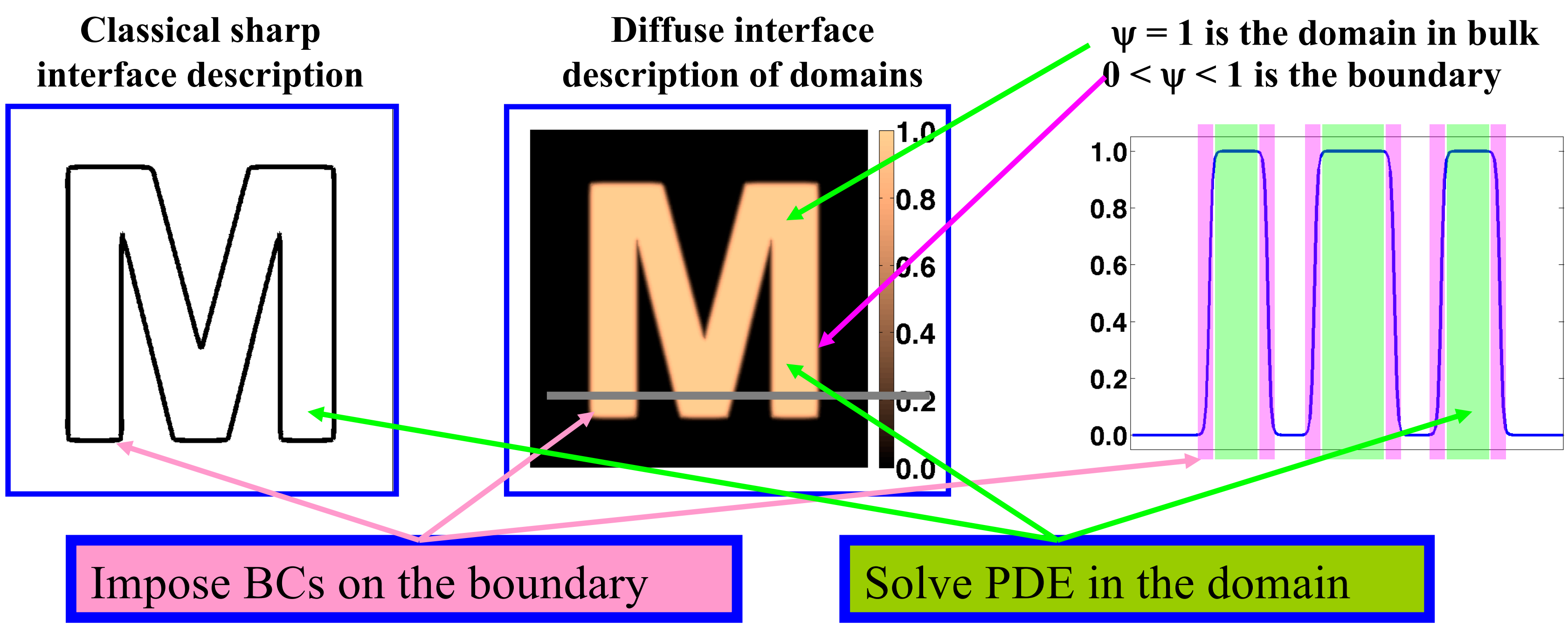


Smoothed Boundary Method

First developed by A. Bueno-Orovio[1] for solving diffusion equation with no-flux BC at a diffuse boundary, but with no derivation.

Use a continuous phase-field-like parameter to define domain of interest, and impose boundary conditions at the diffuse interfaces.

A similar methods were also developed by J. Lowengrub and A. Voigt.[2]



[1] Bueno-Orovio et al, *Appl Math Comput* (2006); Bueno-Orovio et al, *Numer Meth Part D E* (2006); Bueno-Orovio et al, *SIAM J Sci Comput* (2006). [2] X. Li et al, *Commun Math Sci* (2009); K. E. Teigen et al, *Commun Math Sci* (2011).

