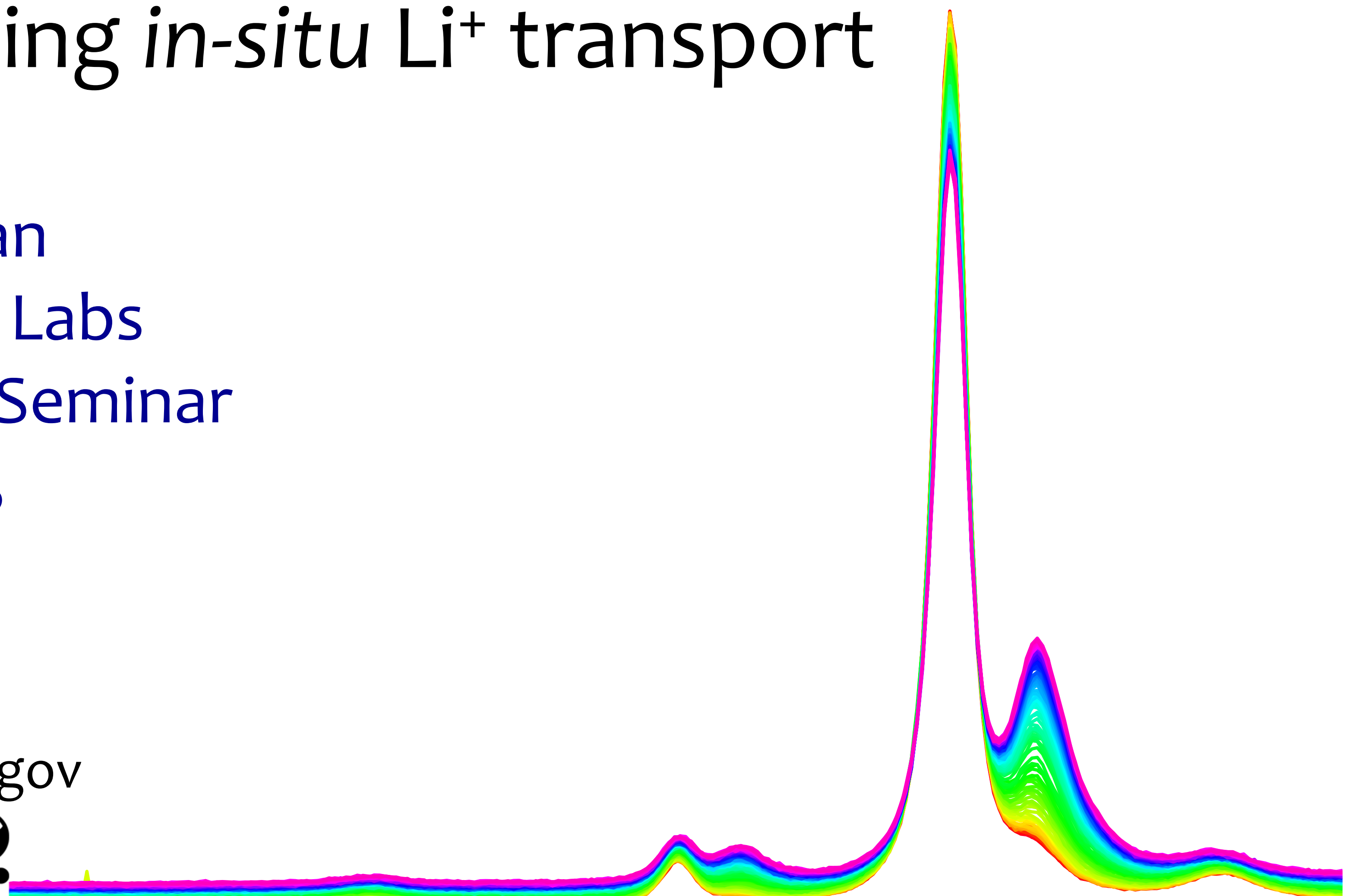
A front-row seat to electrochemical systems in action: observing *in-situ* Li^+ transport

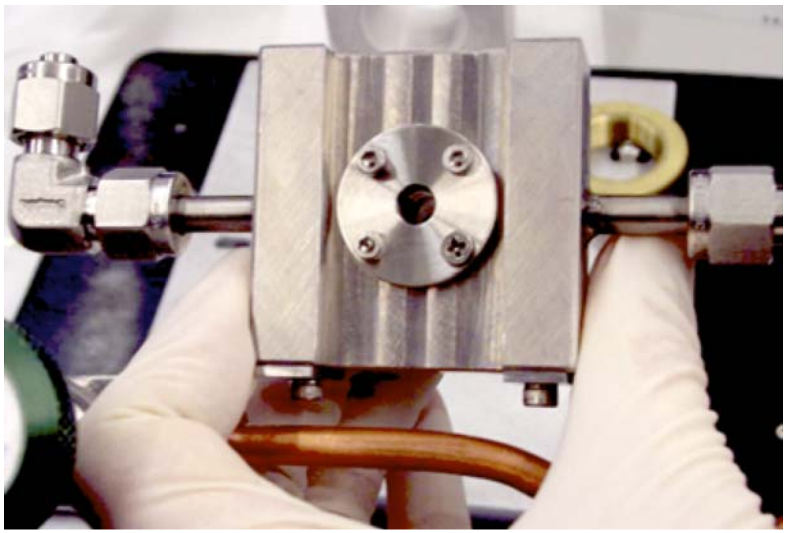


Jeff Urban
Berkeley Labs
NCCAVS Seminar
9/10/2013

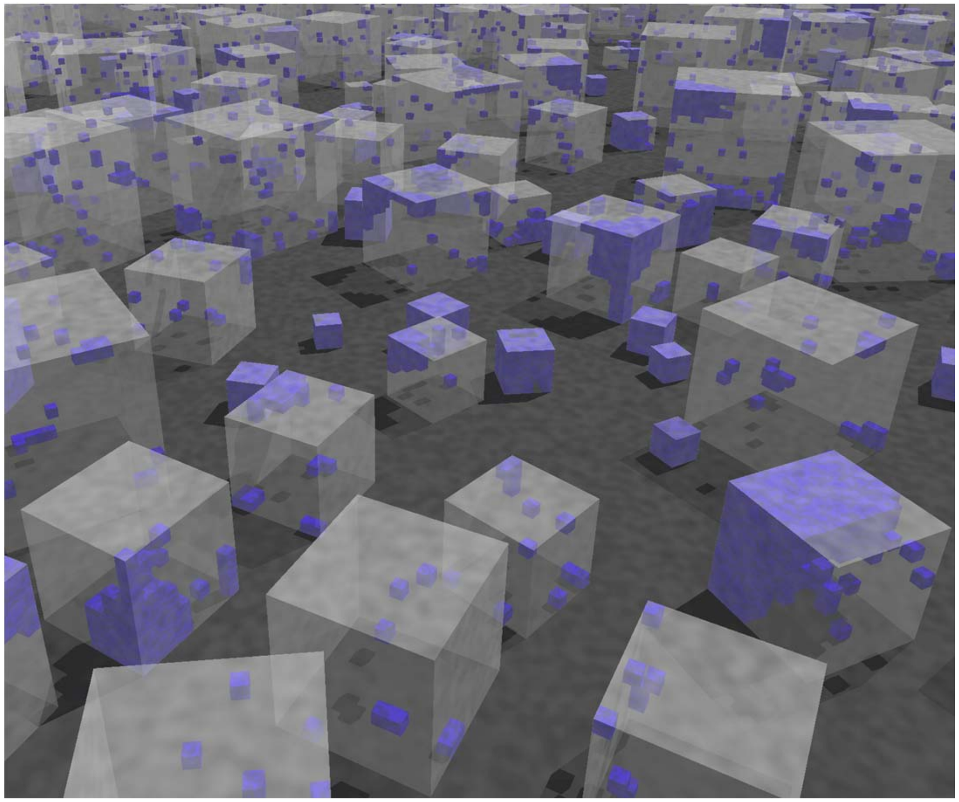
Foundry.lbl.gov

Molecular Foundry

Direct observation of systems *in-situ* provides insight into material transformations

