



## **NREL Energy Storage Projects: FY2014 Annual Report**

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Shriram Santhanagopalan, Aron Saxon,  
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and Chao Zhang

*National Renewable Energy Laboratory*

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Christian E. Shaffer  
*EC Power*

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Prepared under CAEBAT Project

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## Foreword

The Energy Storage Group within the Transportation and Hydrogen Systems Center and the Chemical and Materials Science Center at the National Renewable Energy Laboratory (NREL) performed the work detailed in this report under the Energy Storage Research and Development (R&D) activity of the Office of Vehicle Technologies. This activity is managed by David Howell of the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy, in support of the automotive and battery industries. In fiscal year 2014, NREL performed several R&D projects under its Annual Operating Plan submitted to DOE on anode materials, coatings on cathodes, battery modeling, computer-aided engineering of batteries (CAEBAT), battery testing, life trade-off study modeling, techno-economic analysis of battery-powered vehicles, and secondary use of batteries. A summary of each project was prepared and submitted to DOE for inclusion in its Energy Storage FY14 Annual Progress Report. This report is a collection of the individual reports submitted to DOE.

This research and report would not have been possible without the support and guidance of many people. The authors wish to thank Brian Cunningham, Tien Duong, Peter Faguy, and David Howell from the Office of Vehicle Technologies at DOE for funding support and guidance. We also wish to thank Taeyoung Han of General Motors (GM), Steve Hartridge of CD-adapco, and Christian Schaffer of EC Power for their contributions to the CAEBAT program. More importantly, we would like to thank Marissa Rusinek, Energy Storage Group Administrative Assistant, for her tremendous effort in assembling this report from individual sections written by different principal investigators and adding other documentation.

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## Executive Summary

The National Renewable Energy Laboratory supports energy storage R&D under the Office of Vehicle Technologies at the U.S. Department of Energy. The DOE Energy Storage Program's charter is to develop battery technologies that will enable large market penetration of electric drive vehicles. These vehicles could have a significant impact on the nation's goal of reducing dependence on imported oil and gaseous pollutant emissions. DOE has established several program activities to address and overcome the barriers limiting the penetration of electric drive battery technologies: cost, performance, safety, and life. These programs are:

- *Advanced Battery Development through the United States Advanced Battery Consortium (USABC)*
- *Battery Testing, Analysis, and Design*
- *Applied Battery Research (ABR)*
- *Focused Fundamental Research, or Batteries for Advanced Transportation Technologies (BATT)*

In FY14, DOE funded NREL to make technical contributions to all of these R&D activities. This report summarizes NREL's R&D projects in FY14 in support of the USABC; Battery Testing, Analysis, and Design; ABR; and BATT program elements. The FY14 projects under NREL's Energy Storage R&D program are briefly described below. Each of these is discussed in depth in this report.

### Battery Ownership Model

Fast charging is attractive to electric vehicle (EV) drivers for its ability to enable long-distance travel and quickly recharge depleted batteries on short notice. However, such aggressive charging and the resulting sustained vehicle operation could lead to excessive battery temperatures and degradation. Properly assessing the consequences of fast charging requires accounting for disparate cycling, heating, and aging of individual cells in large battery electric vehicle (BEV) packs when subjected to realistic travel patterns, usage of fast chargers, and climates over long durations (i.e. years). The resultant gains in vehicle utility afforded by fast charging under real-world conditions must also consider these factors. The DOE Vehicle Technologies Office (VTO) has supported NREL's development of the Battery Lifetime Analysis Simulation Tool for Vehicles (BLAST-V) to create a tool capable of accounting for all of these factors. In FY14, specific developments were completed to enable the realistic simulation of EVs operated in the presence of fast chargers. BLAST-V was then employed to evaluate the effects of realistic fast charger use on BEV batteries and utility.

### PEV Battery Second Use

In past years, NREL has created a detailed framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications. The application of this framework to lithium-ion (Li-Ion) plug-in electric vehicle (PEV) batteries has highlighted the need for efficient repurposing strategies, and identified a promising market for repurposed batteries. It has also found that the most pressing remaining uncertainty is the longevity of repurposed batteries in post-automotive applications. To address this uncertainty, NREL has acquired aged batteries, developed a long-term field test site and strategy, and initiated long-term testing via a subcontract with the California Center for Sustainable Energy (CCSE), leveraging a 50-50 cost share partnership with industry. NREL has also acquired additional aged batteries for on-site laboratory testing. Additionally, NREL has worked with Southern California Edison to evaluate the potential of second use batteries in community energy storage applications, and with BMW to demonstrate a pre-commercial second-use battery system.