SBM for diffusion equation

Example: Neumann boundary condition

$$\frac{\partial C}{\partial t} = \nabla \cdot \left(D \nabla C \right)$$

$$\psi \frac{\partial C}{\partial t} = \nabla \left(\psi \cdot D \nabla C \right) - \nabla \psi \cdot \left(D \nabla C \right)$$

$$\psi \left(\frac{\partial C}{\partial t} = \nabla \cdot \left(D \nabla C \right) \right)$$

$$\psi \frac{\partial C}{\partial t} = \nabla \left(\psi \cdot D \nabla C \right) - \nabla \psi \cdot \left(D \nabla C \right)$$

≠0 only where PDE valid

$$\psi \frac{\partial C}{\partial t} = \psi \nabla \cdot \left(D \nabla C \right)$$

$$\psi \frac{\partial C}{\partial t} = \nabla \left(\psi \cdot D \nabla C \right) - \nabla \psi \cdot \left(D \nabla C \right)$$

≠0 only on boundaries

$$\psi \frac{\partial C}{\partial t} \neq \nabla \psi \cdot \left(D \nabla C \right)$$

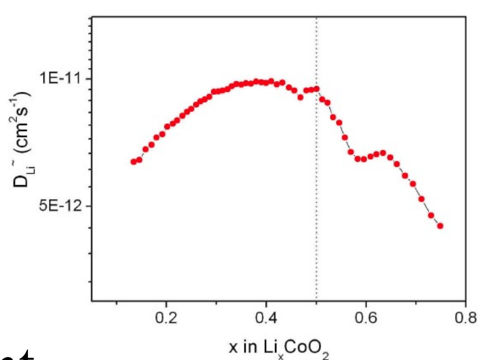
$$\psi \frac{\partial C}{\partial t} = \nabla \left(\psi \cdot D \nabla C \right) - \nabla \psi \cdot \left(D \nabla C \right) \Big|_{BC}$$

Finite difference implementation allows for highly scalable parallel computation

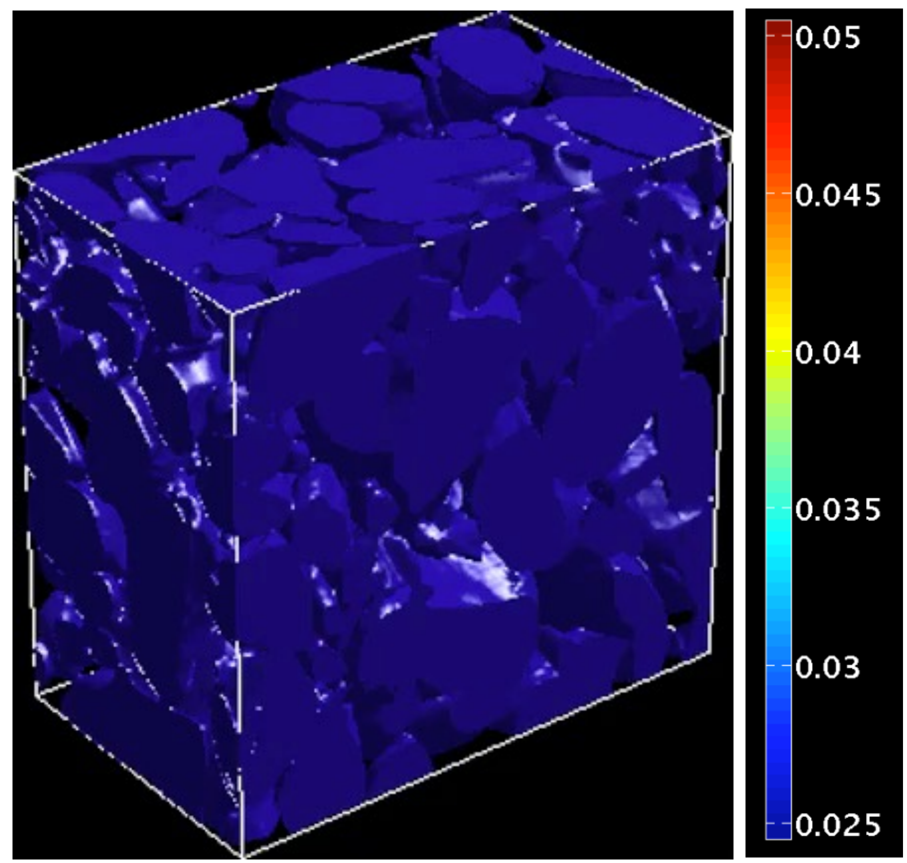
3D Simulation of Electrochemical Process in Complex Microstructure

Li concentration evolution in cathode during discharge-charge process.

