Efficient Safety and Degradation Modeling of Automotive Li-ion Cells and Pack

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Project ID #
ES200

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
• Start date: 10/1/2013
• End date: 9/30/2015
• Project 25% complete

Barriers
• Barriers addressed
  – LiB Safety/Abuse
  – LiB Lifetime
  – LiB Efficiency
  – Computer tools for design exploration

Budget
• Total project funding: $2.0M
  – $1.0M (DOE)
  – $1.0M (cost share)
  – Fed. cost through 12/31/13: $134.5 k

Partners
• Penn State

Funding provided by Dave Howell of the DOE Vehicle Technologies Program.
The activity is managed by Brian Cunningham of Vehicle Technologies, through NETL, Bruce Mixer Technical Monitor.
Project Objectives - Relevance

• Develop an efficient & robust pack-level safety and abuse model
  – Predictive tool with electrochemical-thermal (ECT) coupling
  – Virtual tool to assess/screen safety of cell/pack designs

• Develop mechanism-based, fundamental models for accurately predicting degradation of Li-ion batteries
  – Predictive models valid under user-specified and wide-ranging temperatures and operating conditions

• Perform co-simulation of our software with structural mechanics software via the Open Architecture Standard (OAS)
  – Electrochemical-Thermal-Mechanical (ECT-M) coupled simulation

• Perform testing and validate the cell- and pack-level safety and degradation models

• Expand extensive materials database
  – Experimentally characterizing and adding NCA to our database

• Develop commercial software to be used by licensees

• Support DOE CAEBAT activity
## Project Milestones & Activities

### Recent Milestones Completed

<table>
<thead>
<tr>
<th>Milestone (M)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Project kickoff; all agreements and sub-agreements executed</td>
</tr>
<tr>
<td>M2</td>
<td>Completion of initial model development for safety, abuse, and life</td>
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### Milestones in Progress

<table>
<thead>
<tr>
<th>Milestone (M)</th>
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<tbody>
<tr>
<td>M3</td>
<td>Complete fabrication of large-format cells for safety, abuse, and degradation testing</td>
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<tr>
<td>M4</td>
<td>Safety, abuse, and degradation testing 50% complete</td>
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<tr>
<td>M5</td>
<td>Materials database characterization 50% complete</td>
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<tr>
<td>M6</td>
<td>Initial model implementation complete for safety, abuse and degradation</td>
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**Budget period #1 Exit (12/31/14): Go/No-Go**
Approach – Supporting CAEBAT Activity

End Product: Experimentally validated commercial tool with advanced safety/abuse and life models, along with commercially-relevant materials database
Approach – Materials Database

Tested temperature range for materials
-30°C to 100°C

Existing Anode Materials:
- Graphite (blend natural/syn.)
- LTO

Existing Cathode materials:
- NCM
- LFP
- LMO
- LCO

Adding NCA as part of this project
- GITT for $D_s = f(T,x)$ and $OCP = f(T,x)$
- EIS for $i_0 = f(T,x,c_e)$

Data collected for electrolyte concentrations ranging from 4M to 0.1M

Electrolyte distribution in a Li-ion cell under discharge

Electrolyte Concentration
- 4M
- 1M
- 0.1M

Solid Diffusivity ($D_s$)

DoD

Temperature

Four orders of magnitude change in $D_s$ over typical $(x,T)$ range for automotive use

Modeling parameters needed at low-T, high-T, wide range of chemical compositions and similar conditions of interest for automotive Li-ion batteries and packs
**Approach – ECT Modeling**

**Electrochemical Processes**
- electrochemical reactions
- solid state diffusion
- ion transport through electrolyte
- charge transfer

**Heat generation rate**
\[
q = \sum_j a_{ij} I_j (\Pi_j + \Pi_j) - \sum_k \langle i_k \rangle \cdot \nabla \langle \phi_k \rangle
\]

**Temperature-dependent physico-chemical properties**
\[
\Phi = \Phi_{ref} \exp \left( \frac{E_{act,\Phi}}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right)
\]

**Thermal Processes**
- conservation of thermal energy
\[
\frac{\partial (\rho c_p T)}{\partial t} = \nabla \cdot (\lambda \nabla T) + q
\]

**Model predictions**
- potential and current curves
- temperature history/distribution
- active material utilization
- current distribution

- Understanding thermal phenomena & thermal control has huge impact on
  - Battery safety
  - Cycle life
  - Battery management system
  - Cost

- Electrochemical-thermal (ECT) coupling required for
  - Safety simulations
  - Thermal runaway
  - High power, low-T operation
  - Heating from subzero environment
Accomplishments – Materials Database