### Battery Life Trade-Off Studies

Battery aging behavior directly impacts to what degree an electric-drive vehicle (EDV) battery must be oversized to achieve desired service life across applications and environments. Eliminating extra cost associated with oversizing would positively benefit market acceptance of EDVs. Automotive batteries face large variability in thermal environment and duty cycle, with 10+ degradation factors that must be considered to predict lifetime. Worst-case cell aging conditions within a multi-cell battery pack drives the need to oversize battery cell energy content. Physics-based models describing cell- and pack-level aging processes are needed to support engineering optimization of next generation batteries. Cell life models must capture a multiplicity of degradation modes experienced by Li-ion cells, such as interfacial film growth, loss of cycleable lithium, loss of active material,

degradation of electronic and ionic pathways, with dependence on temperature, state-of-charge, depth-of-discharge, C-rate, and other duty cycle factors. In particular, the mechanical damage induced by high C-rate and depth-of-discharge electrochemical cycling is a poorly understood degradation mechanism which we seek to clarify with physical models. Pack-level life models must capture effects leading to non-uniform cell aging, including temperature imbalance, cell performance and aging variability, and interaction with balance of plant systems such as cell balancing.

### **In-Vehicle Lower-Energy Energy Storage System (LEESS) Component Evaluation**

Automakers have been mass-producing hybrid electric vehicles (HEVs) for more than a decade, and the technology has proven to be very effective at reducing per-vehicle fuel use. However, the cost of HEVs such as the Toyota Prius or Ford Fusion Hybrid remains several thousand dollars higher than the cost of comparable conventional vehicles, which has limited HEV market penetration. The battery energy storage device is typically the component with the greatest contribution toward this cost increment, so significant cost reductions and/or performance improvements to the energy storage system (ESS) can correspondingly improve the vehicle-level cost-versus-benefit relationship. To validate the fuel savings and performance of an HEV using such a LEESS device, this jointly-funded activity between the U.S. Department of Energy Vehicle Technologies Office Energy Storage and Vehicle Systems Simulation and Testing programs has designed a test platform in which alternate energy storage devices can be installed and evaluated in an operating vehicle. We completed comparison testing between the converted Ford Fusion Hybrid test vehicle operating on its production battery pack and operating on lithium-ion capacitor (LIC) LEESS devices supplied by JSR Micro, Inc. We also installed ultracapacitors from Maxwell. Road and dynamometer testing showed that the HEV with LEESS has the same acceleration, driveability, and fuel economy as the HEV with the original NiMH battery.

### **Battery Thermal Analysis and Characterization Activities**

The operating temperature is critical in achieving the right balance between performance, cost, and life for both Li-ion batteries and ultracapacitors. At NREL, we have developed unique capabilities to measure the thermal properties of cells and evaluate thermal performance of battery packs (air or liquid cooled). We also use our electro-thermal finite element models to analyze the thermal performance of battery systems in order to aid battery developers with improved thermal designs. Using NREL's unique R&D 100 Award-winning calorimeters and infrared thermal imaging equipment, we obtain thermal characteristics (heat generation, heat capacity, and thermal images) of batteries and ultracapacitors developed by USABC battery developers and other industry partners. NREL supports the Energy Storage Technical Team by participating in various work groups such as the JCI, LG CPI, SK Innovations, Leyden, Saft, Envia, and Farasis USABC Working Groups.

### **Battery Multi-scale Multi-domain Framework & Modeling**

Physicochemical processes in Li batteries occur in intricate geometries over a wide range of time and length scales. As the size of the battery increases to meet the system demands of high-energy and high-power energy storage in electric vehicle applications, macroscopic design factors in combination with highly dynamic environmental conditions significantly influence the electrical, thermal, electrochemical, and mechanical responses of a battery system. Without better knowledge of the interplays among interdisciplinary multi-physics occurring across varied scales in the battery systems, it is costly to design long-lasting, high-performing, safe, large battery systems. NREL pioneered the multi-scale multi-domain (MSMD) model, overcoming challenges in modeling the highly nonlinear multi-scale response of battery systems. The MSMD provides high extent flexibility and multi-physics expandability through its modularized architecture, as well as computational efficiency to enable the model to run on standard desktop PCs by providing selective, finer meshes for low hierarchical subdomains.