Discharge condition: 3.85 V across the specimen
State of Charge (SOC):
0.5 → 0.99
Charge condition:
4.15 V across
SOC: 0.99 → 0.55

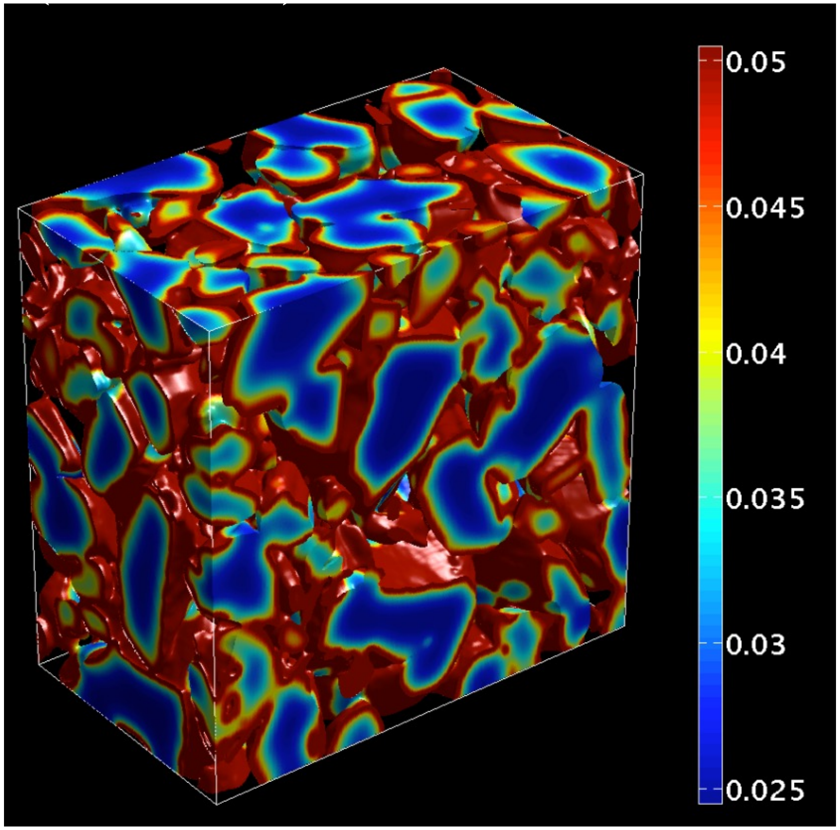


Concentration-dependent diffusivity from first principles (Xia et al. JPS, 159, 1422 (2006))

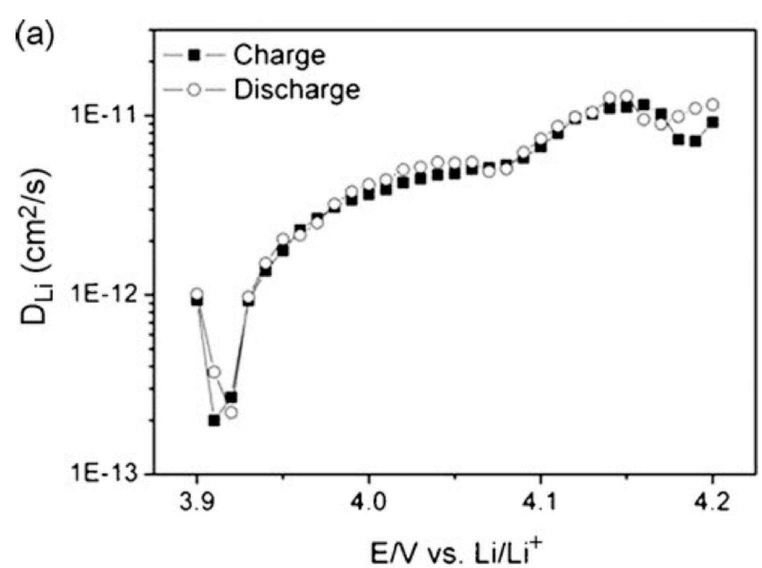


Li concentration (mol/cm^3)

