Computational Design of Batteries from Materials to Systems

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NREL/PR-5400-68770
Physics of Li-Ion Battery Systems in Different Length Scales

- **Electrode Scale**
  - Charge balance and transport
  - Electrical network in composite electrodes
  - Li transport in electrolyte phase

- **Cell Scale**
  - Electronic potential & current distribution
  - Heat generation and transfer
  - Electrolyte wetting
  - Pressure distribution

- **Module Scale**
  - Thermal/electrical inter-cell configuration
  - Thermal management
  - Safety control

- **System Scale**
  - System operating conditions
  - Environmental conditions
  - Control strategy

- **Atomic Scale**
  - Thermodynamic properties
  - Lattice stability
  - Material-level kinetic barrier
  - Transport properties

- **Particle Scale**
  - Li diffusion in solid phase
  - Interface physics
  - Particle deformation & fatigue
  - Structural stability

- **System Scale**
  - System operating conditions
  - Environmental conditions
  - Control strategy

**Computational models offer pathway to advance next generation designs**
**DOE Computer-Aided Engineering of Batteries (CAEBAT) Program**

- **Goal:** Accelerate development of batteries for electric-drive vehicles
- **Successes:**
  - **Multiscale multidomain** model approach linking disparate length-scales (NREL)
  - Open architecture (ORNL)
  - Commercial software toolsets with 150+ users
- **Current priorities** based on feedback:
  - Extend the models to include mechanical failure of cells and packaging components
  - Increase computational efficiency
  - Standardize identification of the model parameters
  - Close gaps between materials R&D and CAEBAT modeling tools

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**MSMD**

*Multi-particle system*

**Examples**

- Preferential utilization in wound cell
- Thermal management design with commercial CAE tools
Outline

• Abuse
  • Internal short
  • Mechanical crush

• Electrode performance
  • Fast electrochemical simulation
  • Parameter identification

• Microstructure role
  • Electrode tortuosity & inhomogeneity
  • Carbon + binder phase

SEM image: Koffi Pierre Claver (ANL)
Safety Modeling Approach

**NREL Electrode Domain Model Library**
- Electrochemical State Variable Model (SVM)
- Abuse Reaction Kinetics Model (ARK)
- Internal Short Circuit Model (ISC)

**NREL ARK Model**
\[
S = HW \frac{d\alpha}{dt}
\]
\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]
\[
k(T) = Ae^{-\frac{Ea}{RT}}
\]
\[
f(\alpha) = \alpha^m(1 - \alpha^n)(-\ln(1 - \alpha))^p
\]

- **S**: volumetric reaction heat;
- **H**: heat of reaction;
- **d\alpha/dt**: reaction rate;
- **k(T)**: temperature-dependent rate constant

**Cell Domain Model**: Single pair potential continuum (SPPC) electrothermal model in ANSYS® Fluent® MSMD-module

- 3D initial short circuit
- Cathode-anode short growth

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Testing Using NREL’s Internal Short Circuit (ISC) Device

Top to Bottom

1. Copper Disc
2. Battery Separator
3. Phase Change Material (wax)
4. Aluminum Disc

Wax formulation used melts around 57°C

ISC device in 3rd wind of jellyroll

Tomography credits: University College of London

2010 Inventors:
NREL: Matthew Keyser, Dirk Long, and Ahmad Pesaran
NASA: Eric Darcy

US Patent # 9,142,829 awarded in 2015

2016 R&D100 Award Winner
Validation of the 3D Simulation – 18650 Cell

- Simulation result shows a good agreement with testing data
- ISC device is able to trigger thermal runaway of cell successfully
- Due to different thermal conductivity of cell, heat transfer rate along azimuthal and axial directions is faster than in the radial direction
**Simulation vs. Testing**

- Simulation results show the same trend as testing data, and the maximum temperature of simulation results at TC1 and TC2 is similar to the testing data.
- There are two reasons that might affect the accuracy of simulation: complicated thermal conditions during testing and the location of thermocouples.
- Thermal runaway models are generally accurate at predicting cell runaway (or not) and propagation.

