Consortium for Advanced Battery Simulation (CABS)
Project ID: ES295

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Team: Srikanth Allu, Wael Elwasif, Kenny Higa, Sergiy Kalnaus, Scott Roberts, Srdjan Simunovic, Venkat Srinivasan, Hsin Wang
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2016 U.S. DOE Hydrogen and Vehicle Technologies Program
Annual Merit Review and Peer Evaluation
Brian Cunningham, Vehicle Technologies Program

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Overview

**Timeline**
- **Start** — October 2016
- **Finish** — September 2019
- **Percent complete:** 15

**Budget**
- **FY16** — $1.575M

**Barriers Addressed**
Advanced simulation capabilities enable improved / optimized design, allowing the following barriers to be addressed:

- **C. Performance**
- **D. Abuse Tolerance, Reliability, and Ruggedness**
- **E. Life**

**Partners**
- **LBNL**
- **SNL**
- as well as the NREL-led CAEBAT project team
Relevance
Relevance and Project Objectives (1)

- Major barriers for increasing battery energy density and power, increasing safety and reducing cost include
  
  1. insufficient understanding of the underlying physical phenomena that limit battery performance and safety, particularly the role of microstructure, and
  
  2. lack of validated predictive simulation tools.

- CABS is addressing (1) by developing new experiments for properties with largest uncertainties and developing new validated models that allow researchers to explore battery response under both normal and abusive conditions, and is addressing (2) by deploying increasingly capable and computationally efficient releases of the Open Architecture Software (OAS) and components of the Virtual Integrated Battery Environment (VIBE), developed as part of CAEBAT 1.

- First released in Fall of 2014, VIBE has been downloaded over 100 times.
Relevance and Project Objectives (2)

• CABS enables researchers and battery designers to explore and optimize batteries using new materials, configurations, and designs by
  – developing improved mechanistic models,
  – obtaining data from new and existing experiments, and
  – deploying successively more capable, efficient, and usable releases of VIBE

• This supports EERE’s *EV Everywhere* goals by enabling increases in energy density, specific energy, and power while maintaining safety
  – Outcome: increased adoption of EVs
    • reduced emission of greenhouse gases
    • improved economic competitiveness of the U.S., in large part by reducing dependence on foreign oil.
Approach / Strategy

High-level approach/strategy is shown in the following 3 slides, but is also embedded in the milestone slides within Technical Accomplishments.
Approach (1)

Efficient hybrid models
Constitutive models for electrode deformation
Constitutive and failure models for cells
Microstructure models
Homogenization methods
Criteria for internal short circuit

Models

Pack

Mechanical Properties
Deformation
Thermal Properties
Electrochem. Performance
Imaging
Kinetic/Transport

Experiments

Electrode
Approach (2)

• Computational efficiency
  – Hybrid models
  – Software design – reducing file-based communication
  – State management library for OAS components
  – Continuous execution
<table>
<thead>
<tr>
<th>ID</th>
<th>FY16</th>
<th>Lead</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.1</td>
<td>Baseline performance profile of VIBE/OAS/AMPERES</td>
<td>ORNL</td>
<td>P</td>
<td></td>
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<td></td>
<td>Complete</td>
</tr>
<tr>
<td>I.1</td>
<td>Report on experimental techniques supporting models</td>
<td>ORNL</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>Complete</td>
</tr>
<tr>
<td>E.1</td>
<td>Produce segmented tomographic reconstructions of electrodes for</td>
<td>LBNL</td>
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<td>On Track</td>
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<tr>
<td></td>
<td>conversion to spatial domains for microstructural models</td>
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<tr>
<td>E.2</td>
<td>Demonstration of single side indentation test with incremental</td>
<td>ORNL</td>
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<td>On Track</td>
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<td></td>
<td>deformation to determine faulting in spirally wound, wound prismatic,</td>
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<td></td>
<td>and stacked electrodes in hard case</td>
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</tr>
<tr>
<td>C1.1</td>
<td>Collect constitutive models for NMC materials and report on use of</td>
<td>SNL</td>
<td></td>
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<td>On Track</td>
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<tr>
<td></td>
<td>mesoscale data to project lead</td>
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</tr>
<tr>
<td>I.2</td>
<td>Deployment of VIBE/OAS with enhanced extensibility and hybrid models</td>
<td>ORNL</td>
<td></td>
<td></td>
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<td></td>
<td>On Track</td>
</tr>
</tbody>
</table>
Technical Accomplishments