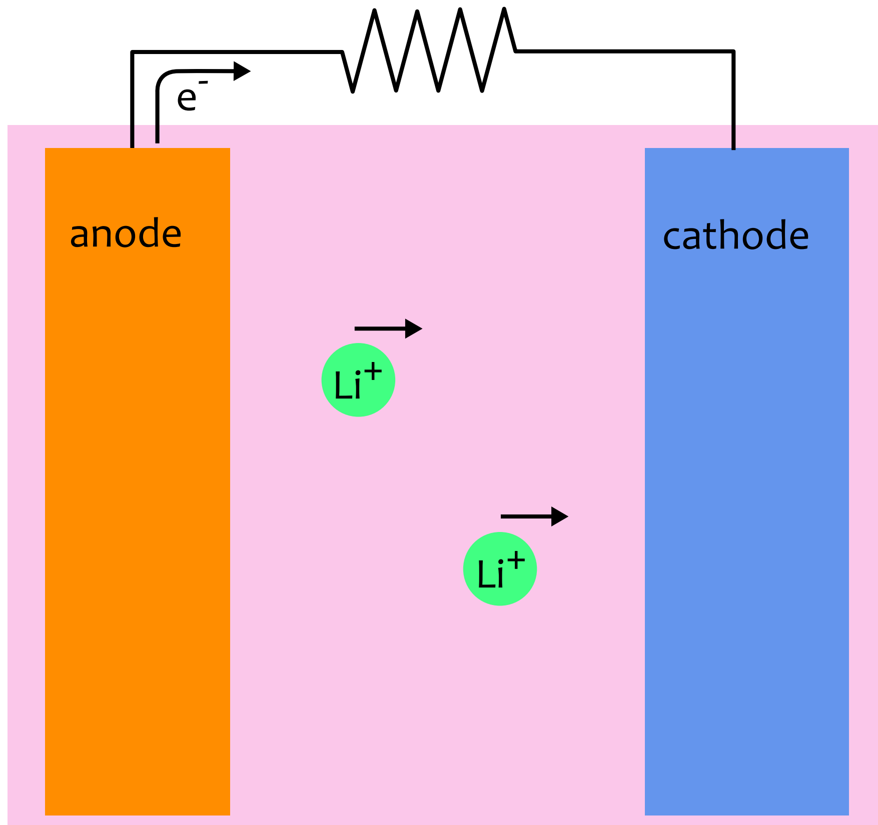


Derived first size-dependent scaling laws for alloying phase transitions (Pd-H_2)

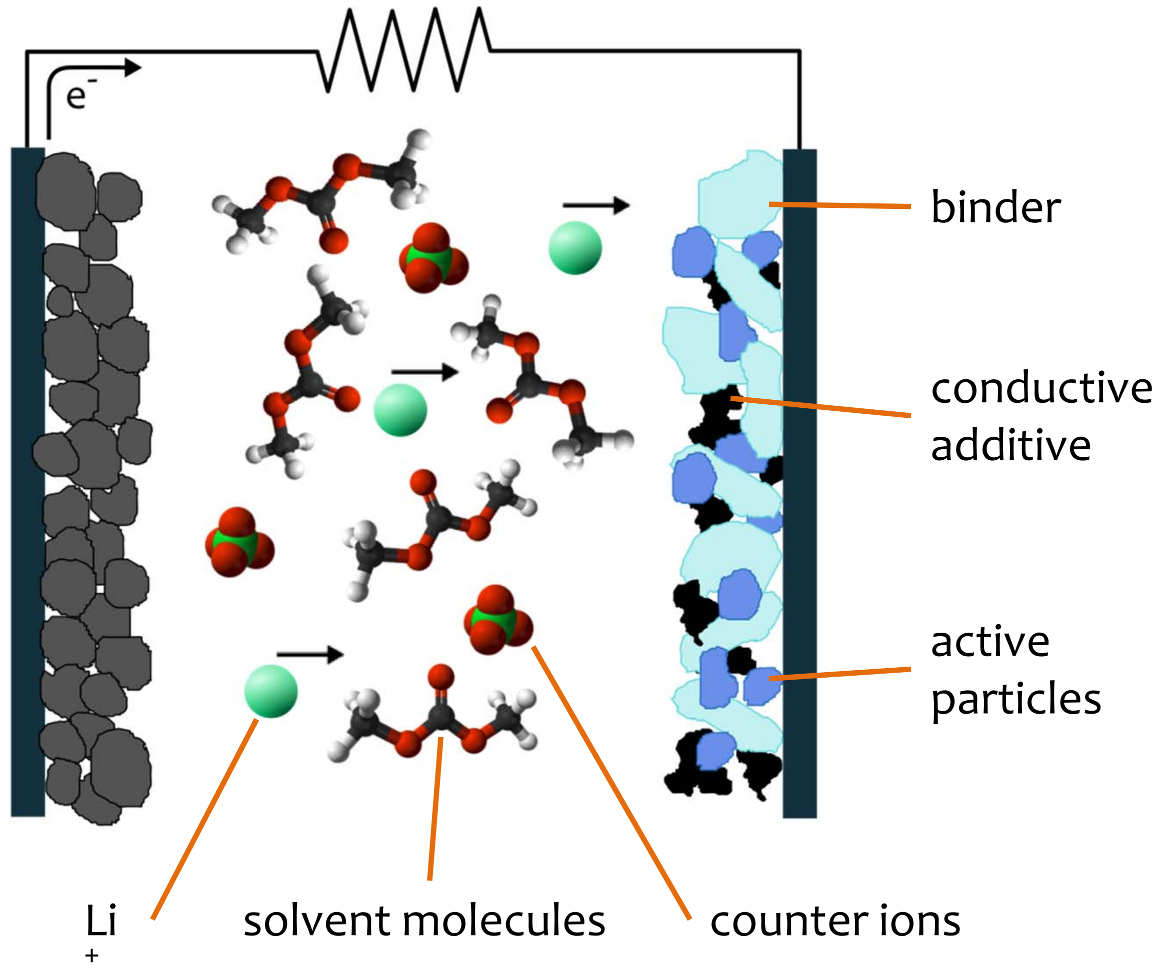


- Bardhan, Hedges, et al., *Nature Materials* (ASAP) **2013**

Li^+ transport—Fundamental, but not Simple

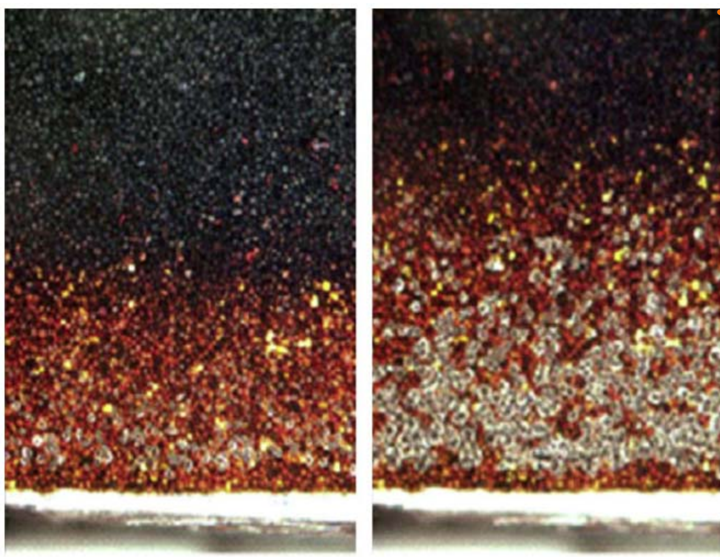


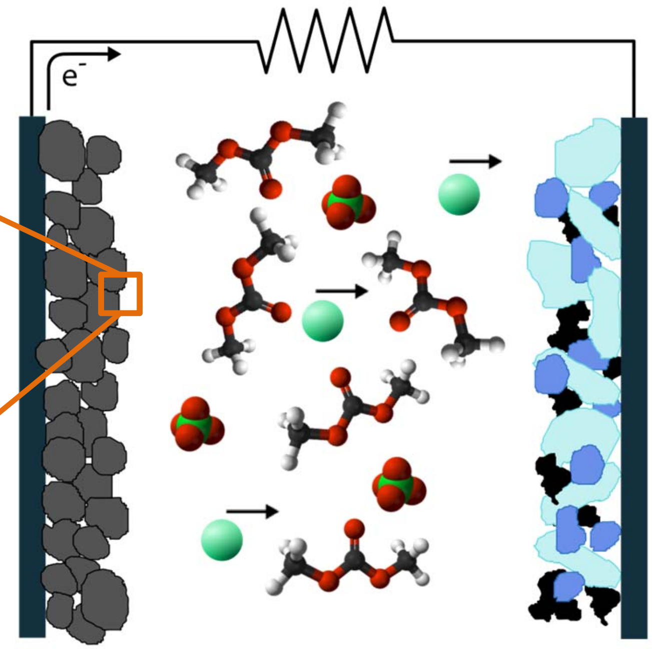
Li⁺ transport—Fundamental, but not Simple