### **Computer-Aided Engineering of Batteries (NREL)**

The goal of the Computer-Aided Engineering of Automotive Batteries (CAEBAT) activity is to “develop suites of software tools that enable automobile manufacturers, battery developers, pack integrators, and other end-users to simulate and design cells and battery packs in order to accelerate the development of energy storage systems that meet the requirements of the electric drive vehicle.” To oversee the successful execution of the CAEBAT program, NREL was assigned to coordinate the industry and academic activities on Cell-Level Modeling and Pack-Level Modeling. In order to engage serious involvement of industry, NREL, with guidance from DOE, issued a Request for Proposals (RFP) in FY10 to seek development of cell and pack battery design tools for a period of three years with 50-50% cost sharing. The CD-adapco, GM, and EC Power teams were awarded in the middle of 2011. The



three subcontract teams started technical work in July 2011, made steady progress, and have either met their milestones or are on track to complete them in early FY15 after no-cost extensions. All three subcontractors have completed the first version of their software and released it to the public, and there are more than 50 users designing batteries with these CAEBAT tools. In FY14, NREL continued working on developing and further improving its 3D electrochemical-thermal models. NREL also collaborated with ORNL in their development of the Open Architecture Software.

#### **Development of Computer Aided Design Tools for Automotive Batteries (General Motors)**

The principal objective of the GM team is to produce an efficient and flexible simulation tool that predicts multi-physics responses for battery pack thermal management and predicts an optimum cell energy capacity in terms of electrical performance, cooling requirements, life, safety, and cost. GM has assembled a CAEBAT Project Team composed of GM researchers and engineers, ANSYS software developers, and Prof. R.E. White of the University of South Carolina and his ESim staff. In partnership with DOE/NREL, the Project Team has interacted with the CAEBAT working groups to integrate and enhance existing sub-models, develop cell- and pack-level design tools, and perform experimental testing to validate the simulation tools. The GM team has also created interfaces to enable these new tools to interact and interface with current and future battery models developed by others. NREL has provided the technical consultations and monitored the overall progress. ORNL has provided the standard for Open Architecture Software (OAS). With a rapid deployment to industry, these project results will contribute to accelerating the pace of battery innovation and development for future electric-drive vehicles. The first version of the ANSYS battery software was officially released to the public with Release 15 of FLUENT in the winter of 2014.

#### **Development of Computer Aided Design Tools for Automotive Batteries (CD-adapco)**

The U.S. Department of Energy established the CAEBAT activity to develop multi-physics design tools. NREL, with guidance from DOE, co-funded three subcontractors including CD-adapco, to develop software tools for CAEBAT. CD-adapco has extended its class-leading computer-aided engineering code, STAR-CCM+, to analyze the flow, thermal and electrochemical phenomena occurring within spirally-wound lithium-ion battery modules and packs. This coding has been developed in collaboration with Battery Design, LLC, a sub-contractor to CD-adapco with considerable experience in the field of electrochemistry modeling. As well as resolving the electrochemically-active regions in a spiral cell, the model accounts for tabbing of the electrode in the overall performance. The created electrochemical model has now been applied to lithium-ion cells. The project was successfully completed in 2014. Star-CCM+, CD-adapco's flagship commercial software, was released with a battery modeling module developed under this CAEBAT project. Many around the world use this tool for accelerating battery design.

#### **Development of Computer Aided Design Tools for Automotive Batteries (EC Power)**

The design, build, and testing process for batteries and packs is extremely time consuming and expensive. The CAEBAT activity was initiated by DOE and monitored by NREL to develop software tools to accelerate the development and design of batteries. EC Power's Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model (ECT3D) directly addresses the issues related to the design and engineering of these cells. Many technical characteristics of batteries and packs that are critical to battery performance and safety are impossible to measure experimentally. However, these same characteristics are easily analyzed using ECT3D in a virtual environment. The use of advanced software such as ECT3D allows the design engineer to gain unique insights into the performance of his/her system that would be inaccessible via experimental measurements. Furthermore, the analysis is done completely in a virtual environment, eliminating the need for any physical production of test cells. The AutoLion™ commercial software developed in part under this project has been well received, with approximately 30 licensees employing the software. The AutoLion™ software is now being applied in markets beyond the automotive market, including batteries designed for personal and wearable electronics devices and large-scale energy storage.