Includes:

- Foundation provided by previous CAEBAT projects and related efforts
- Summary of completed FY16 milestones, including approach
Technical Accomplishments

• The Virtual Integrated Battery Environment (VIBE) was developed under the initial CAEBAT program as a mechanism for demonstrating and deploying the Open Architecture Software (OAS) system used to foster interoperability between battery simulation tools.

• Although the earlier CAEBAT project ended in FY15, since CABS builds on that work, we include a brief overview of VIBE and selected accomplishments in the following slides.
Virtual Integrated Battery Environment (VIBE)

- OAS plus components representing physics models, together with the Battery State, constitute VIBE
- Current capabilities include coupled electrochemical, thermal, and electrical models integrated within VIBE

\[ J = Y(V_p - V_n - U) \]
\[ U = a_0 + a_1(DOD) + a_2(DOD)^2 + a_3(DOD)^3 \]
\[ Y = a_4 - a_5 \times DOD + a_6 \times (DOD)^2 - a_7 \times (DOD)^3 + a_8 \times (DOD)^4 - a_9 \times (DOD)^5 \]

\[
\frac{\partial (\varepsilon_e c_e)}{\partial t} - \nabla \cdot (\varepsilon_e D_e^{\text{eff}}(\varepsilon_e) \nabla c_e) - \frac{1 - \varepsilon}{F} j^\text{Li} = 0
\]

Species concentration in the solid phase:
\[
\frac{\partial (\varepsilon_s c_s)}{\partial t} - \nabla \cdot (\varepsilon_s D_s^{\text{eff}}(\varepsilon_s) \nabla c_s) + \frac{j^\text{Li}}{F} = 0
\]

Electrolyte Potential:
\[
\nabla \cdot (\varepsilon_e \kappa^{\text{eff}}(\varepsilon_e) \nabla \phi_e) + \nabla \cdot (\varepsilon_e \kappa^{\text{eff}}(\varepsilon_e) \nabla \ln c_e) + j^\text{Li} = 0
\]

Electrode Potential:
\[
\nabla \cdot (\varepsilon_s \sigma^{\text{eff}}(\varepsilon_s) \nabla \phi_s) - j^\text{Li} = 0
\]

\[
\rho C_p \frac{\partial T}{\partial t} - \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) - \frac{\partial}{\partial y} \left( k \frac{\partial T}{\partial y} \right) - \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) = q
\]

where \[ q = aJ \left[ E_{oc} - E - T \frac{\partial E_{oc}}{\partial T} \right] + a_P r_P i_P^2 + a_n r_n i_n^2 \]
Virtual Integrated Battery Environment

Software components comprising VIBE.
VIBE components have been coupled in multiple combinations depending on application need

- DualFoil electrochemistry + AMPERES thermal
- DualFoil electrochemistry + AMPERES thermal + AMPERES electrical
- AutoLion (ECPower) + Dakota (for optimization / parameter sweep)
- 1DElectrode electrochemistry (SNL) + AMPERES thermal
- 1DElectrode electrochemistry + AMPERES thermal + AMPERES electrical
- AMPERES NTG electrochemistry + AMPERES thermal
- AMPERES NTG electrochemistry + AMPERES thermal + AMPERES electrical
- AMPERES 3D electrochemistry + LS-Dyna mechanics

http://ecpowergroup.com/autolion-2/
https://dakota.sandia.gov/
VIBE – Download Statistics

- >150 downloads via http://batterysim.org/
- Downloads from all over the world from labs, academia, and industry. Some of the institutions are listed below:

<table>
<thead>
<tr>
<th>Institution</th>
<th>Institution</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple</td>
<td>Fisker Automotive</td>
<td>Northeastern University</td>
</tr>
<tr>
<td>NASA</td>
<td>Texas A&amp;M Univ.</td>
<td>Fiat Chrysler Automobiles</td>
</tr>
<tr>
<td>Lockheed Martin</td>
<td>Stanley Black &amp; Decker</td>
<td>Georgia Tech</td>
</tr>
<tr>
<td>Ford Motor Company</td>
<td>BASF Corporation</td>
<td>Iowa State University</td>
</tr>
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<td>Bosch, LLC</td>
<td>Saft America</td>
<td>University of Maryland</td>
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<tr>
<td>Honda R&amp;D Co, Ltd</td>
<td>Motorola</td>
<td>University of Michigan</td>
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<tr>
<td>Samsung Electronics</td>
<td>Pan Asia Technical Automotive Center</td>
<td>Purdue University</td>
</tr>
<tr>
<td>Virtual Vehicle Research Center</td>
<td>CEA – Commissariat Energie Atomique</td>
<td>North Carolina State University</td>
</tr>
<tr>
<td>Zee Aero</td>
<td>ICT Fraunhofer</td>
<td>University of Dayton</td>
</tr>
<tr>
<td>IK4-CIDETEC</td>
<td>Washington University</td>
<td>University of Nevada, Las Vegas</td>
</tr>
<tr>
<td>Institute for Energy and Environmental Research, Heidelberg, GmbH</td>
<td>TU Muenchen</td>
<td>SAIT Polytechnic</td>
</tr>
</tbody>
</table>
Overview of VIBE simulations

Detailed 3D Modeling

Charge Transfer Zone

Pouch Zone

Discharge Curves (Validation with IR Imaging)

1C Discharge

5C Discharge

Cylindrical Cell with Current Collectors Resolved (Electrochemical – Thermal - Electrical)

Mechanical Abuse of Cylindrical Cell with Current Collectors Resolved (Electrochemical – Thermal – Electrical – Mechanical)

Temperature in 4P and 4S Module with Fully Coupled Electrochemical, Electrical and Thermal Simulations in CAEBAT OAS / VIBE

Journal of Power Sources
Available online 21 August 2013
In Press, Accepted Manuscript — Note to users

A new open computational framework for highly-resolved coupled 3D multiphysics simulations of Li-Ion Cells

Srinanth Aliu, Sergiy Kalnais, Wael Elwasif, Srdjan Simunovic, John Turner, Sreekanth Pannala
Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

CABS Consortium for Advanced Battery Simulation
Electro-chemistry Modeling Hierarchy

CABS Consortium for Advanced Battery Simulation

Particle Resolved Formulation

3-D Volume Averaged Formulation

Pseudo-2D

Single Particle

Problem (Typical Lithium-Ion Cell)

Fully resolved Discretization

Volume Averaged Representation

Pseudo-2D

Single-particle
AMPERES is robust enough to handle high discharge rates needed for short simulations

- External short is similar to internal short from an electrochemistry perspective
- Rapidly dropping the potential difference across the terminals in a short time produces exponential rise and decay of current through the battery
  - **Now evolving current as part of simulation rather than imposing**
- Fully 3D – maps directly to electrical / thermal and mechanical
- Runs in a few minutes
Technical Accomplishments:
FY16 Completed Milestones
Milestone C.1 - Baseline performance profiling
ORNL Lead, Status: Complete

Goals

• Measure VIBE performance
  — Identify components for improvement / optimization

• Perform simulations involving real automotive battery pack configuration (Nissan Leaf pack is the current choice)
  — Constant current discharge
  — Coupled electrochemical-electrical-thermal simulations under US 06 driving profile

Approach / Strategy

• Select problem
• Generate mesh
• Experimental data for thermal-electrochemical two-way coupling
• Profiling and performance analysis

Results

• Constant current discharge of representative 4P module was simulated using NTG and DualFoil models for electrochemistry, nonlinearly coupled to thermal and electrical solutions
• Performance profiling identified opportunity to speed up simulation by 25%
Milestone I.1 - Report on exp. techniques
ORNЛ Lead
Status: Complete