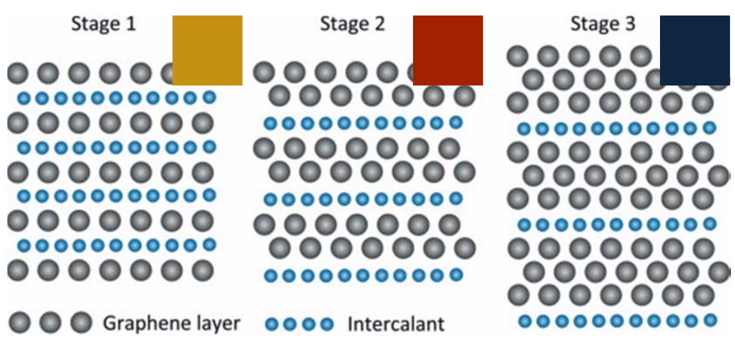


Imperfections in Li^+ Transport: Plating, and Other Problems

Lithium plating on a graphite electrode







Harris, *et al., Chem. Phys. Lett*.**2010**

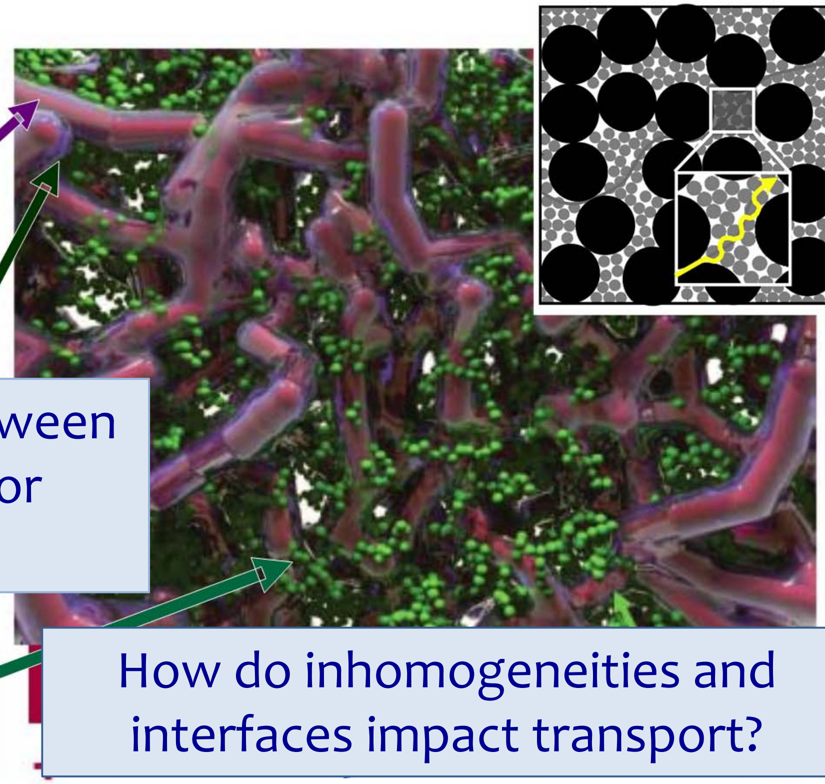
Basic Science Questions in Ion Transport for Electrochemical Cells

Positive electrode

Negative electrode

Current Battery Structure

Image courtesy Phillips



What is the relationship between tortuosity and porosity for complex geometries?

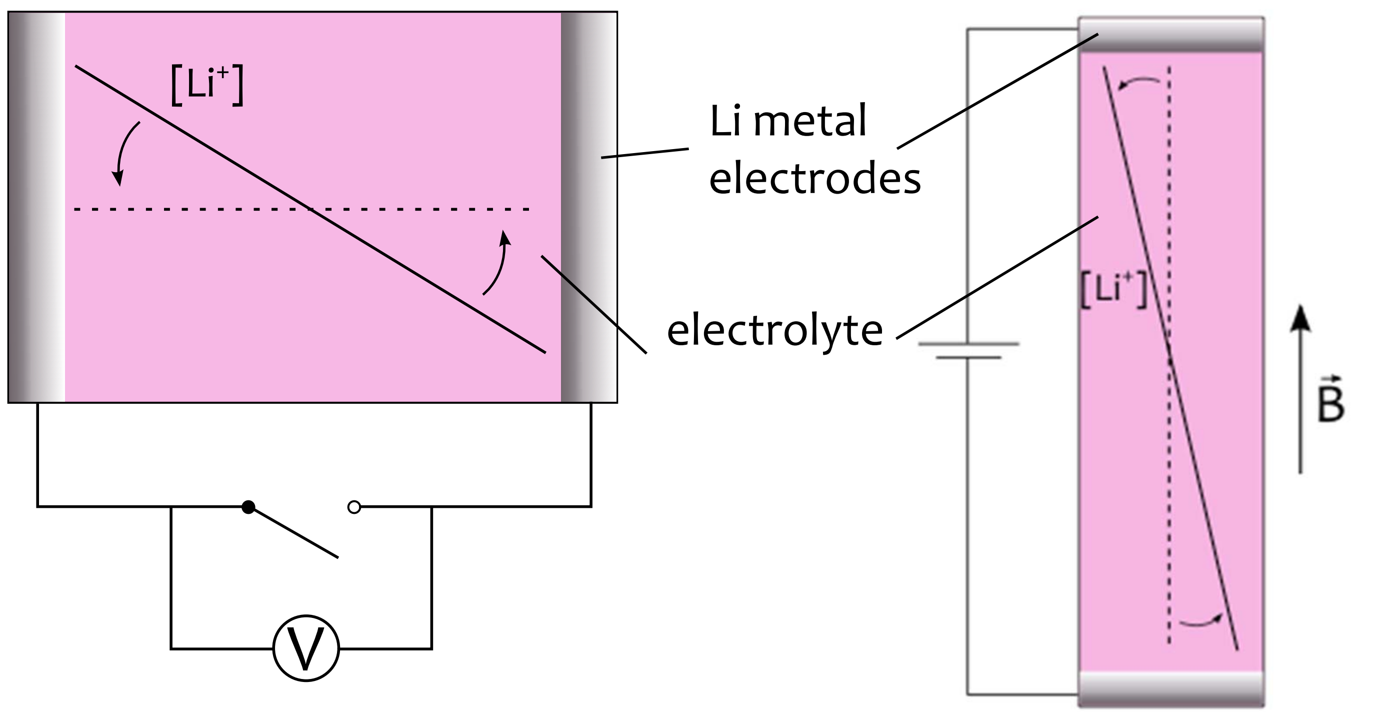
How do inhomogeneities and interfaces impact transport?

$$D = \frac{\varepsilon}{\tau} D_{\mathrm{void}}$$

Techniques for Measuring Li⁺ Transport

Galvanostatic polarization with restricted diffusion model

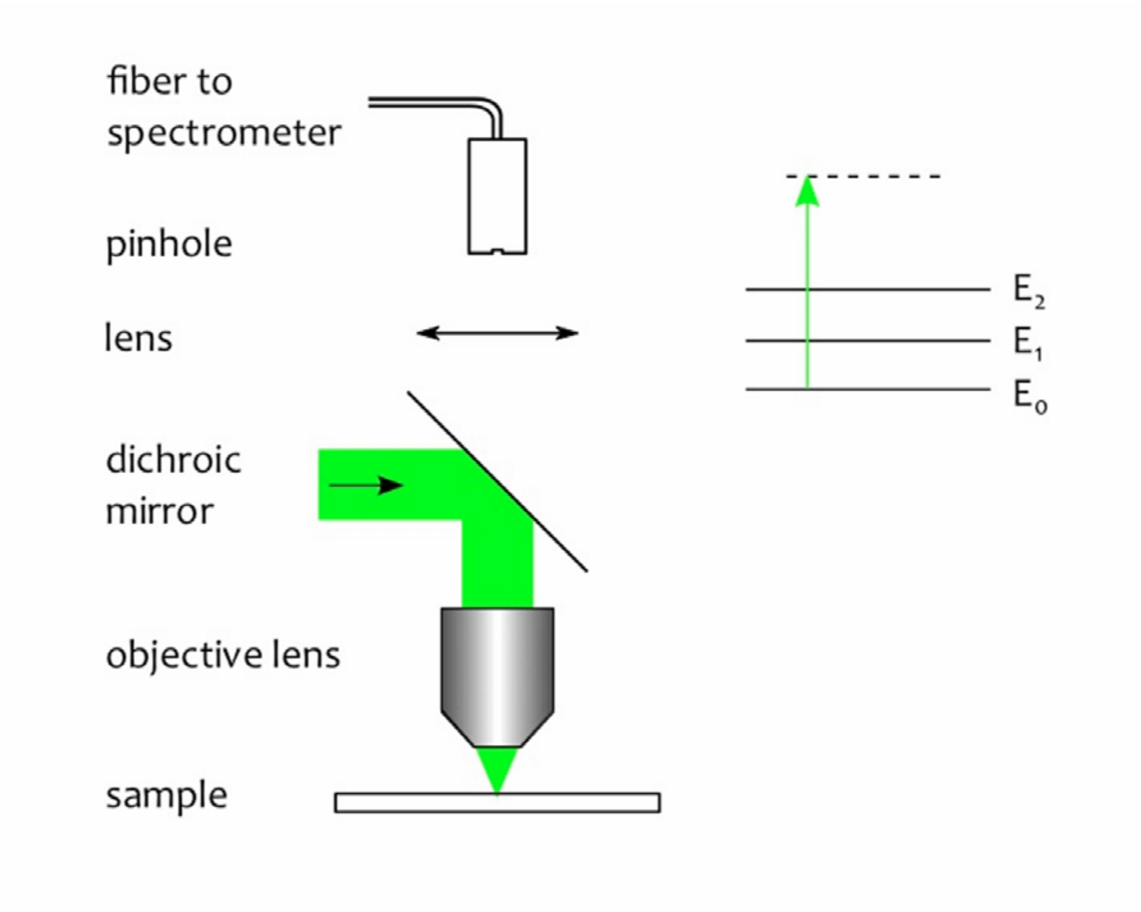
NMR imaging of ^{7}Li during polarization