#### **Coupling of Mechanical Behavior of Cell Components to Electrochemical-Thermal Models**

During the first phase of CAEBAT, performance models simulating the electrochemical and thermal performance of lithium-ion batteries were developed and incorporated into commercially-available software tools, and efforts toward modeling abuse response were initiated. Existing models in literature, as well as those developed under the previous phase of CAEBAT, assume a predetermined value for the short circuit resistance when calculating the heat generation rate during thermal runaway events. Depending on the value of contact resistance chosen for a particular simulation case, the outcome of the cell response can be varied arbitrarily. Thus, the existing models are limited in their ability to predict the outcome of an internal short circuit or mechanical crush. In the current effort, we develop

a methodology to couple the mechanical response of different cell components (anode, cathode, separator, etc.) with NREL's electrochemical-thermal models. This will provide a comprehensive set of tools to compute properties such as the nature of the short circuit or evolution of short resistance as a function of chemical composition, thermal, and electrical properties, as well as the mechanical constraints on the material, thereby accounting for experimental observations using realistic modeling tools.

### **Significant Enhancement of Computational Efficiency in Nonlinear Multi-scale Battery Model for Computer-Aided Engineering**

DOE's CAEBAT program has focused on developing innovative modeling capabilities to help industries accelerate mass-market adoption of EDVs. NREL pioneered the MSMD model, overcoming challenges in modeling the highly nonlinear multi-scale response of battery systems. However, there are still remaining challenges. Significant efforts continue being invested to improve energy-power capability and reliability of batteries through engineering at the material level by controlling particulate morphology and size, modifying the particle surface, or redesigning thermodynamics. Due to the complex nonlinear interactions across a wide range and scale of physics, computational cost becomes excessively high to quantify such improvements for the benefits in device-level response, even with state-of-the-art models. The CAEBAT program has resulted in software packages providing 3-D battery pack simulation modeling capability. However, because of the system's extreme complexity, the computational cost of simulating a battery pack response is still very high. Therefore, further improvement of computational efficiency is needed, and the intrinsic nonlinearity of battery physics must be resolved properly. This would enable the use of models in design and management tradeoff studies of performance/life in large vehicle battery systems, which are typically composed of several hundred large-format individual cells. In this project, we develop a computational methodology for a significant improvement in computational efficiency of nonlinear multi-scale battery modeling while maintaining or enhancing the solution accuracy from the most advanced state-of-the-art models.

### **Crash Propagation Simulation and Validation**

NREL has actively participated in building mathematical models to simulate performance and life of lithium-ion batteries as part of the DOE/VTO CAEBAT activity. These models accommodate a wide variety of physics, including thermal and electrochemical aspects. Existing thermal/electrochemical models in the literature assume a short circuit resistance when calculating the heat generation rate and temperature evolution during thermal runaway events, and are thus limited in their ability to predict the outcome of mechanical crash. On the other hand, existing mechanical simulations of vehicle batteries treat the batteries as passive components and do not include the energetics that ensues from mechanical failure of a battery. Thus, design of structural components based on these calculations is not straightforward. In the current effort, we are developing a modeling approach that incorporates the effects of mechanical failure (e.g., during a crash) on the energetics that follow the event.

### **Development of Industrially Viable ALD Electrode Coatings**

In previous work, NREL, in partnership with the University of Colorado, has shown that extremely thin, conformal coatings of aluminum oxide deposited with the Atomic Layer Deposition (ALD) technique are capable of dramatically improving cycleability of lithium-ion cells. This project seeks to convert the common ALD processing format into a new reactor geometry that is compatible with battery electrode manufacturing. As part of this effort for FY14, NREL and the CU-Boulder team, working with limited carryover funding, has successfully completed design and construction of a new in-line ALD reactor. Work in this area has focused on modification of previous reactor designs to build a system capable of assessing the ability to obtain ALD-type coating processes in an in-line format and under acceptable battery manufacturing conditions. Earlier reactors were constructed to conduct initial feasibility testing of the ALD process when converted to an in-line format and with deposition occurring at atmospheric pressure; however, these early designs focused on planar substrates. More recent work has focused on creating a system that is capable of deposition onto moving coated battery electrode foils, as used in present manufacturing. Special emphasis was placed on designing a system to understand the impact of coating on porous substrates. An in-line ALD reactor system for flexible substrates compatible with existing commercial battery electrode coating facilities was constructed. Controlled deposition of aluminum oxide on a flexible substrate at an effective processing line speed of >400 ft/min was demonstrated, nearly an order of magnitude higher than current industrial processes.