Goals

• Summarize experimental techniques available to address mechanical and electrochemical behavior of the Li-ion cell and cell components and active materials
  – determination of material properties for model input
  – determination of geometric features of electrodes (microstructure reconstruction) for meshing
  – validation of models
  – benchmark experiments defining failure mode of cells under mechanical abuse
Technical Accomplishments:
Other FY16 Accomplishments
Effective properties with binder

Effective conductivity: Stress/cycling degrades binder conductivity, reduces accessibility of some LCO concentrations

Effective modulus: Soft binder significantly decreases stress state throughout network

Mendoza, Roberts, et al. (submitted); Roberts (unpublished)
Separate cP spheres: Geometric convergence

- Geometric parameters now show clear 2\textsuperscript{nd}-order convergence w/ low initial error
- < 1\% error in SA and volume at \( h \approx r/5 \)!
  - With single LS, required \( h \approx r/100 \).

\[ O(1.94-2.01) \quad O(1.99-2.00) \]
Performance scaling: Many particles

- Currently performing verification activities on 200 particle mesh; largest currently feasible
- Goal of simulating domain with 700 particles
- Recent improvements for particle-number scaling
  - Former behavior < $n^3$
  - Recent improvements > $n$

<table>
<thead>
<tr>
<th>Particles</th>
<th>4.39.5</th>
<th>STK Part Creation</th>
<th>Crossings Map</th>
<th>Volume-Surface Map</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.68</td>
<td>1.70</td>
<td>0.77</td>
<td>0.40</td>
</tr>
<tr>
<td>200</td>
<td>12.25</td>
<td>9.00</td>
<td>4.17</td>
<td>1.00</td>
</tr>
<tr>
<td>Scaling</td>
<td>7.3x</td>
<td>5.3x</td>
<td>5.4x</td>
<td>2.5x</td>
</tr>
</tbody>
</table>
FY17 preparation: PFG-NMR and concentrated solution theory

• High electrolyte concentrations develop in batteries under demanding conditions
• At high concentrations, all species in solution interact with all others; Fick’s law no longer appropriate, accurate models require concentrated solution theory
• Pulsed field gradient (PFG)-NMR yields tracer diffusivities
• Have developed method for connecting PFG-NMR measurements to concentrated solution theory multicomponent diffusivities

\[
\begin{pmatrix}
  j_1/\rho_1 \\
  j_2/\rho_2 \\
  j_3/\rho_3
\end{pmatrix} =
\begin{pmatrix}
  L_{11} & L_{12} & L_{13} \\
  L_{12} & L_{22} & L_{23} \\
  L_{13} & L_{23} & L_{33}
\end{pmatrix}
\begin{pmatrix}
  d_1 \\
  d_2 \\
  d_3
\end{pmatrix}
\]

\[
d_k = x_k \left( 1 + \frac{d\ln \gamma_k}{d\ln x_k} \right) \nabla x_k
\]
Response to Previous Year Reviewers’ Comments

This is a new project for FY16
Collaboration and Coordination
Collaboration and Coordination

- Bi-weekly telecons of working groups on meshing and testing between CABS and NREL project team.
- Monthly videocons with CABS partners at SNL and LBNL
- Joint quarterly meetings with VTO program office and NREL project team
- Partner with Ford on VTO-funded project on simulation of mechanical abuse (Project ID: ES296)
- Project with DOT / NHTSA on crashworthiness
- Naval Surface Warfare Center, Carderock for large-scale testing
- Interactions with VIBE users and potential users, e.g.
  - Motorola
  - NASA
Remaining Challenges and Barriers
Upcoming challenges

• Software and numerical challenges of
  – scaling to larger problems (pack level, with multiple domains)
  – scaling microstructure simulations
  – multiscale simulations (embedding subgrid models in continuum simulations)

• FY17, Q2: Quantifying the error in transport properties due to ion pairing.
• FY18, Q1: Constructing appropriate sample holders for X-ray tomography of cycled electrodes.
Future Work

Includes:
- Detail on FY16 milestones
- Overview of FY17 and FY18 milestones
Milestone E.1 - Microstructure imaging  
LBNL Lead, Status: On Track

Goal

• Obtaining tomography images from uncycled electrodes.
• Perform microstructure imaging of electrodes calendered to different pressures