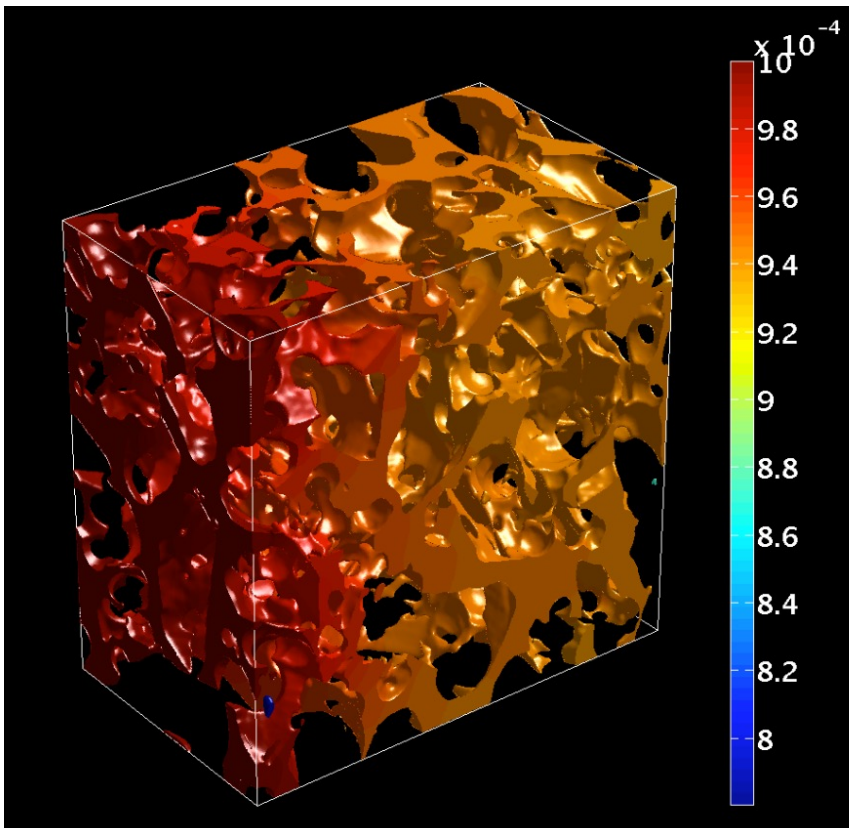
Li Concentration in Complex Microstructure: Particles



- Even without the miscibility gap, morphologies similar to “shrinking core” observed due to the concentration dependence of diffusivity.
- Details of diffusivity must be taken into account.
- Interpretation of thermodynamics and experiments needs care.



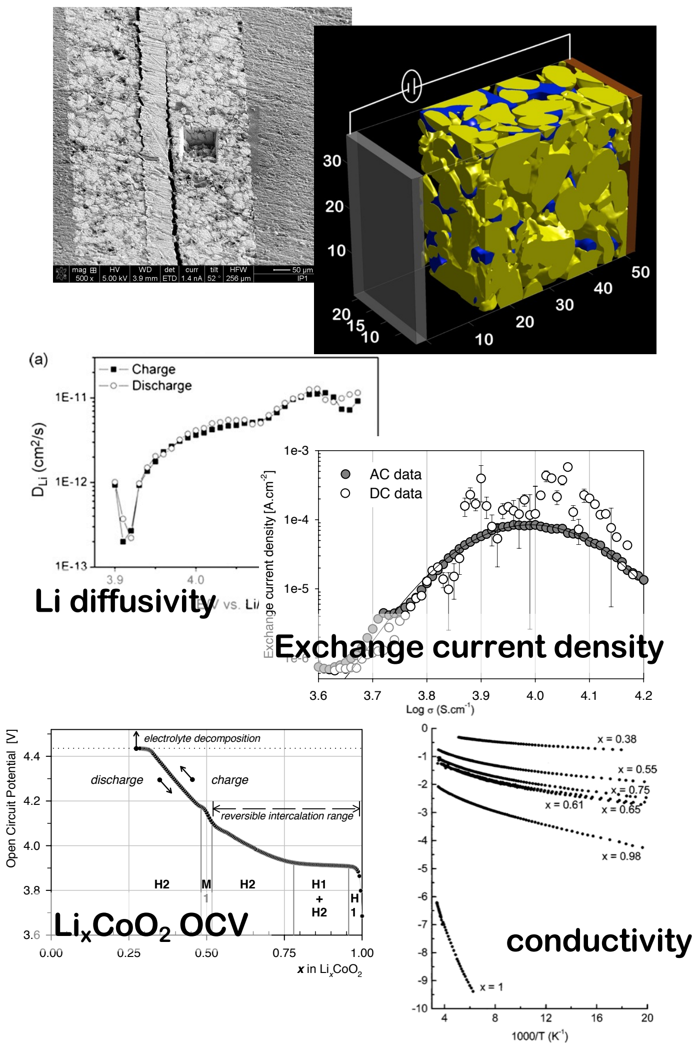
Li Concentration in Complex Microstructure: Electrolyte



