Electrochemical Shock in Polycrystalline Lithium Storage Materials

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“Whiskers, Wires, and Walls” Workshop – NIST
30 September 2010

\[ V = \frac{-\Delta \mu_{\text{Li}}}{e} \]
Lithium-ion Batteries – Operating Principles

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Most Materials Change Shape with Varying Lithium Content

- LiCoO$_2$
- LiMn$_2$O$_4$
- Si
Most Materials Change Shape with Varying Lithium Content

\[ \text{LiCoO}_2 \rightarrow \text{Li}_{0.5}\text{CoO}_2 \]
\[ \Delta V = +1.9\% \]

\[ \text{LiMn}_2\text{O}_4 \rightarrow \text{Mn}_2\text{O}_4 \]
\[ \Delta V = -7.3\% \]

\[ \text{Si} \rightarrow \text{Li}_{4.4}\text{Si} \]
\[ \Delta V = +311\% \]
Previous Models Have Calculated Diffusion-Induced Stresses

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Critical combinations of particle size and rate

Need fracture toughness measurements!

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What About Polycrystals?

Phase Transformations?

Need fracture toughness measurements!

Microstructure Matters for Electrochemical Shock

EBSD orientation maps for LiCoO$_2$ polycrystalline particles in composite (Lishen) electrodes

Microstructure Matters for Electrochemical Shock

**Goal:** Develop Models for Electrochemical Shock that incorporate this microstructural complexity and address (anisotropic) phase transformations
Microstructure Generation

2D Voronoi Construction
- 2N Random numbers per grain \((x_i, y_i)\)

Random Grain Orientations
- Use OOF2’s EulerABG Convention
- 3 Random numbers per grain for \((\alpha_i, \beta_i, \gamma_i)\)
- All done in Mathematica
Each grain is numbered

Each boundary is numbered and we know which grains it separates

- $n \rightarrow -n$ for opposite direction along same edge
- Exclude Boundary Edges from Analysis

We know the location of each triple point
LiMn$_2$O$_4$: A Model System

LiMn$_2$O$_4$ + Li$^+$ + e$^-$ → Li$_2$Mn$_2$O$_4$

cubic

tetragonal

$\alpha$ [Å]

3.0% shrinkage

$X$ in Li$_X$Mn$_2$O$_4$

12.3% expansion

Start with end point analysis... (Analogies to thermal shock)

Assumptions: Plane Stress Condition; Zero-Displacement normal to external boundaries

Note: Stresses here are referred to the OOF/Lab frame coordinates
Use tensor transformation to extract grain boundary normal stress.
Extraíendo información local de esfuerzo
Still have $r^{-1/2}$ singularity!

\[
K = \frac{2}{\sqrt{\pi a}} \int_0^a \sigma_{nn}(x') \sqrt{\frac{x'}{a-x'}} \, dx'
\]

K: Stress-Intensity Factor

\[K > K_{IC}\]

Still have $r^{-1/2}$ singularity!

\[ K = \frac{2}{\sqrt{\pi a}} \int_0^a \sigma_{nn}(x') \sqrt{\frac{x'}{a-x'}} \, dx' \]

\( K \): Stress-Intensity Factor

\( K > K_{IC} \)

Stress-Intensity Factor – Nonuniform Loading

\[ \sigma_{nn}(x) \]

Still have \( r^{-1/2} \) singularity!

\[ K = \frac{2\sqrt{\pi}a}{\sigma_{nn}(x) - \sigma_{nn}(x')} \]


\[ K > K_{IC} \]
Method:

1) Choose an edge
   Remember, they have been numbered...

2) Choose a random flaw size from a flaw size distribution
   Need flaw distribution information!

3) Choose a random position along the edge

4) Calculate K using polynomial model for stress distribution
Flaw Size Distributions

- Flaws are **not** Weibull distributed

\[ f(a) = \frac{c^{n-1}}{(n-2)!} a^{-n} e^{-c/a} \]

\[ \frac{c}{n} \sim a^{-n} \]

K Distribution from Random Flaws

570 Tensile Flaws (Random Size and Position)

Frequency vs. Stress Intensity Factor

1000 Random Flaws (Size and Position)
Is this distribution characteristic of the underlying microstructure?
Other Potentially Interesting Microstructure Variables

Grain Orientation
Triple Points
Grain Size
Porosity
Calculate Stress Intensity Flaw-Size Relations for All Grain Boundaries

Extract Failure Probabilities and Extreme Values Statistics

Finite Element Stress Calculations in OOF2

Generate Random Voronoi Microstructure in Mathematica

Extract Local Stresses Along Each Grain Boundary

Populate the Microstructure with Random Flaws

Calculate Stress Intensity Flaw-Size Relations for All Grain Boundaries
Microstructure matters for electrochemical shock — opportunity for design

- Mathematica + OOF2 is a convenient, powerful tool set

This is a snapshot of current development

Potential Future Directions:

- Introducing Second Phases (or porosity)
- Electrochemical Kinetics

Experiments – X-Ray Tomography?
Acknowledgements

- National Science Foundation Graduate Research Fellowship
- Dept. of Energy, Basic Energy Science, Award No. DE-SC0002633
Questions?