### **Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes**

Significant advances in both energy density and rate capability for Li-ion batteries will be critical for their implementation in next generation EVs. Due to the high theoretical capacity of silicon (Si), 3,579 mAh g<sup>-1</sup> for

$\text{Li}_{15}\text{Si}_4$ , and its natural abundance, silicon has attracted much attention as a promising Li-ion anode material. However, progress towards a commercially viable Si anode has been impeded by Si's rapid capacity fade caused by the large volumetric expansion. Such a massive volumetric change can result in cracking and pulverization of the Si particles, which then lead to the interruption of electronic transport pathways and the electrochemical isolation of pulverized particles. As part of the DOE's BATT activity under the Focused Fundamental Research Program, the overall goal of this project is to stabilize the silicon anodes with conformal ultrathin coatings. Both ALD and MLD have been developed to fabricate the nanoscale coatings with desirable elastic properties and good conductivity, accommodate the volumetric expansion, protect the surface from the reactive electrolytes, as well as ensure the electronic paths through the composite electrodes. A new aluminum alkoxide polymer (alucone) film using sequential reactions of trimethylaluminum (TMA) and hydroquinone (HQ) was developed. A sustainable cycling behavior with 2,000 mAh g<sup>-1</sup> at 50 cycles and an enhanced rate performance for new MLD-engineered thick Si anodes was achieved. The morphology and structure evolution of both uncoated and MLD-coated silicon anodes during cycling were characterized.

## List of Acronyms and Abbreviations

A123	A123 Systems
AB	acetylene black
ABDT	ANSYS Battery Design Tool
ABR	Applied Battery Research
AIGL	aluminum glycerol
AIHQ	aluminum hydroquinone
Al <sub>2</sub> O <sub>3</sub>	aluminum oxide
ALD	atomic layer deposition
AP-ALD	atmospheric pressure atomic layer deposition
AP-CVD	atmospheric pressure chemical vapor deposition
API	application programming interface
BATT	Batteries for Advanced Transportation Technologies
BEC	bussed electrical center
BECM	battery energy control module
BEV	battery electric vehicle
BLAST-V	Battery Lifetime Analysis Simulation Tool for Vehicles
BMS	battery management system
BOM	Battery Ownership Model
BPSM	battery pack sensor module
BTMS	battery thermal management system
CAD	computer-aided design
CAE	computer-aided engineering
CAEBAT	Computer Aided Engineering of Automotive Batteries
CAN	controller area network
CCSE	California Center for Sustainable Energy
CD	cell domain
CD	charge depletion
CDM	cell domain model
CDNUF	current density non-uniformity factor
CFD	computational fluid dynamics
CS	charge sustaining
CU	University of Colorado at Boulder
CV	conventional vehicle
DCFC	direct current fast charger
DCM	demand charge management
DDPM	discrete diffusion particle model
DOD	depth of discharge
DOE	U.S. Department of Energy
ECM	equivalent circuit model
ECT	electrochemical-thermal
ECT3D	Electrochemical-Thermal Coupled 3-Dimensional Li- ion Battery Model
ED	electrode domain

EDLC	electrochemical double-layer capacitor
EDM	electrode domain model
EDV	electric drive vehicle
ESS	energy storage system
EV	electric vehicle
FTP	Federal Test Procedure
GM	General Motors
GPC	growth per cycle
GUI	graphical user interface
HEV	hybrid electric vehicle
HPC	high-performance computer
HPPC	hybrid pulse power characterization
HQ	hydroquinone
HVTB	high-voltage traction battery
HWFET	Highway Fuel Economy Test
INL	Idaho National Laboratory
IR	infrared
JCI	Johnson Controls Inc.
LCO	lithium cobalt oxide
LEESS	lower-energy energy storage system
LGCPi	LG Chem Power, Inc.
Li	lithium
LIC	lithium-ion capacitor
Li-ion	lithium-ion
LPV	linear parameter varying
LTi	linear time invariant
MABx	Micro Auto Box
MLD	molecular layer deposition
MSMD	multi-scale multi-domain
NiMH	nickel metal hydride
NMC	nickel manganese cobalt
NTGK	Newman, Tiedemann, Gu, Kim
OAS	open architecture software
OCP	open circuit potential
OEM	original equipment manufacturer
ORNL	Oak Ridge National Laboratory
PAN	polyacrylonitrile
PD	particle domain
PDM	particle domain model
PEV	plug-in electric vehicle
PHEV	plug-in hybrid electric vehicle
POD	Proper Orthogonal Decomposition
PVDF	polyvinylidene difluoride
R&D	research and development