Approach / Strategy

• X-ray microtomography of electrode samples under light compression, immersed in electrolyte solution
• Refine methods for associating voxel intensity with phase identity
• Generate segmented reconstructions of NMC electrodes, uncalendered and calendered, at 3 pressures

Challenges

• Ability to determine phase identity
• Mitigation – use alternative measurements (BET, etc.) to supplement reconstruction data
Milestone E.2 - Single side incremental indentation
ORNL Lead, Status: On Track

Goals
• Explore internal deformation of the cell including internal faulting
• Provide experimental support for formulation of cell failure criterion

Approach / Strategy
• Design enclosure to preserve internal state of the cell after removal of load.
• Investigate effect of indentation speed on onset of short circuit

Challenges
• Safety concerns for high SOC scenarios may result in using backup test facility (NSWC)
# CABS FY17 Milestones

IDs indicate whether milestones are primarily experimental (E), computational (C), or integrated (I).

<table>
<thead>
<tr>
<th>ID</th>
<th>FY17</th>
<th>Lead</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>Risk(s)</th>
<th>Mitigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.3</td>
<td>Demonstration of ability to construct 3D meshes of electrodes using reconstructions from micro-tomography</td>
<td>SNL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Availability of data, ability to create meshes</td>
<td>Use existing data and meshes</td>
</tr>
<tr>
<td>E.3</td>
<td>Potential-dependent solid diffusivities for Li-ion and EIS</td>
<td>LBNL</td>
<td></td>
<td></td>
<td></td>
<td>P</td>
<td>Ability to obtain nucleation rate, location</td>
<td>Use average quantities</td>
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<tr>
<td>I.4</td>
<td>Demonstrated ability of VIBE/OAS to simulate onset of short-circuit due to mechanical abuse informed by microstructure</td>
<td>ORNL</td>
<td></td>
<td></td>
<td></td>
<td>D</td>
<td>Ability to handle mesh distortions</td>
<td>Use alternative element formulation</td>
</tr>
<tr>
<td>E.4</td>
<td>Data from mechanical deformation tests (nano-indentation and scratch tests) available</td>
<td>ORNL</td>
<td></td>
<td></td>
<td></td>
<td>P</td>
<td>Ability to procure and configure test equipment</td>
<td>Adjust schedule</td>
</tr>
<tr>
<td>C.2</td>
<td>Validated constitutive models and failure criteria for electrode materials and spirally wound, wound prismatic, and stacked electrodes under indentation</td>
<td>ORNL</td>
<td></td>
<td></td>
<td></td>
<td>P</td>
<td>Convergence of constitutive models</td>
<td>Explore alternative solution algorithms</td>
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<tr>
<td>I.5</td>
<td>Deployment of VIBE/OAS with integrated multiscale capability</td>
<td>ORNL</td>
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<td></td>
<td></td>
<td>S</td>
<td>Ability to simulate sufficiently large domains</td>
<td>Obtain additional comp. resources</td>
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# CABS FY18 Milestones

IDs indicate whether milestones are primarily experimental (E), computational (C), or integrated (I).

<table>
<thead>
<tr>
<th>ID</th>
<th>FY18</th>
<th>Lead</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>Risk(s)</th>
<th>Mitigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.3</td>
<td>Coupled thermo-electro-mechanical microstructure simulations of overcharge and mechanical abuse scenarios</td>
<td>SNL</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>Ability to accurately handle large deformation and fracture</td>
<td>Accept more approximate models</td>
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<tr>
<td>E.5</td>
<td>Obtain electrode image data from cycled electrode material</td>
<td>LBNL</td>
<td>P</td>
<td></td>
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<td></td>
<td>Ability to cycle consistently</td>
<td>Increase samples</td>
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<tr>
<td>C.4</td>
<td>Demonstrated mesoscale simulations</td>
<td>ORNL</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>Input param. uncertainty</td>
<td>Careful design of exp. param. space</td>
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<tr>
<td>C.5</td>
<td>Demonstrate improved computational efficiency on benchmark pack-level sim using hierarchy of electrochemical models for US06 drive cycle</td>
<td>ORNL</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>Unforeseen software and numerical challenges</td>
<td>Adjust priorities and reallocate staff</td>
</tr>
<tr>
<td>C.6</td>
<td>Demonstration of validated constitutive models &amp; failure criteria for electrode materials &amp; spirally wound, wound prismatic, &amp; stacked electrodes under bending for pouch cell</td>
<td>ORNL</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>Convergence of constitutive models</td>
<td>Explore alternative solution algorithms</td>
</tr>
<tr>
<td>I.6</td>
<td>Deployment of VIBE/OAS with efficient, validated mechanistic models</td>
<td>ORNL</td>
<td></td>
<td></td>
<td></td>
<td>S</td>
<td>Availability of data, software challenges</td>
<td>Reallocate staff, approx. data &amp; models</td>
</tr>
</tbody>
</table>
Summary