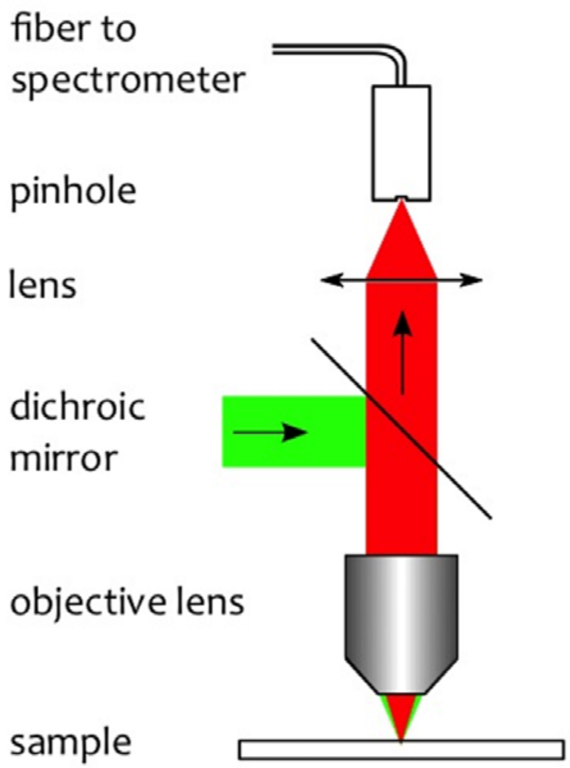
- Newman, *et al.*, *AIChE J.* **1973**
- Hafezi, *et al.*, *J. Electrochem. Soc.* **2000**

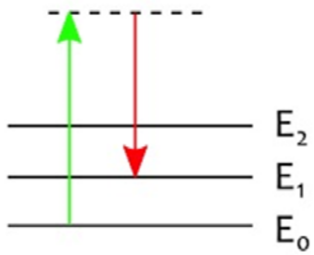
- Klett, *et al.*, *JACS* **2012**

Confocal Raman Spectroscopy

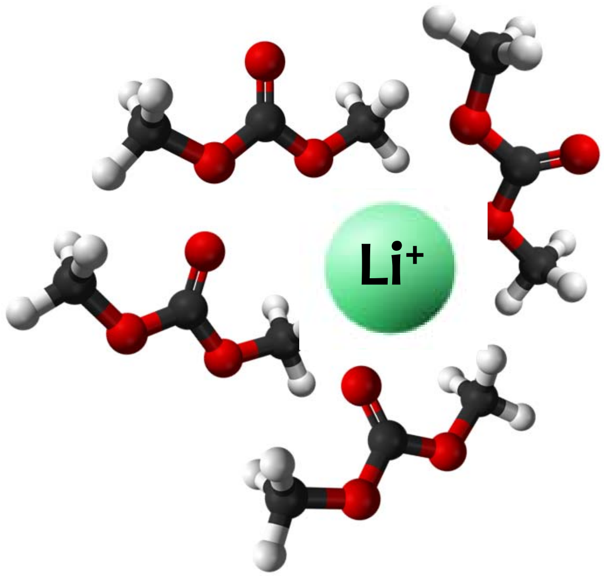


Confocal Raman Spectroscopy



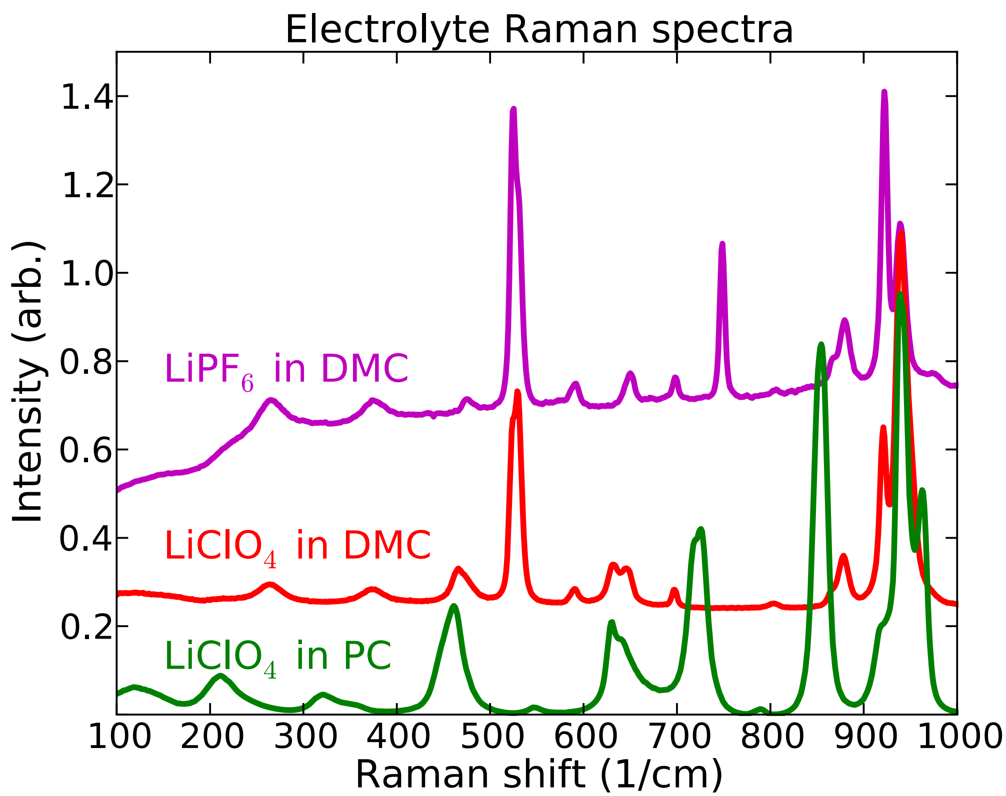


$$E_{out} = E_{in} - (E_1 - E_0)$$

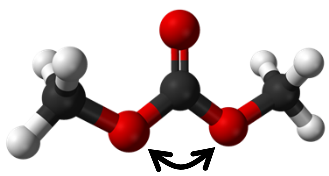


Raman Scattering Provides Chemical Specificity

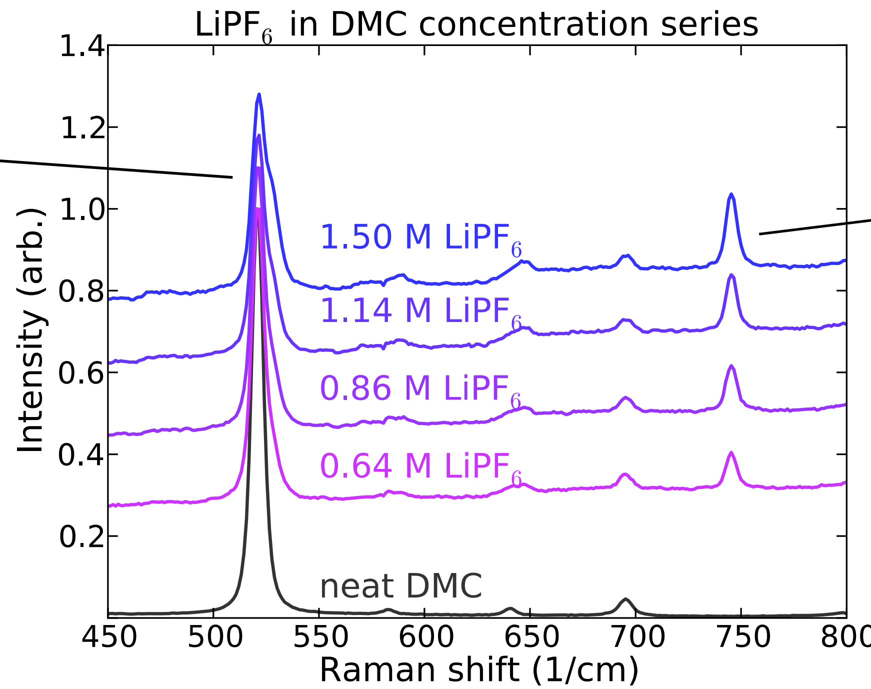
- Different solvents have unique spectra
- Spectral lines are "fingerprints", and evolve as ions (Li^+) are added