R2R	roll-to-roll
REM	regulation energy management
RFP	request for proposals
ROM	reduced order modeling
RS	representative sandwich
RTS	reaction temperature sensor
RVE	representative volume element
SEI	solid electrolyte interphase
Si	silicon
SPPC	single potential-pair continuum
SOC	state of charge
SVM	state variable model
TEM	transmission electron microscopy
TMA	trimethylaluminum
UDDS	Urban Dynamometer Driving Schedule
USABC	United States Advanced Battery Consortium
VTO	Vehicle Technologies Office
WLTP	worldwide harmonized light vehicles test procedure

# Battery Ownership Model

## Jeremy Neubauer

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Start Date: FY2009  
Projected End Date: FY2015

## Objectives

- Identify cost-optimal electric vehicle (EV) use strategies and pathways capable of achieving national oil displacement goals in support of the U.S. Department of Energy's (DOE's) EV Everywhere Grand Challenge
- Evaluate various business models and impact of other factors such as driving patterns, geography, battery wear, and charge profiles using the NREL-developed Battery Ownership Model (BOM) and Battery Lifetime Analysis Simulation Tool for Vehicles (BLAST-V)

## Technical Barriers

- The economics of plug-in electric vehicles (PEVs) are highly sensitive not only to vehicle hardware and fuel costs, but also to infrastructure costs, driving patterns, all-electric range, battery wear, charging strategies, third-party involvement, and other factors; *proper analysis requires a detailed, comprehensive, systems-level approach*
- The broad range of complex EV usage strategies proposed, including battery leasing, battery swapping, fast charging, opportunity charging, vehicle-to-grid service, battery second use, etc., presents a large number of scenarios to assess
- Battery life is typically a major factor in the total cost of ownership of EVs, but accurate modeling of battery degradation under the complex and varied conditions of potential automotive use is challenging
- Economics are highly sensitive to vehicle drive patterns; thus, different drive patterns require different use strategies to minimize cost; drive pattern

data sufficient for economic analysis is also in short supply

## Technical Targets

- Quantify the total cost of ownership of EVs when complex usage scenarios and business models are employed
- Understand how battery performance, life, and usage affect cost and other engineering parameters
- Design use strategies that achieve cost parity between EVs and gasoline-powered conventional vehicles (CVs)

## Accomplishments

- Added multi-cell battery simulation capability to BLAST to study heterogeneous battery electrical, thermal, and wear response and evaluate its effect on EV performance
- Added geospatial data to travel patterns employed in BLAST, and developed an intelligent rerouting algorithm for EVs to utilize available charging infrastructure that enables travel not otherwise achievable
- Simulated a range of scenarios of EVs operating in the presence of real-world fast charger deployments; found that the primary challenge for battery electric vehicle (BEV) with fast charging is controlling maximum battery temperature resultant from repeated drive-charge cycles with minimal rests in between, which can be achieved with active battery cooling systems; once battery temperature is controlled, we found that access to fast charge infrastructure can enable BEVs to travel 785 more miles per year, on average, across the travel patterns studied



## Introduction

Fast charging is attractive to EV drivers for its ability to enable long-distance travel and quickly recharge depleted batteries on short notice. However, such aggressive charging and resulting sustained vehicle operation could lead to excessive battery temperatures and degradation. Properly assessing the consequences of fast charging requires accounting for disparate cycling, heating, and aging of individual cells in large BEV packs when subjected to realistic travel patterns, usage of fast chargers, and climates over long durations (i.e. years). The resultant gains in vehicle utility afforded by fast charging

under real-world conditions must also consider these factors.

The DOE Vehicle Technologies Office (VTO) has supported NREL's development of BLAST-V to create a tool capable of accounting for all of these factors. In FY14, specific developments were completed to enable the realistic simulation of EVs operated in the presence of fast chargers. BLAST-V was then employed to evaluate the effects of realistic fast charger use on BEV batteries and utility.

## Approach

NREL's BLAST-V is an electric vehicle simulator focused on computing long-term effects of complex operational scenarios on vehicle utility and battery performance. It considers the vehicle powertrain, battery control strategy, driving and charging patterns, local climate, the vehicle-battery-environment thermal system, battery chemistry, and other factors in computing short-term vehicle and battery performance (e.g., vehicle range, battery voltage, state of charge (SOC), and temperature) and long-term vehicle utility and battery degradation.