**Temperature Contours at Center Plane**

- At t = 9.6 s
- At t = 52.6 s
Heat Dissipation to Control Thermal Runaway

- 3S1P module
- 24-Ah LCO/graphite
- Shut-down separator
- Fin cooling
- Initial ISC in the middle cell

LCO = Lithium cobalt oxide
Mechanical Abuse Modeling Approach

**Objective:** Predict battery behavior during a crash event to optimize safety and weight reduction

**Step 1:** Start with Component and Cell-Level Test Results as Input

**Sample Input:**
- Stress-strain curves for cell components (separator, current collector, etc.)
- Failure strengths for particles
- Mechanical data for cell packaging
- Temperature vs. C-rate for cell
- Abuse reaction data from calorimetry for specific chemistries

**Step 2:** Explicit Simulations
Parameterize Material Response

**Step 3:** Simulate Cell-Level Response for Multiple Cases

**Step 4:** Scale to Module-Level

**Step 5:** Validate against Experimental Data

**Sample Output:**
- Current distribution among the different cells within the module
- Localized heat generation rates far away from damage zone
- Stress distribution across multiple parts of the battery module

**Goal:** Identify localized failure modes and onset loads to within 30 MPa
**Mechanism of Failure Initiation following a Crush**

**Outcome:**
- Comprehensive understanding of failure thresholds and propagation mechanism for each component within the cell
- Better explanation of test data results in recommendations for test-method development
- Light-weighting/right-sizing of cells without compromising safety

Copper foil Layer 1
Anode Layer 4
Cathode Layer 6

Cathode-Anode Short

**Side-facing indenter**

1st layer
4th layer
7th layer


Shear failure of active material layers within a battery

Copper foil fails before separator ruptures

Multi-cell Crush Test and Simulation

Testing

Bar crush of a 12-cell string

Josh Lamb, SNL

• Models capture qualitative features; numerical comparison of failure strains underway.
• The packaging can prevent deformation of the cells by as much as 50% under these crush test conditions.
• There is a significant scope to lightweight the pack, even after the safety threshold is met.

Compression from buckling

Separation of electrode layers

Initial validation

Packaging study
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SEM image: Koffi Pierre Claver (ANL)
Approach for Fast Electrochemical Simulation

1) Nonlinear Multiscale Implicit Formulation

\[ \phi = f(i; x, p) \]

2) Timescale Separation & Variable Decomposition

\[ \phi = g(i; x, p) + h(i; x, p) \]

3) Partial/Selective Linearization

\[ G(i; x, p) = \frac{dg}{di} \]

\[ \phi = G(i; x, p)i + H(i; x, p) \]

Example Speed-up of Electrode-domain Simulation

The selective G-H linearization approach drastically reduces computational burden

<table>
<thead>
<tr>
<th>Simulation case</th>
<th>Computation time for Electrode Domain Models (EDM) in seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load Profile</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>1C</td>
<td>25</td>
</tr>
<tr>
<td>1C</td>
<td>0</td>
</tr>
<tr>
<td>Drive cycle</td>
<td>25</td>
</tr>
<tr>
<td>Drive cycle</td>
<td>0</td>
</tr>
</tbody>
</table>
Model Parameter Identification Workflow

Pre-processing and filtering of raw data

Setup baseline MSMD Inputs

Fitting of model to data

- Python script parses data to meet model needs
- Parameter estimation based on Levenberg-Marquardt algorithm
- Workflow independent of model(s)/data set(s)
- Can use the same approach for multiple models and/or datasets – as long as the list of inputs and outputs are standardized (e.g., using the OAS)
- Process can be easily wrapped with a GUI as workflow stabilizes.
Parameter Identification Results

Examples of Parameters and Confidence Intervals

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{Li}^{max}$ (mol/m$^3$)</td>
<td>2.9511e+04 ± 2.5377e+02</td>
<td>4.9050e+04 ± 7.0677e+01</td>
</tr>
<tr>
<td>$D_s^{ref}$ (m$^2$/s)</td>
<td>3.015e-15 ± 2.469e-15</td>
<td>4.393e-15 ± 2.563e-17</td>
</tr>
</tbody>
</table>

Automated procedure calibrates models with data from cyclers to a max. relative error < 5%
Underway: Analysis of Material/Data Quality

- Determine what level of fidelity in calibration data is necessary by comparing against QC data/spec.