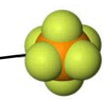


Raman Peaks Report on Ion Concentration and Local Chemical Environment



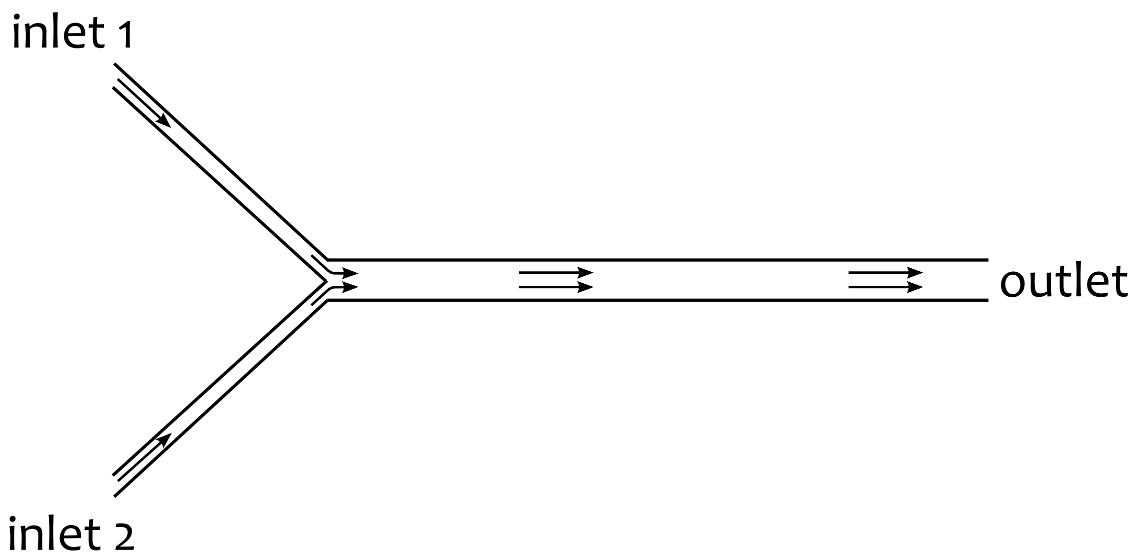
Peak at 520 cm^{-1} from O-C-O deformation of dimethyl carbonate

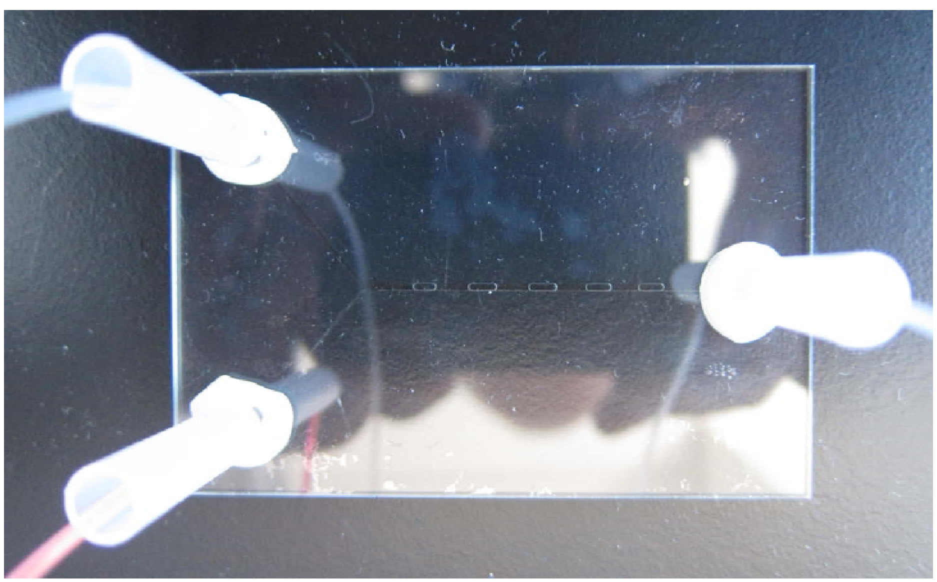




Peak at 747 cm^{-1} from PF_6^- breathing mode

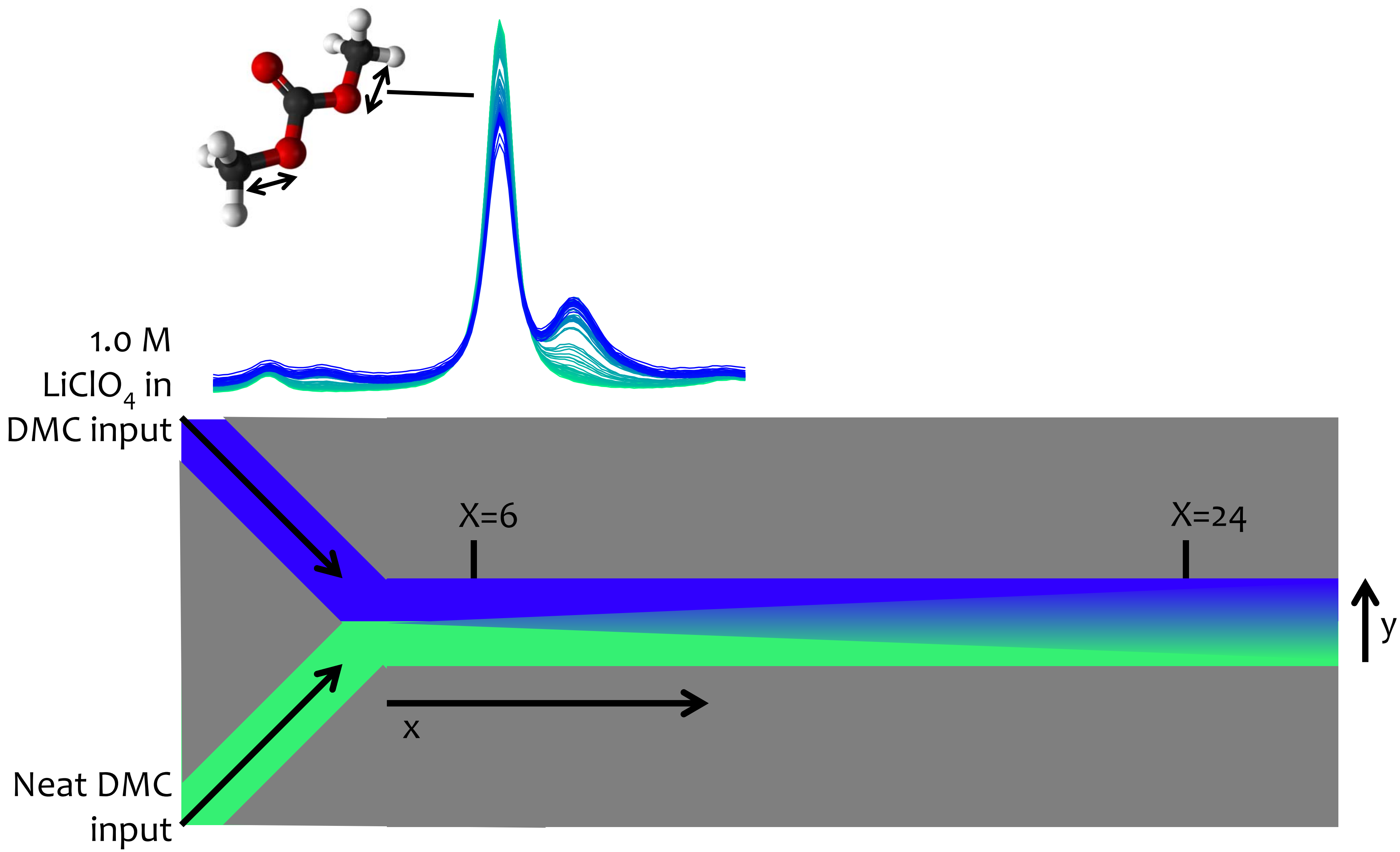
Generating Controlled Concentration Gradients in Microfluidic Devices