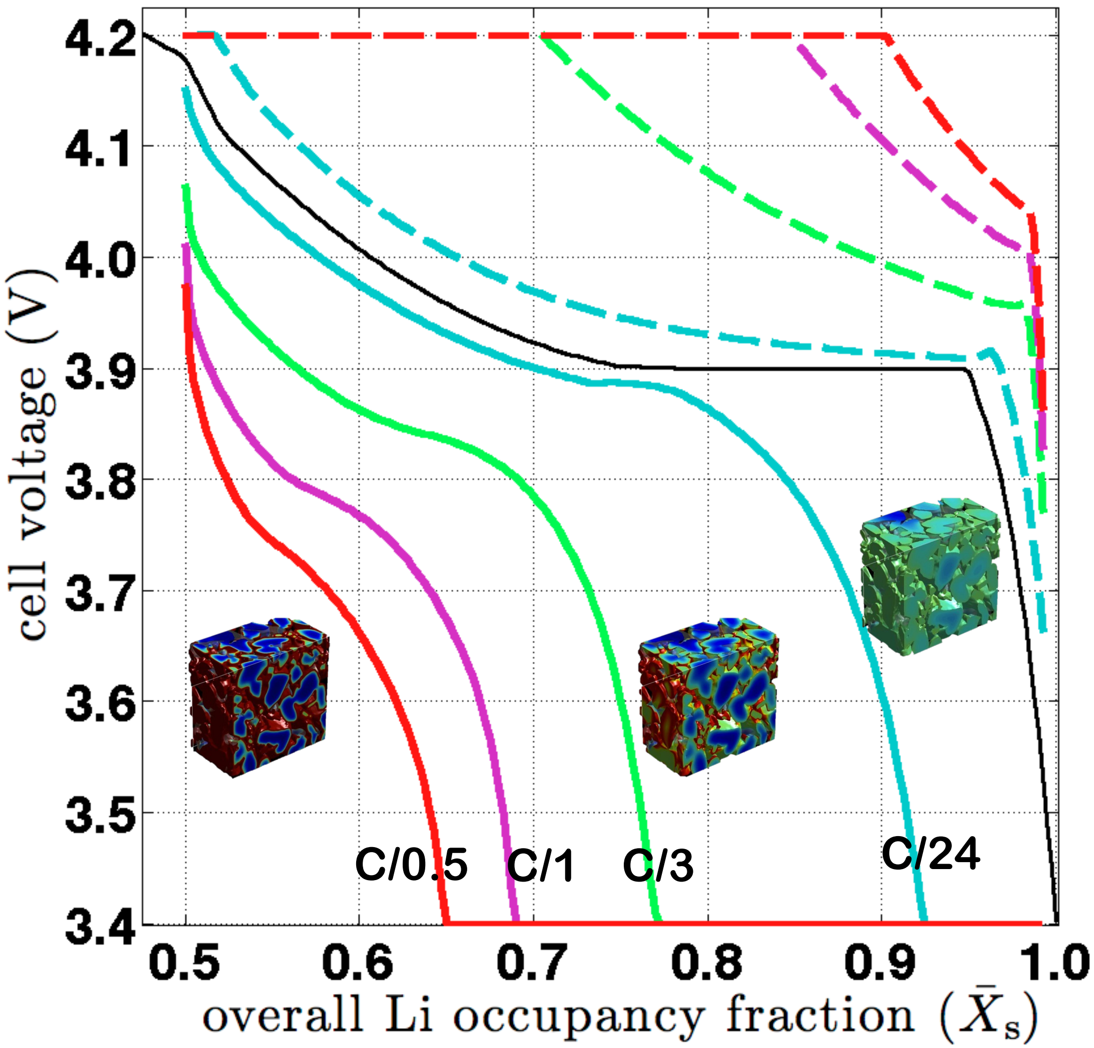
- Even though the diffusivity in electrolyte is six magnitude greater than in solid particles, the concentration is not constant.
- Significant concentration depletion across the cathode due to the complex diffusion channel.
- An accurate model must take this into account.

Electrochemical Simulation: Li_xCoO_2

Experimentally measured input parameters



Simulated cell voltage at different C-rates



[1] H. Xia *et al.*, *Electrochim Acta* (2007)
[2] P. J. Bouwman, Ph.D. Thesis (2002); [3] D. Carlier *et al.*, *J Electrochem Soc* (2002)

Questions simulations can be used to answer

Virtual discharge-charge cycling of batteries:

- How do microstructure affect the rate?
- How much stress results during the cycle? How can we reduce it?
- What kind of materials would perform better?
- **If there are new theories/expressions/values for material parameters, how does it affect the overall performance of the device?**