Key to BLAST-V is the calculation of battery degradation. NREL has developed a semi-empirical life model, offering a combination of increased confidence in interpolations and projections, while maintaining simplicity of implementation and a basis in actual laboratory data. BLAST-V incorporates the NREL model for a lithium-ion (Li-ion) cell with a nickel-cobalt-aluminum cathode and graphite anode to supply a representative model of battery degradation. Recent updates enable BLAST-V to simulate individual cells within a pack, deploying this degradation model in a highly parallel fashion to investigate heterogeneous cell aging.

Another recent addition to BLAST-V is the ability to include geospatial travel data and reroute travel histories based on route efficiency and available infrastructure. This algorithm evaluates alternative routes to reach destinations using the Google Maps application programming interface (API), searches for available charging infrastructure within a user-defined distance from each route, selects a sequence of charging infrastructure to utilize that minimizes travel time and maintains acceptable battery SOC on each route, then selects the route and charging schedule that is most convenient to the driver.

To seed travel histories, we employ historical travel data from the Puget Sound Regional Council's Traffic Choices Study. We filter these histories to those that accrued 8,000 miles or more over a one-year period for simulation to focus on higher mileage drivers. Typical meteorological year data from both moderate and hot climates (Seattle, WA, and Phoenix, AZ, respectively) are employed to explore the impact of environmental temperatures. We employ a mid-size sedan with

technology and performance levels anticipated for a 2020 model year vehicle that yields an 80 mile range on an approximate EPA cycle. Three battery thermal management systems (BTMS) were employed in our analyses: a passive system, an active cooling system that operates when the vehicle is being driven, and an active cooling system that operates when the vehicle is either being driven or parked at a charger. A 6.6 kW AC level 2 charger is assumed to be installed in the vehicle owner's home and available for use at all hours of the day. A network of 50 kW direct current fast chargers (DCFC), representative of the current deployment of fast chargers in the Seattle metro area, was employed as well.

## Results

Baseline simulations were run using the Seattle climate to check the typical usage of DCFCs resultant from our implanted methodologies and assumption. Results show that most drivers in this study use fast chargers 10 times per year or less, but extreme cases reach up to 8 times per month. This results in relatively small fractions of total BEV electricity coming from DCFCs, typically less than 10%. When visiting a DCFC, we predict that drivers will stay between 10 and 22 minutes, arriving with a battery SOC of 18 to 60%. Although data on real-world usage of DCFCs is sparse, this appears to agree reasonably well with data reported by the EV Project<sup>1,2</sup>.

Next we compared battery response when operated in our two selected climates with and without access to a fast charger network. In Seattle, we saw that neither the use of fast chargers nor the variation of BTMS had any significant effect on time-averaged battery temperatures or capacity loss over ten years for the average driver. In Phoenix, we see similar trends when comparing the absence and presence of fast chargers, though the difference between BTMS is much more apparent – the presence of active cooling while driving, and the additional use of that system in standby mode at a charger noticeably reduces average battery temperature and capacity loss.

While the nearly negligible impact of fast charger usage on battery capacity fade may be surprising to some, it is important to point out that DCFCs are used quite sparingly by our driver histories. Where the effect of fast charger usage is most noticeable is in the maximum battery temperature. As shown in Figures 1 and 2,

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<sup>1</sup> Fast DC Charging for Electric Vehicles, Navigant Research Webinar, April 9, 2013. <http://www.navigantresearch.com/webinar/fast-dc-charging-for-electric-vehicles>

<sup>2</sup> Smart, J. "Latest Insights from The EV Project and ChargePoint America PEV Infrastructure Demos," presented at GITT meeting, Idaho National Laboratory, August 12, 2014.



comparison of cases with and without fast charger availability shows that maximum battery temperatures are ~15 deg C higher for the median driver when fast charging is employed with a passive BTMS. In fact, in the presence of fast charging, our simulated maximum battery temperatures regularly exceed 45 deg C in Seattle and 60 deg C in Phoenix – so high that they could in fact pose a safety risk if charging and/or driving is not impeded by onboard vehicle control systems. The addition of active battery cooling, however, can significantly moderate maximum battery temperatures, especially when employed both while driving and charging.

