Li\(^+\) Transport: 
Relationships to Heterogeneity and Failure

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How Materials Fail
How Materials Fail

- Ductile fracture
  - *In situ* tensile test
  - Viewed through octagonal eyepiece

- To predict failure we need microstructural detail
  - Not just average Si density
  - Clustering of Si structures

What to study
  Identify, quantify heterogeneity
  Si clustering

How to improve durability
  Control heterogeneity

cast Al-7Si-0.3Mg, Sr modified Si structures

1 mm
Is Battery Failure Heterogeneous?

With L. Cai, K. An, Z. Feng, C. Liang, ORNL

*in situ* Neutron Diffraction

Cycle until capacity is down by 40%
Is Degradation Spatially Homogeneous?

18 cm

Degraded Cell

Good as new
Is Degradation Spatially Homogeneous?

Area Y degraded more than Area X
Within Area Y the LMO degrades heterogeneously

What to study
Identify, quantify heterogeneity

How to improve durability
Control heterogeneity
A High Level Picture of Li Battery Failure

- Hypotheses:
  - Battery failure begins at heterogeneities
  - Identify relevant heterogeneities by observing Li\(^+\) transport

If these are true, then we know:

- What to study
  - Identify, quantify heterogeneities
  - Variability of [Li\(^+\)] at the mesoscale

- How to improve durability
  - Control heterogeneities

Monitoring Where the Li$^+$ Goes

• In the Electrolyte
  – Heterogeneity within and among the pores
  – Complements previous work mapping Li in graphite
  – Technique validation only

• In the SEI: How the SEI works
  – What is Li transport like at the molecular level?
  – Isotope and ion tracers
Lithiation of Graphite

Photoshop to enhance colors

A. Timmons


Heterogeneous Lithiation of Graphite

- Particles are not monodisperse (Garcia, Bazant)
- Particles are not internally isotropic
Heterogeneous Lithiation of Graphite

- Particles are not monodisperse (Garcia, Bazant)
- Particles are not internally isotropic
- \([\text{Li}^+]\) does not vary smoothly among neighboring pores (heterogeneity in tortuosity)
Heterogeneous Tortuosity
with N. Brandon and P. Shearing, Imperial College; D. Kehrwald, GM

Heterogeneous Tortuosity

- In #3, get inefficient charging with wasted material
- In #11, get plating, or overcharging and electrolyte destruction
- Homogeneous electrodes have higher safe charging rates and maximum SOC compared to electrodes with “bad” spots
• A substantial fraction of the commercial electrode is inefficiently charged or dangerous, even at 50% SOC at 1.5 C

• Automotive batteries may use only 65% or 70% of total SOC window
Measuring \([\text{Li}^+]\) in the Electrolyte
With Jason Forster and Jeff Urban, LBL
Measuring [Li+] in the Electrolyte
With Jason Forster and Jeff Urban, LBL

O-C-O deformation of DMC

CH$_3$-O vibration of DMC

![Graph showing Raman shift (1/cm) vs. intensity (arb.) for different concentrations of LiClO$_4$ in DMC.](image)
Measuring [Li\(^+\)] in the Electrolyte

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O-C-O deformation of DMC

CH\(_3\)-O vibration of DMC

Microfluidic Cell*

Re < 5, \(\sim\) mm/min
Laminar = diffusion

COMSOL Simulations: \( f = 4 \, \mu l/min \)
COMSOL Simulations: \( f = 2 \text{ μl/min} \)
COMSOL Simulations: \((f = 1 \mu l/min)\)
Concentration Profile Width Increases with $x$
Concentration Profile Width Changes with $[\text{Li}^+]$

$$D(c) = 1.2 \times 10^{-5} \exp(-1.1c) \text{ cm}^2/\text{s}$$
Heterogeneous Lithiation of Graphite

- *in-situ* time-dependent 2D \([\text{Li}^+]\) maps
- Simultaneous mesoscale measurements in graphite and in pores
- Compare to predictions based on 3D microstructures
Transport in the SEI
with Peng Lu, GM R&D and Chen Li, Zee Aero

• A large literature on SEI, practically all concentrating on
  • Formation mechanisms
  • Composition and morphology
  • Impedance measurements

• How does SEI function as a Li\(^+\) transport medium?
  • Via grain boundaries between SEI components (E. Peled)
  • Via interstitials and vacancies (J. Newman)
  • As though SEI were a polar ionic liquid (G. Smith)

• Little direct experimental data on how the SEI works (M. Tang)
  • Does it participate chemically, or is it a passive, inert structure?
  • How do SEI properties evolve as it forms?
  • What compounds would make an “ideal” SEI? Nanocrystalline/amorphous
Transport in the SEI: Approach

1. Create SEI with natural abundance $^7\text{LiClO}_4$ ($^6\text{Li}:^7\text{Li} \sim 0.08$)
   - Cu electrode isolates $\text{Li}^+$ to within SEI (no insertion)

2. Soak SEI in isotopically labeled $^6\text{LiBF}_4$ for 15 minutes
   - $\text{BF}_4^-$ and $^6\text{Li}^+$ are tracers for ion transport in the original ($^7\text{LiClO}_4$) SEI

3. Depth profile with TOF SIMS
   - Without exposure to air
Transport in the SEI: $\text{BF}_4^-$ Tracer

- $\text{BF}_4^-$ identifies the porous part of the SEI
• Almost 2/3 of SEI $^7$Li is exchanged in a 15 minute soak
  • Grain boundary diffusion cannot explain Li transport
  • SEI is not a passive, inert structure to Li$^+$ transport
    • Qi et al, JACS 134, 15476 (2012).
• Electrolyte degradation products may be incorporated into the SEI
Which SEI Compounds are “Good” or “Bad?”