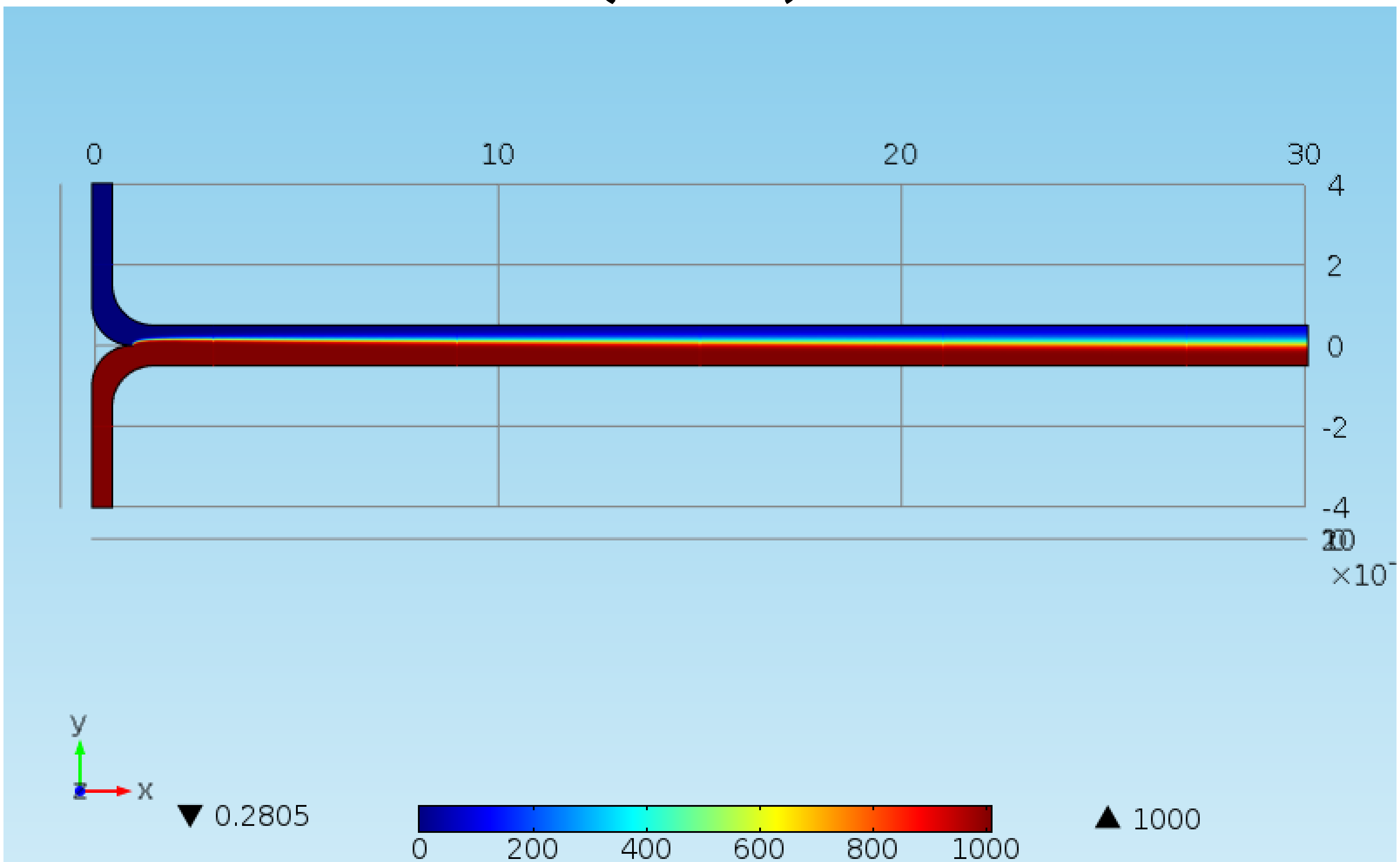


- Small Reynolds number: laminar flow
- Diffusion is the only way to transport solute across streamlines
- Flow is driven by a syringe pump
- Channel is ~ 1 mm wide, 50 microns deep and ~ 30 mm long

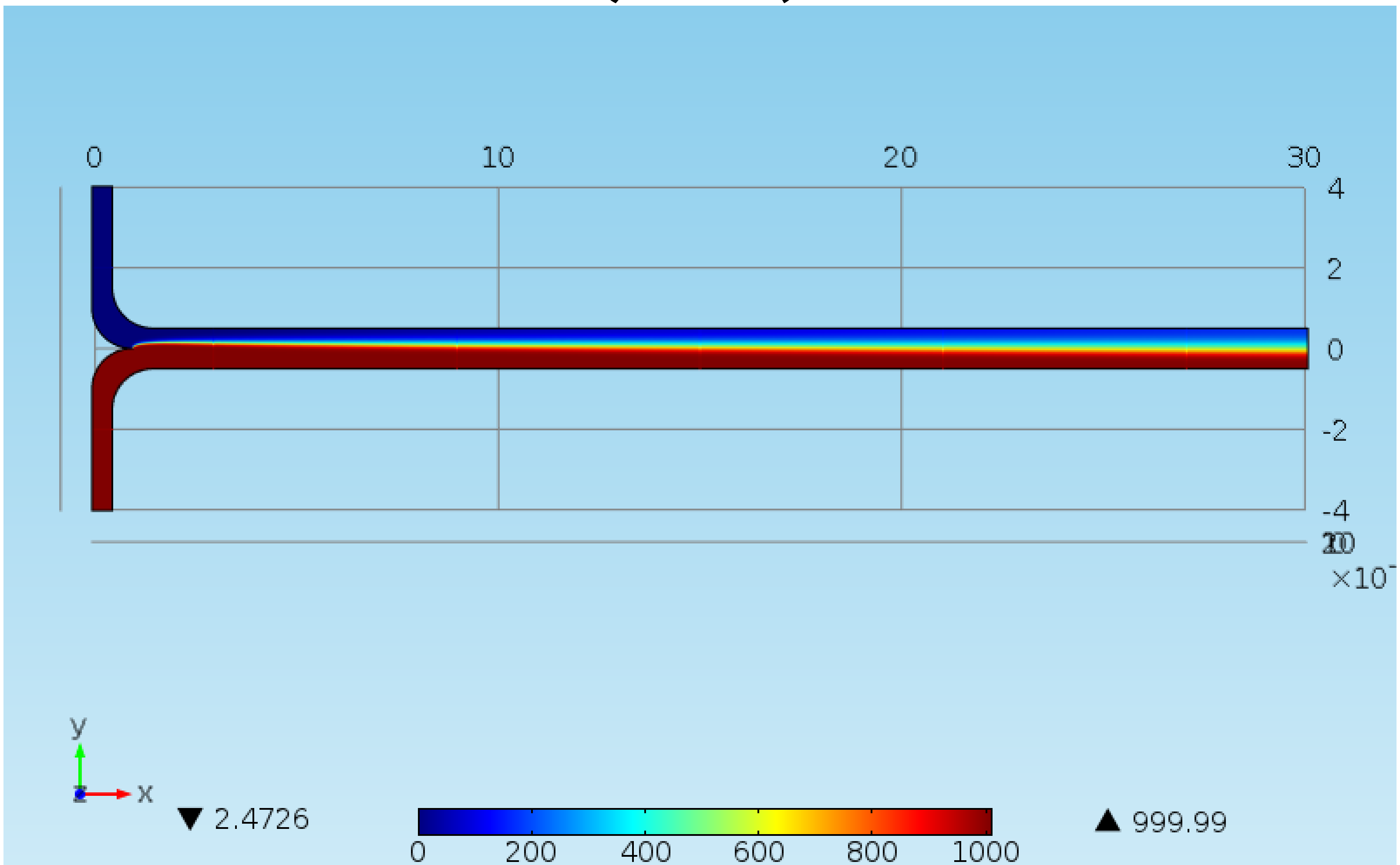
Concentration Gradient Develops as $LiClO_4$ Diffuses