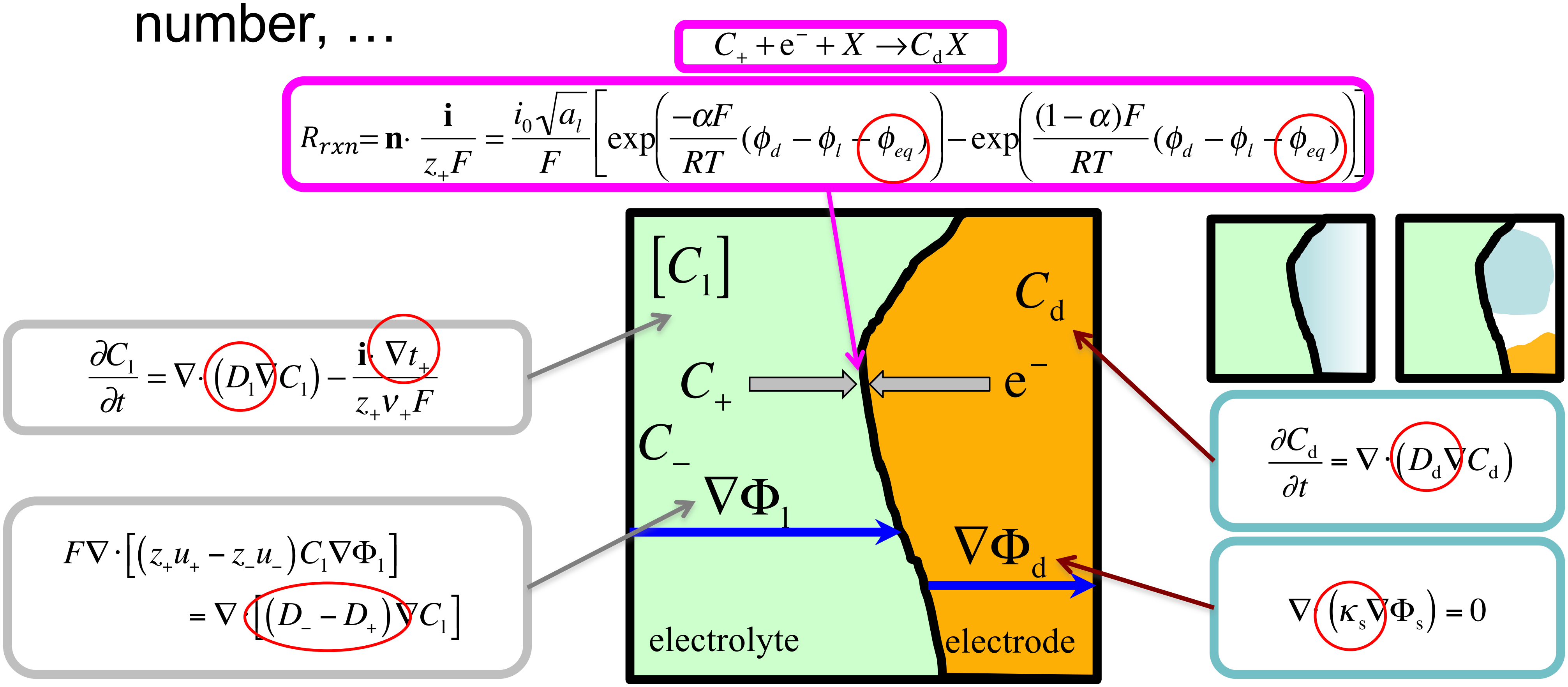
A quick review & question break

- Governing equations
  - Different equations in different material phases
  - Based on mass conservation and current continuity (charge conservation, coupled with reaction rate (Butler-Volmer)
- Microstructure of electrodes
- Smoothed Boundary Method (SBM)
- Example simulation results
- Material properties needed for electrochemical dynamics modeling

- Questions?