- “Good” means good Li$^+$ transport
- Soak $^7$Li salts in $^6$LiClO$_4$/DMC
  - 30 second soak (15 minutes in previous slide)

- Build SEI component library
  - What are the best compounds?
  - What about compound mixtures?
  - Crystalline or amorphous?
  - What does an ideal SEI look like?
    - Can we design our additives?
How Does the SEI Evolve During Formation?

- Grow SEI films in ½-cell with Cu foil electrodes
  1. Initially grow 4 films at 700 mV until current < 1 μA/cm²
  2. For 3 of them, continue SEI growth at 500 mV
  3. For 2 of them, continue SEI growth at 300 mV
  4. For the last one, continue SEI growth at 25 mV
- 4 samples showing the evolution of a single SEI film
  - Representative of the very slow formation step for commercial cells
  - Not 4 SEI films grown at 4 voltages
- Transfer to TOF-SIMS under Ar for tracer experiments
How Does the SEI Evolve?

- Porosity falls smoothly with depth
- Films > 300 mV are porous all the way to the Cu
- At every depth, the films lose porosity monotonically as voltage drops
  - SEI film growth does not simply involve adding material at the top or bottom
How Does the SEI Evolve?

- $\text{Li}_2\text{O}^+$ can fragment from $\text{Li}_2\text{O}$, $\text{Li}_2\text{CO}_3$, $\text{ROCO}_2\text{Li}$, or almost any carbonite-like species
- Formation of inorganic material occurs throughout the SEI
  - Implies conversion of primordial material (whose concentrations fall)
How Does the SEI Evolve?

- Porosity depth profiles have the same shape at higher voltages.
- The 2-layer SEI fully formed only below 300 mV.
- Porous layer thins at 25 mV, also indicating conversion.
- Using Cu means that changes < 300 mV cannot relate to onset of insertion.
High-Level Picture of SEI Growth

- Cell capacity falls as $t^{1/2}$ ➞ SEI growth is diffusion limited
- What is diffusing?
  - Solvent molecules (Bazant)
    - Diffuse through the dense layer
    - React at the electrode-dense layer interface
    - Tang: but then growth wouldn’t depend on formation voltage. Wrong
  - Electrons (Newman)
    - Diffuse through the dense layer
    - React at the dense layer-porous layer interface
    - Tang: but then growth wouldn’t depend on transport from the bulk. Wrong

High-Level Picture of SEI Growth
With Kjell Schroder and Keith Stevenson, U. Texas, Austin

- What diffuses, solvent or electrons?
  - Grow SEI on Si with LiPF$_6$ in PC at 500 mV
  - Complete SEI growth with LiPF$_6$ at 10 mV in d$_6$PC

TOF-SIMS Depth Profiles

- New material appears at the electrode-dense layer interface
  - Solvent diffusion

- Conversion, organic to inorganic, occurs throughout the SEI
  - Electron diffusion

- Can this account for the $t^{1/2}$-dependence + Tang’s discrepancies?
Summary I

- We have proposed a high-level view of battery failure
  - Failure begins at heterogeneities
  - Focus on the interaction of Li$^+$ transport with spatial heterogeneities
  - More homogeneous electrodes
    - Higher safe charging rate
    - Higher maximum SOC = higher energy density

Summary I

- We have proposed a high-level view of battery failure
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  - Focus on the interaction of Li\(^+\) transport with spatial heterogeneities
  - More homogeneous electrodes
    - Higher safe charging rate
    - Higher maximum SOC = higher energy density
- Progress with spatially resolved, time dependent, *in situ* Li maps
  - Detect Li optically (1 \(\mu\)m resolution) from perturbation of host
    - Changes in color for graphite, in Raman spectra for solvent

Summary II

• How the SEI works
  – Transport mechanism
    • SEI is chemically active: it incorporates electrolyte species
      – Electrolyte degradation products may be incorporated into the SEI
    • Grain boundary diffusion is at best a minor contributor
  – Initial studies to build a library rating individual SEI components
    • Crystalline and amorphous
  – Porosity profile evolution during SEI formation
    • Composition becomes more inorganic at every depth
    • Porous layer gets thinner as SEI gets thicker
    • Conversion, not just addition
  – High level picture of SEI growth
    • Material added at low voltage comes from solvent diffusing to electrode
    • Conversion of organic to inorganic material from electrons diffusing out

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