- We are developing an improved battery simulation tools building upon previously released OAS/VIBE
  - We have done baseline performance profiling of VIBE/OAS/AMPERES and identified strategies for improvement
    - e.g. 25% speedup by eliminating driver setup at each time-step
- We are developing experimental procedures for support of constitutive models and validation. Experimental work is on track
  - Mechanical compression of cells and cell components
  - Resonant ultrasound spectroscopy (RUS)
  - Calendering of electrodes
  - Electrodes for X-Ray tomography prepared and shipped to LBNL
  - Design single side indentation experiments and tensile testing
  - Design experiments for measuring diffusivities in concentrated solutions
- Microstructure simulation capabilities are developed
  - Simulations show significant role of binder in relieving stress inside particles of active electrode material
  - Improved treatment of conformal decomposition FEM (CDFEM) for better convergence
Initial investigation of 3D architecture as a mechanism for increasing energy and power density

- Constant electrode volume for both trench and planar configurations
- To use uniform separator thickness need to maintain equal depth trenches for both electrodes
- Same constant current boundary condition used in both configurations
Comparison between Trench and Planar configurations for 2C discharge

Total capacity extracted from trench configuration exceeded the planar configuration at 2C constant current.
Comparison between Trench and Planar configurations for 5C discharge

Total capacity extracted from trench configuration exceeded the planar configuration at 5C constant current.
Comparison between Trench and Planar configurations for 1C, 5C, and 10C discharge

Total capacity extracted from trench configuration exceeded the planar configuration
Integration of resistivity models

• Integrating the mechanics simulations with resistivity models that feeds into the electrochemistry-thermal simulations.
• Images show potential distribution during internal short with increasing conductance.
Models for Electrode Microstructure

- Raw Tomography
- Meshed Particles
- Spherical Approximation
- Ellipsoidal Approximation
Fabric Tensor Formulation

- Use established methods and models from mechanics of saturated granular materials and bonded porous aggregates.
  - Same methods are used to describe damage in materials.
- Clear physical interpretation and relation to experiments.

Fracturing of the Particles at High Calendaring Pressures

- Particle contact and interaction changes with fracture
- Fabric tensor captures evolution of contact with particle breakage

Top View with selections

Lower Selection

Upper Selection
Mechanical Models for Electrode Materials with Particle Fracture

- Upscaling of microstructure simulations using FT formulations
- We are investigating FT methods for upscaling other battery processes and their coupling
Conformal meshing of complex microstructures

Conformal Decomposition Finite Element Method

2D image stack

Surface mesh (STL)

3D reconstruction

Background mesh

Decomposition of background mesh using CDFEM

Hutzenlaub (2012); Noble (2010); Roberts (2014)
Mathematical model for electrochemistry

In the particle

- **Ohm’s Law**
  \[ \nabla \cdot (\sigma \nabla \phi_s) = 0 \]

- **Intercalated Li conservation**
  \[ \frac{\partial C_{Li}}{\partial t} + \nabla \cdot \left[ MC_{Li} \nabla \left( \mu_{Li}^{\text{chem}} + \mu_{Li}^{\text{stress}} \right) \right] = 0 \]