Coin-cell dataset 1..N

Particle Domain fit for cells 1..N

Range of fitted Particle Domain parameters

Cell Domain fit with bounds on Particle Domain parameters

Distribution of cell-level metrics

Predict actual cell performance

Cell Domain fit + Confidence Intervals

Closing the loop between lab-scale calibration data and production cell specs. will reduce development costs by directing improvements to processes that impact on cell quality the most.
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  • Fast electrochemical simulation
  • Parameter identification (bottleneck)

• Microstructure role
  • Electrode tortuosity & inhomogeneity
  • Carbon + binder phase
Enhancing Electrodes through Microstructure Modeling

Stochastic reconstruction & meso-scale physics

Validation of virtual 3D geometry

Electrode fabrication, tomographic measurement, electrochemical response

Electrochemical performance validated for multiple electrode designs

Design inputs
• Chemistry
• Morphology
• Size distribution
• Binder
• Conductive additive
• Calendaring

Microstructure Model
• Geometry
• Physics
• High Performance Computing (HPC)

Homogenization

Linkage to CAEBAT macroscopic simulation toolsets

Image credits:
Microstructure – Partha Mukherjee, TAMU
HPC – NREL image gallery
Coated electrode – hirano-tec.co.jp

Cell Analysis, Modeling & Prototyping (CAMP) Facility
Comparison of seven NMC electrode designs vs. C-rate

Capacity depends mainly on porosity due to electrolyte transport limitations

Average voltage drops due to ohmic and polarization losses

NMC: nickel manganese cobalt
Multiple measurements needed to resolve relevant characteristics across length scales

Focused Ion Beam - Scanning Electron Microscopy
- Particle surface & morphology
- Secondary phase (conductive additive + binder)

Nano- & Micro-Tomography
- Ionic & electronic tortuous paths (lacks secondary phase, however)

*Graphite electrode image courtesy of Paul Shearing & Donal Finegan of UCL. All other images courtesy of Pierre Yao & Daniel Abraham of ANL.
Meso-scale Modeling of Conductive/Binder Phase

- Numerical algorithm stochastically generates conductive/binder phase taking on different morphologies

A) Film-like deposits (solid lines)

B) Finger-like deposits (dashed lines)

Finger-like deposits improve electronic conductivity but introduce additional tortuosity for electrolyte-phase transport

Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU
• Microstructure property relations used in today’s macro-homogeneous models hold well in the limit of low solid volume fraction / high porosity...

\[ a = 3\varepsilon_s \]

\[ \tau = \varepsilon^{-0.5} \]

Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU
Meso-scale Modeling of Effective Electrode Properties (2/2)

- ... but lose validity for dense electrodes
- Meso-scale models were used to develop more accurate property relations for dense electrodes across entire electrode design space. To be validated and extended to non-spherical geometries

\[
a = 3\varepsilon_s
\]

\[
\tau \left[ R^2 = 0.9394 \right] = 0.8025 \cdot \varepsilon^{-1.0244}
\]

\[
\tau = \varepsilon^{-0.5}
\]

Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU
Microstructure Analysis

- Particle size and morphology of calendared electrodes
  - Clear differences between graphite and NCM morphologies
  - Calendaring slightly elongates and re-aligns of particles

- Tortuosity* via homogenization calculation
  *Micro-pore, neglects conductor + binder phase for now

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<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Through-plane</td>
<td>3.8</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>In-plane</td>
<td>1.8</td>
<td>1.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Summary and Future Work

• Safety models able to represent and predict thermal runaway propagation in a battery module
  o Model-based design cost-effective and repeatable
  o ISC device preferred to other test methods (nail, pinch, etc.)
  o Mechanical abuse/crash validation underway

• Addressing bottlenecks for adoption of electrochemical models into battery CAE design process
  o Parameter identification
    – Enabled by fast running models
    – Optimizing experiments and test articles
  o Addressing heterogeneity in electrode microstructure
  o Prediction of effective properties for electrode models
    – Thick electrode, fast charge optimization
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  CAMP Facility

• Paul Shearing – Univ. College of London

www.nrel.gov/transportation/energystorage/
Publications and Presentations


Publications and Presentations, cont.

- A. Mistry et al., “Secondary Phase Stochastics in Li-ion Battery Electrodes,” *in preparation*.
- François Usseglio-Viretta et al., “Non-parametric Discrete Particle Algorithm and Application to Microstructure of Li-Ion Battery Electrodes,” *in preparation*.