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

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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
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Diagram showing Li\(^+\) transport through a composite material consisting of active particles, binder, conductive additive, solvent molecules, and counter ions. The process involves electron transport (e\(^-\)) and Li\(^+\) transport through a solvent medium.
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

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

How do inhomogeneities and interfaces impact transport?

\[ D = \frac{\varepsilon}{\tau} D_{\text{void}} \]
Techniques for Measuring Li$^+$ Transport

Galvanostatic polarization with restricted diffusion model

NMR imaging of $^7$Li during polarization

- Klett, et al., JACS 2012
Confocal Raman Spectroscopy
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$$E_{out} = E_{in} - (E_1 - E_0)$$
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⁺
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Determine Width of Concentration Profile: Calculate Diffusion Coefficient

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

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