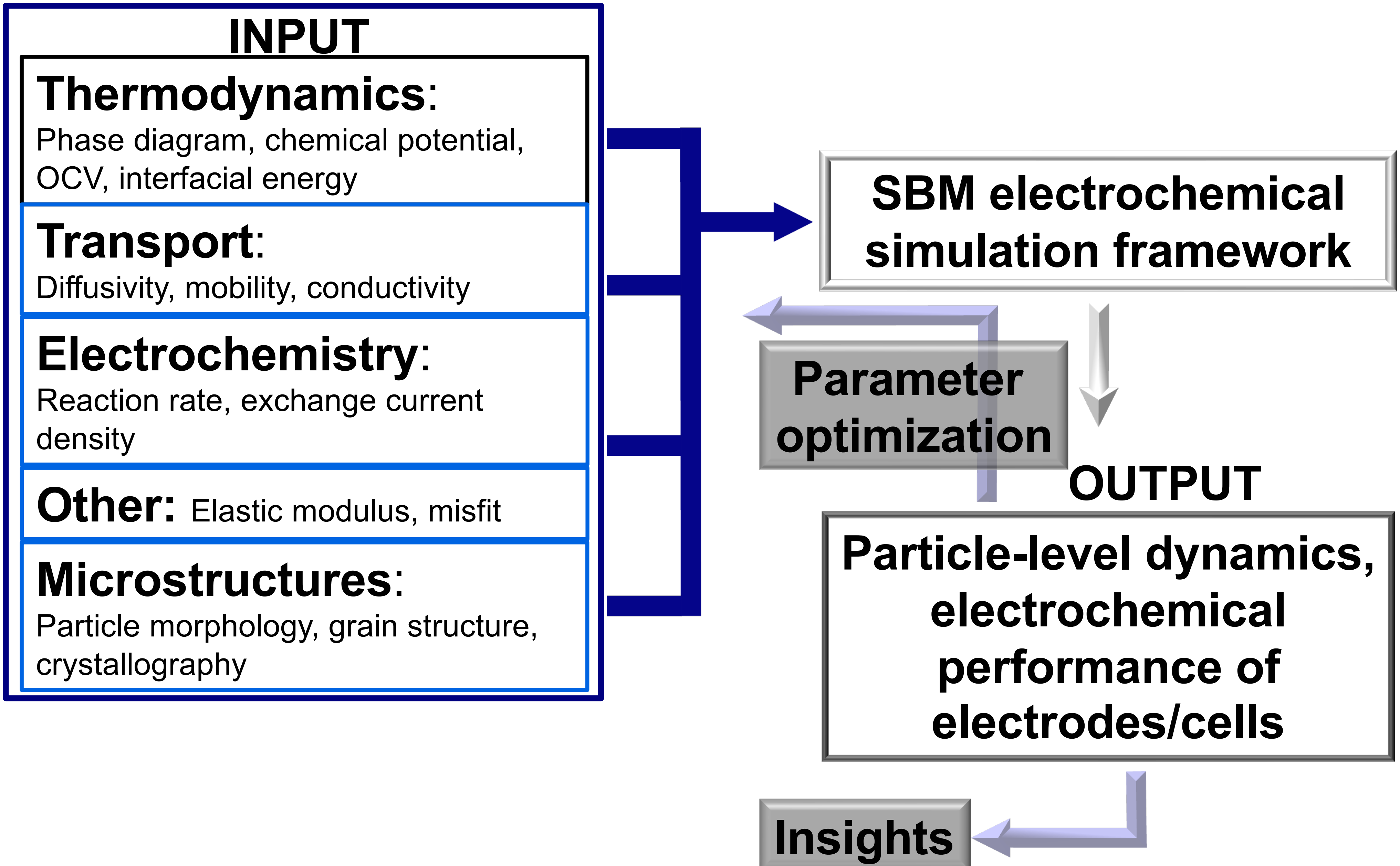
What material properties do we need?

Key parameters: Open circuit voltage (or chemical potential); ionic diffusivity/conductivity; electronic conductivity; exchange current density; transference number, …



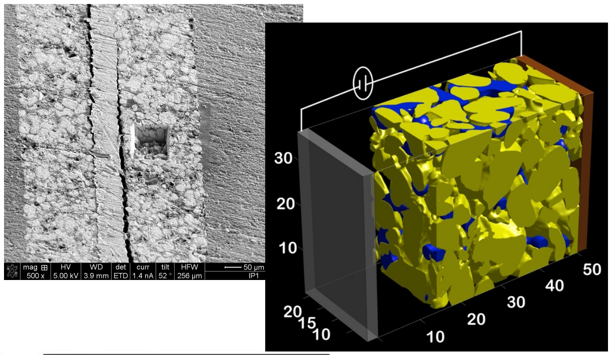
John Newman and Karen E. Thomas-Alyea. Electrochemical Systems. Wiley Inter-Science, third edition, 2004.

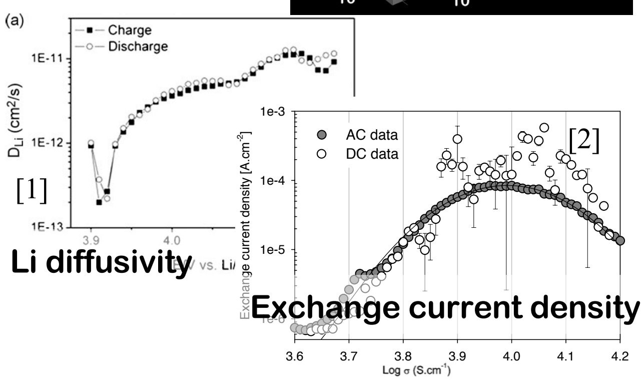
Structure of Simulation Framework

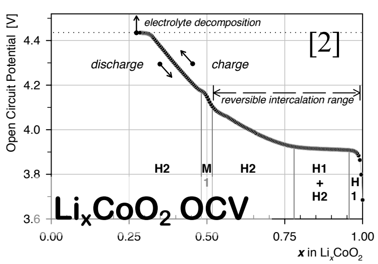


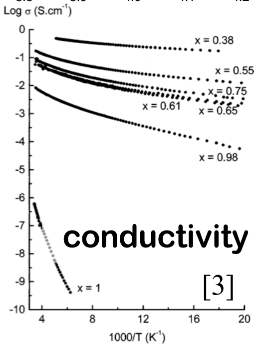
Electrochemical Simulation: Lithium Cobalt Oxide (LCO)