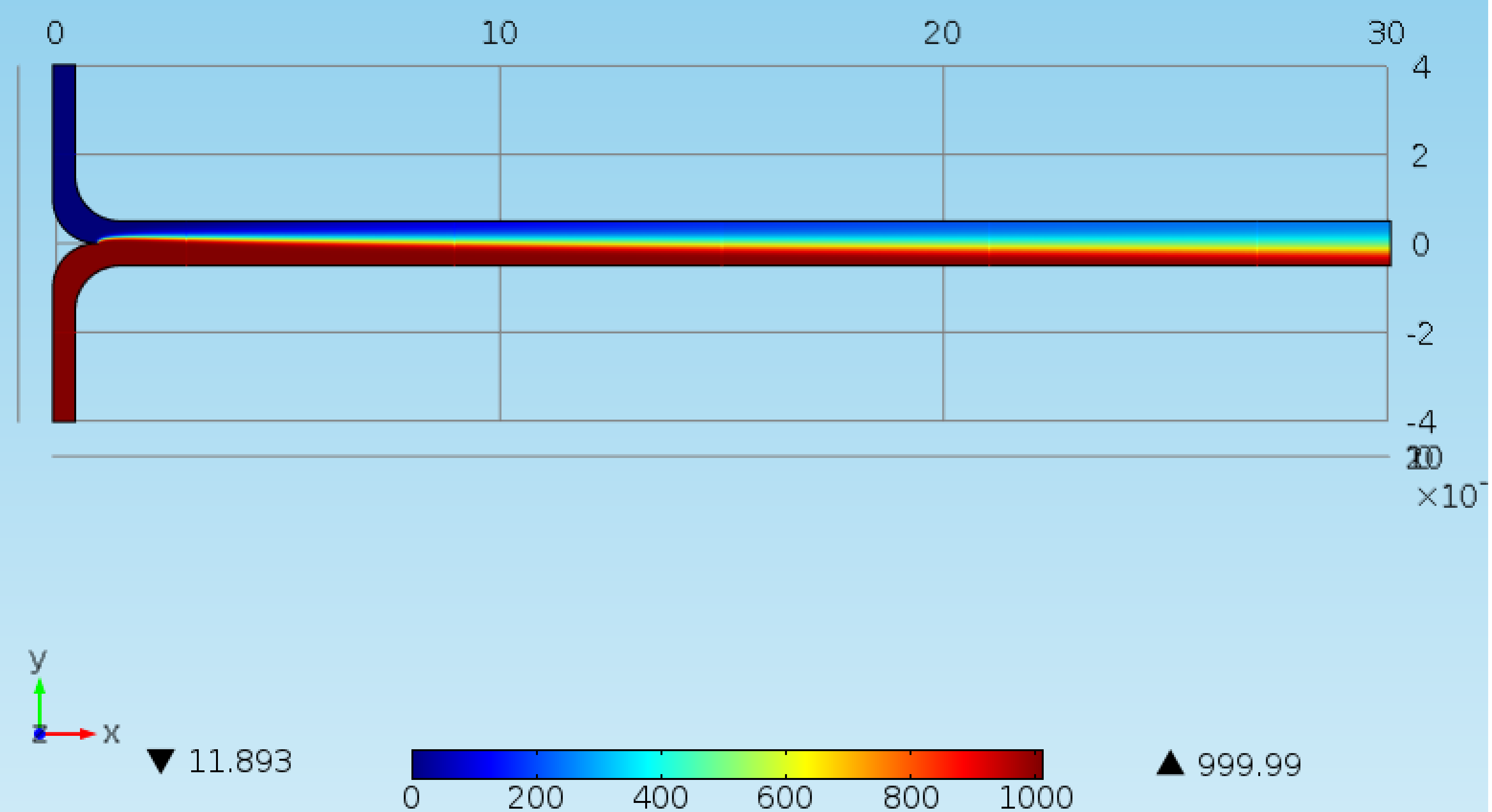
Comsol Simulations: Fast Flow Rate (v = 4)



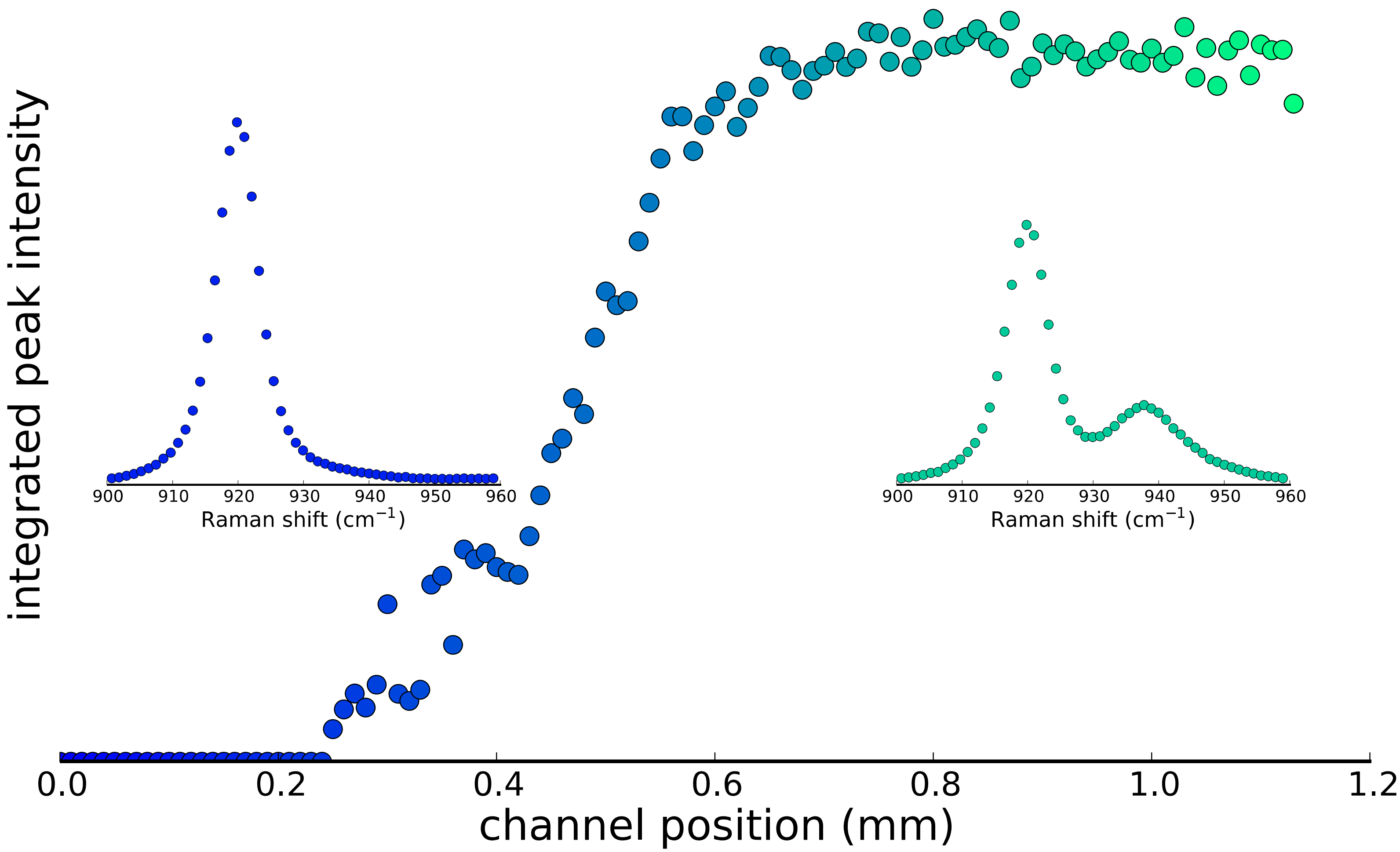
Comsol Simulations: Medium Flow Rate (v = 2)



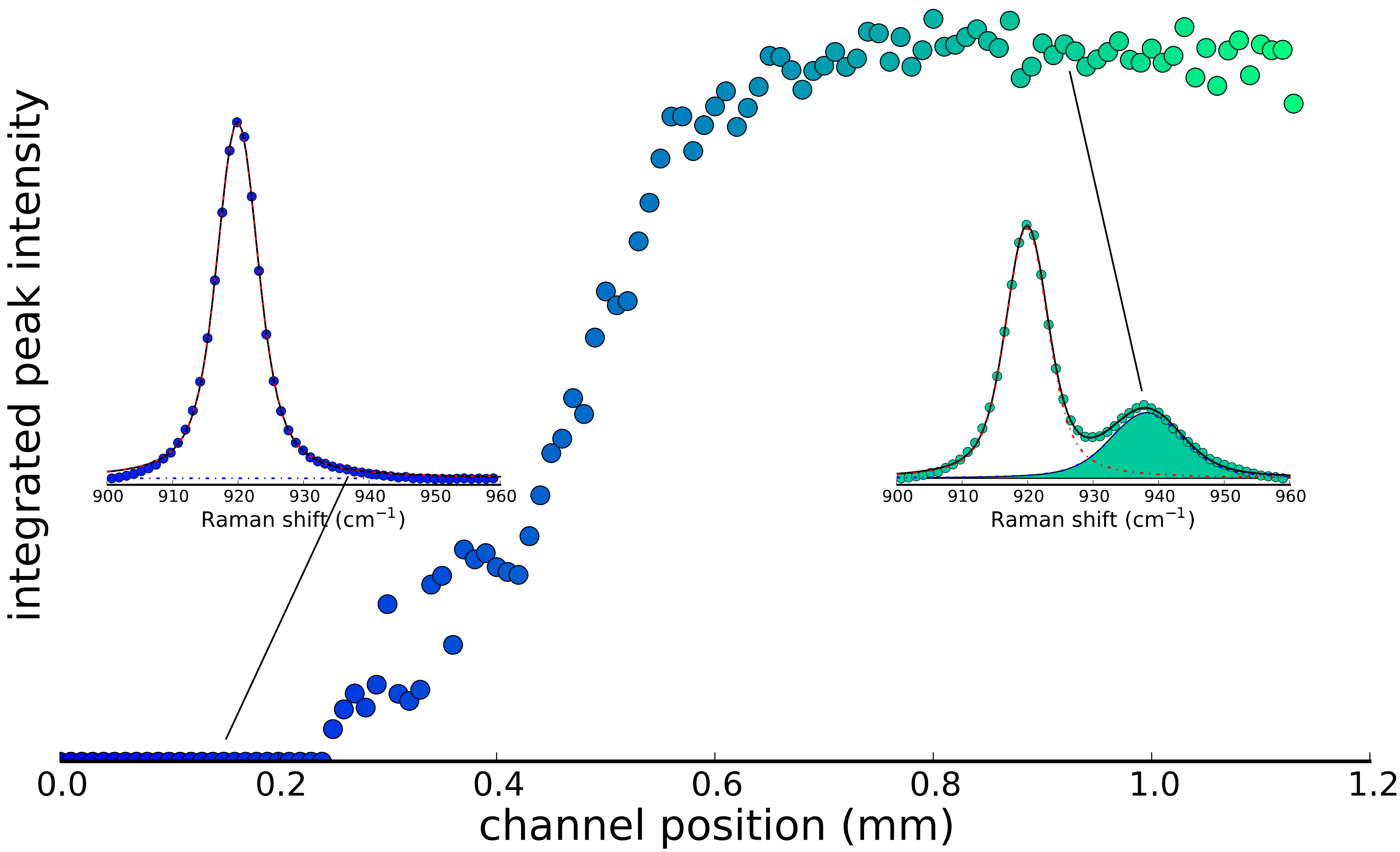
Comsol Simulations: Slow Flow Rate (v = 1)