NCA Property Measurement

**GITT Test – OCP and Ds**
- To get OCP = f(x,T) and D_s = f(x,T)
- 6-8 months to carry out full matrix of (x,T) combinations
- At one T, 40+ data points to get data for entire (0 < SOC < 1) range
- NCA/Li half cells used
- Nearly complete

**EIS – Exchange Current Density**
- To get OCP = f(x,T) and D_s = f(x,T)
- 6-8 months to carry out full matrix of (x,c_e,T) combinations
- NCA/Li half cells
- Recently started

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**GITT Input:**
Current discharge pulse and rest period

**Z' (Ω cm²)**

Sample: NCA Cell #5, 1.2M

S=$1.539$ cm² ($\phi=14$mm)

Temperature: 20°C

ac=5mV, f=1000 kHz to 0.005Hz

**Temperature**

**Solid Diffusivity (D_s)**

**Z'' (Ω cm²)**

Curves for different SOC

Adding NCA properties to materials database for accurate Li-ion battery prediction under automotive conditions
Accomplishments – Pack-level Safety

Initial Implementation of Pack-level Shorting Model

- We have developed a robust approach and algorithms to efficiently simulate nail penetration of multi-cell packs
- Typical nail penetration simulation takes a few hours for one processor per cell (coupled ECT simulation)
- Goal: develop a software that can reliably assess safety of any cell or pack and evaluate effectiveness of various mitigation strategies
  - Nail type, nail size
  - Cell material types, electrode design, capacity, cell/pack geometry
  - Evaluate proposed safety mechanisms under different safety conditions

The coupled thermal and electrochemical response of pack-level shorting is captured with the model implemented, in an efficient manner.
Accomplishments – Pack-level Safety

Number and Arrangement of Cells in Pack (1/2)

Case #1
- One 30Ah NMC/graphite cell
- The two cases are identical electronically (same V, same total capacity)
- Both are shorted by 20mm diameter stainless steel nail
- The 6p/1s arrangement is substantially safer due to more global heating

Case #2
- 6p/1s configuration of 5Ah NMC/graphite cells

Kalupson et al., ECS Spring Conference, Orlando, FL April 11-15, 2014
Accomplishments – Pack-level Safety

Number and Arrangement of Cells in Pack (2/2)

Pack safety is dictated by complex interplay between electrochemical, thermal, and geometric factors; safety can only be determined by models that account for all three factors.

Kalupson et al., ECS Spring Conference, Orlando, FL April 11-15, 2014
Accomplishments – Safety Validation

Preliminary Nail Penetration Testing

- Goal: measurement of detailed electrochemical and thermal response during nail penetration test (not just temperature)
  - Current and/or contact resistance
  - Multiple sensors embedded in nail and/or cell to validate ECT model
- To date: preliminary testing of various designs
  - Will down-select best designs for future use
- In year two – also perform nail penetration of multi-cell pack (pack-level validation)

Successful in-situ measurement of temp & current from past work
Accomplishments – Life & Abuse

- Enhanced life and abuse models – completed initial model development (model equations)
  - Enhanced electrode pulverization model
  - Enhanced SEI growth model, including effects of electrolyte additives
  - Life model for user-defined mixed electrodes
  - Overcharge model

- Currently working on implementing these refined models
- All models are mechanism-based, temperature-dependent, predictive models, i.e. non-empirical

*Enhanced models for more accurate prediction of life and features to expand usefulness (e.g. mixed electrode with life)*
Collaboration w/Other Institutions

Project Lead – Software development and sales, project administration.

Academic Partner – materials testing and detailed model validation
Future Work

- Complete NCA characterization
- Carry out nail penetration testing and validation
  - Single cell
  - Multi-cell pack
- Continue implementation and validation of enhanced models for life and abuse
  - Accelerated life testing
  - Overcharge testing
- Add additional features to pack-level safety model
  - Add capability to simulate partial penetration of pack (e.g. 3/16 cells shorted) for parallel configuration
- OAS: co-simulation with structural mechanics software (ECT-M simulation)
- These activities reflected in future milestones
Response to Previous Year Review

• This is the first year for this project (no review from last year)
Summary

• Project on track
  – Demonstrated simulation of pack-level nail penetration
  – NCA characterization ongoing
  – Nail penetration testing with innovative approach to acquire data for validation
  – Initial model development complete for enhanced life and abuse models

• Future work tied to milestones and addresses project objectives
  – Completing ongoing tasks
  – Implementation of models developed
  – Validation of safety and life models
  – OAS

• Software is commercially available

• Meeting CAEBAT/DOE goals
  – Helping to accelerate the adoption of automotive Li-ion batteries by addressing barriers to adoption (e.g. life and safety)
  – Enabling technology for EV, PHEV