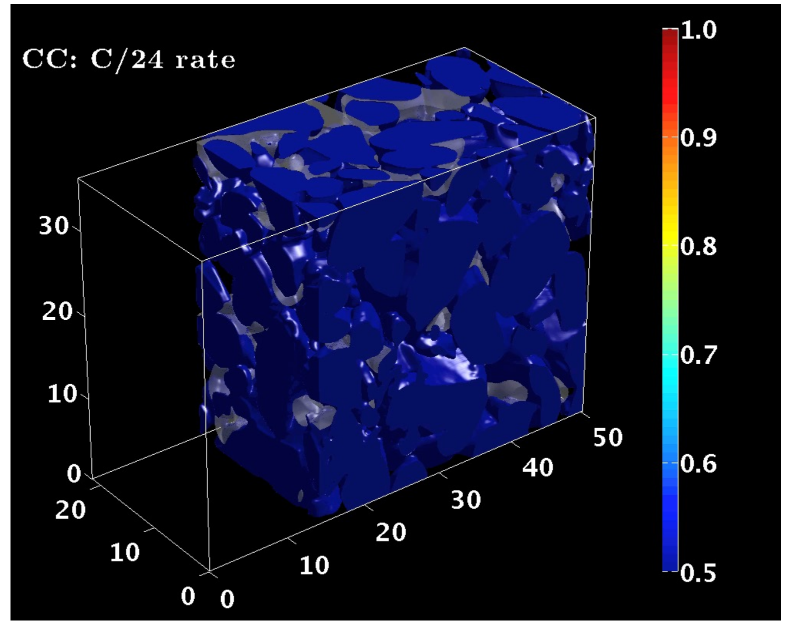
Experimentally measured input parameters

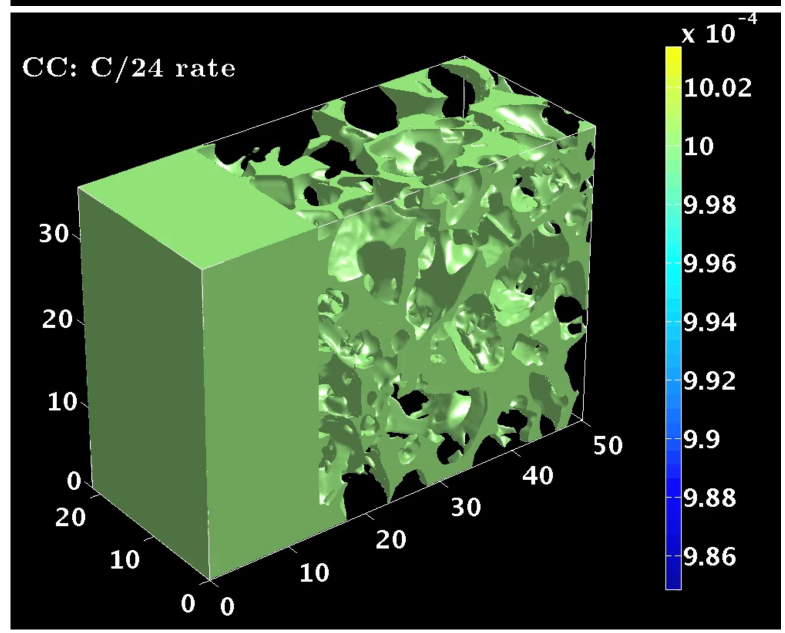












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How are they measured?

Open circuit voltage: Charge/discharge a battery, ideally with a reference electrode, VERY SLOWLY (~C/30).

Diffusivity in the active materials: PITT (potentiostatic intermittent titration technique) or EIS (electrochemical impedance spectroscopy) and fit. But different techniques often give contradictory values.

Exchange current density: Potential sweep to obtain I-V curves to obtain a Tafel plot, and then extrapolate to the equilibrium potential. Challenge: not the entire electrode is active; the active area is not known.

Conductivity: I-V curve on individual component.

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But sometimes these quantities can be obtained via lower-scale (e.g., atomistic) simulations!