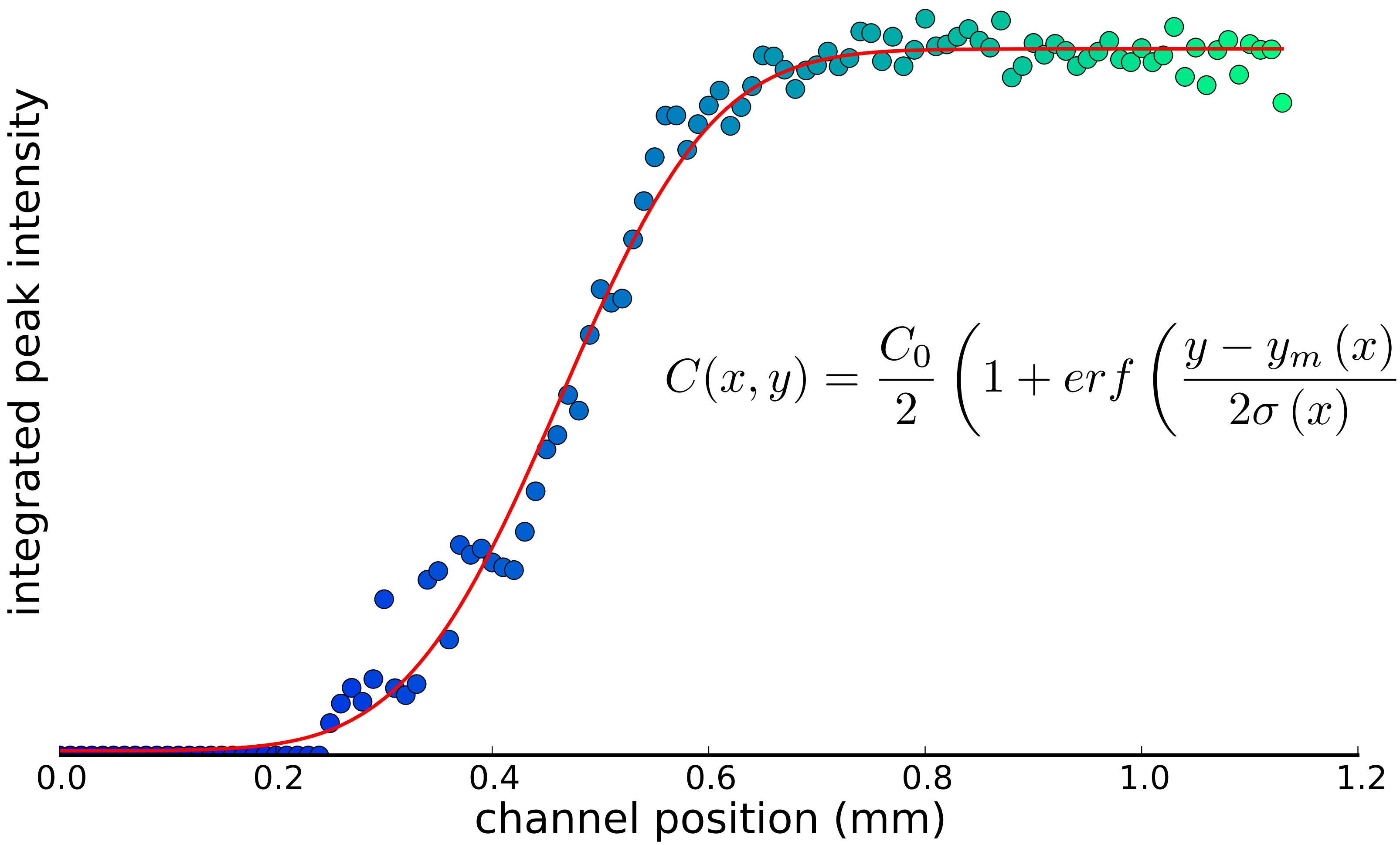
Measure Concentration by Fitting Peak Corresponding to DMC:Li$^+$



Measure Concentration by Fitting Peak Corresponding to DMC:Li$^+$

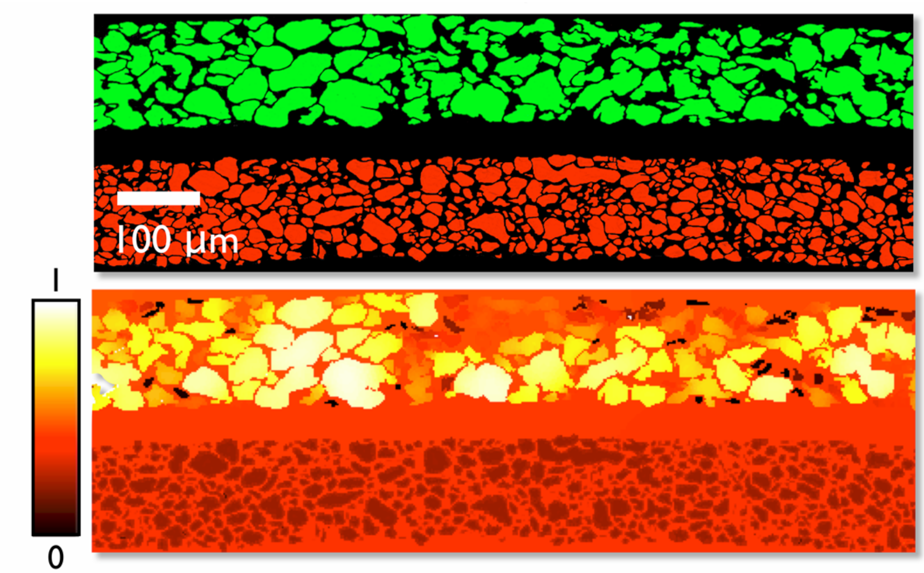


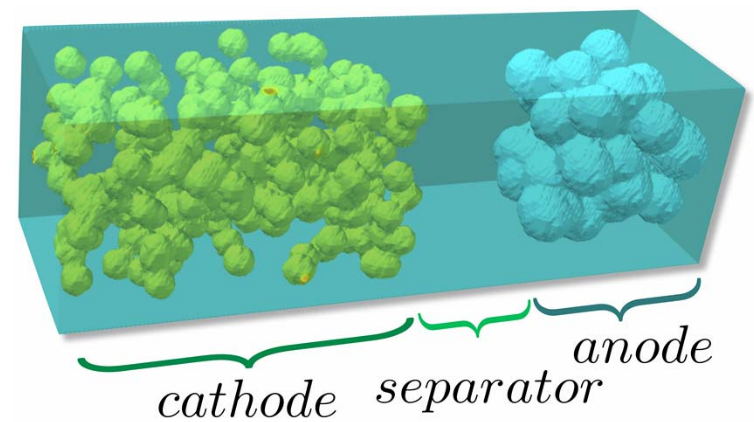
Determine Width of Concentration Profile: Calculate Diffusion Coefficient



$$C(x,y) = \frac{C_0}{2}\left(1 + erf\left(\frac{y - y_m(x)}{2\sigma(x)}\right)\right)$$

Future directions: *in-situ* Raman Imaging of Real Systems





- Measure concentration profiles at electrode/electrolyte interfaces: how do electrodes fail, microscopically?
- Study the transport of Li^+ through tortuous (geometrically interesting) networks, combine with modeling

Edwin Garcia (Purdue), Steve Harris (LBL)

Acknowledgements

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Steve Harris

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U.S. DEPARTMENT OF ENERGY

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