At the interface

- **Butler-Volmer reaction rate**
  \[ \mathbf{J} \cdot \mathbf{n} - j_0 \left[ \exp \left( \frac{\alpha_a F (\phi_s - \phi_l - \phi_{eq})}{RT} \right) - \exp \left( \frac{-\alpha_c F (\phi_s - \phi_l - \phi_{eq})}{RT} \right) \right] \]

In the electrolyte

- **Current conservation**
  \[ \nabla \cdot \left[ F \left( \mathbf{J}_{Li^+} - \mathbf{J}_{PF_6^-} \right) \right] = 0 \]

- **Nernst-Planck fluxes**
  \[ \mathbf{J}_i = -D_i \left( z_i C_i \frac{F}{RT} \nabla \phi_l + \nabla C_i \right) \]

- **Li+ conservation**
  \[ \frac{\partial C_{Li^+}}{\partial t} + \nabla \cdot \mathbf{J}_{Li^+} = 0 \]

- **Electroneutrality**
  \[ C_{PF_6^-} = C_{Li^+} \]
Electrochemical behavior with non-ideal lithium transport

- Ideal transport (Fickian) model:
  \[ J_{Li} = -D \nabla C_{Li} \]

- Non-ideal (potential) model:
  \[ J_{Li} = -MC_{Li} \nabla \mu_{Li}^{\text{chem}} \]

Ideal transport model shows unrealistically high concentration gradients

Mendoza, Roberts, et al. (submitted)
Mathematical model for mechanics

- Intercalation-induced swelling causes a volumetric strain
  \[ E = E_{\text{elastic}} + E_{\text{swelling}} = E_{\text{elastic}} + \alpha \Delta C_{Li} \]

- For a linear elastic constitutive behavior, swelling is converted to stress
  - Analogous to standard “coefficient of thermal expansion” approach
    \[ \sigma = C : E_{\text{elastic}} = C : E - C : \alpha \Delta C_{Li} = C : E - \beta \Delta C_{Li} \]

- Generally, volumetric strain is isotropic
  \[ \beta = \beta \delta \]

- Stress governed by quasi-static momentum conservation
  \[ \nabla \cdot \sigma + F = 0 \]
Stress development in LCO network

Particle confinement leads to 100x higher stresses than in isolated particles

Mendoza, Roberts, et al. (submitted)
Srinivasan group core strength: battery model development

- Building on Prof. John Newman’s work on porous electrodes
- Spatially-averaged equations & parameters, simple geometries
- Qualitative understanding at low computational cost
- Past work on LFP, NMC, graphite; currently building Li-S model
Macroscale models provide insight into performance (NMC example)

- Rapidly provide predictions of spatial variation
- Allows examination of capacity limitations
- Allows exploration of potential drops and capacity loss mechanisms
Systematic experiments provide model parameters (NMC example)

- Li surface reaction kinetics from low-current experiments with Li-Li symmetric cell
- DLi(SOC) in NMC from open-circuit relaxation experiments with thin electrode, single particle model
- NMC surface reaction kinetics from rate experiments with thin electrode, single particle model
Mechanical simulations consider other performance limitations (graphite)

- Single particle diffusion-induced stress model investigates particle cracking
- Diffusivity of Li in graphite at two temperatures from thin electrode experiments, single-particle model
- SEM images after cycling tests show damaged and undamaged particles consistent with model results
Expanded mechanical simulations consider interaction with binder

- Active material particles attached to surrounding material
- Silicon shows 300% expansion, fully lithiated
- Large-deformation mechanics, built on work by Christensen and Newman
- Axisymmetric model system: particle with attached binder
Realistic electrode geometries might improve model accuracy

• What is the cost of spatial averaging?
• Using X-ray microtomography at ALS to obtain electrode reconstructions
• Yields intensity in 3D region divided into volume elements (“voxels”)
• “Segmentation” of voxels according to phase
Developed workflow from sample preparation to microscale simulation

- Reconstructions turned into surface meshes
- Governing equations without spatial averaging
- Fine detail with high computational cost
- How different from macroscale simulation, and why?

10 μm x 10 μm x 57 μm sample

Lithium/Salt Concentration (kmol/m^3)

18.079  23.645  29.211  34.777  40.343  45.909