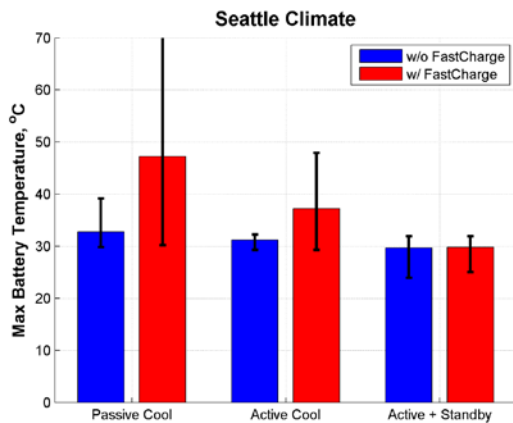


Figure 1. Effect of DCFCs and BTMS on battery capacity loss in Seattle

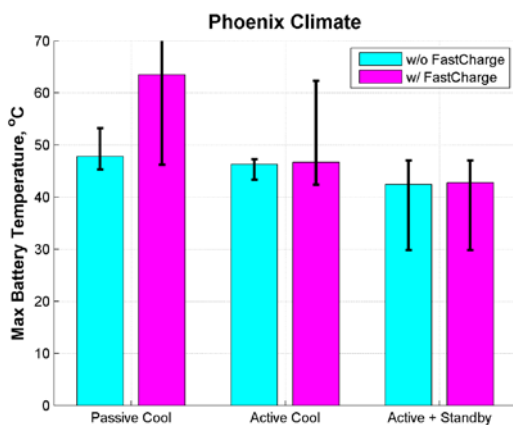


Figure 2. Effect of DCFCs and BTMS on battery capacity loss in Phoenix

Closer investigation of these high temperature events reveals their cause: repeated, back-to-back drive and charge events with short or no rests in between. Fast charging is shown to elevate battery temperature at a faster rate than driving (compare, for example, an estimated battery discharge power of 18 kW when driving at 300 Wh/mi and 60 mi/hr to a fast charge rate of 50 kW), and the presence of fast charging allows the vehicles to travel further more continuously than is otherwise

possible in their absence. Thus, it is not unreasonable that a battery and BTMS designed for use without fast charging could overheat when this option is presented.

Subsequent simulations investigated the utility improvements DCFC access can afford BEV drivers as a function of vehicle range (see Figure 3). Where active BTMS is employed to manage battery maximum temperature, we find that access to fast chargers can enable BEVs to travel 785 more miles per year, on average, across the travel patterns studied for our baseline 80 mile BEV. In extreme cases, though, drivers can achieve several thousand additional miles with the use of fast charging. Clearly, the impact on travel patterns can be high. We also observe that the benefits of fast charging for the average driver falls slowly to 409 miles per year as vehicle range increases to 218 miles. Travel patterns that make use of fast charging infrastructure most frequently are found to fall much more sharply as vehicle range increases.

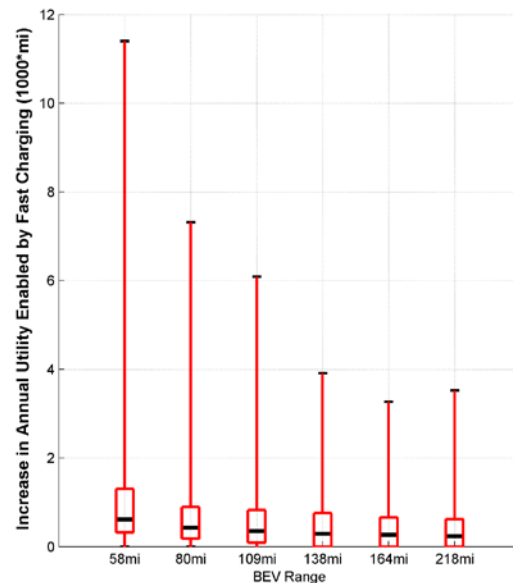


Figure 3. Additional mileage enabled by fast charger access as a function of vehicle range

## Conclusions and Future Directions

BLAST-V has been employed to study the impact of realistic fast charging on simulated battery electrical, thermal, and degradation response, as well as the resultant gains in vehicle utility. We have found that the largest challenge presented by fast charging to the battery is its effect on maximum battery temperature. In the presence of a passive BTMS, maximum battery temperatures can exceed safe operating limits due to repeated drive-charge sequences with short or no rests in between. This can be controlled, however, via the employ of BTMS with active cooling capabilities, or onboard vehicle controllers

limiting charging and driving activities. The prior is expected to be much more attractive in terms of driver satisfaction.

Where active BTMS is employed to manage battery maximum temperature, we find that access to fast chargers can enable BEVs to travel 785 more miles per year, on average, across the travel patterns studied for our baseline 80 mile BEV. This benefit is found to decrease as vehicle range increases, as would be expected.

### FY 2014 Publications/Presentations

1. Neubauer, J.; Pesaran, A.; Bae, C.; Elder, R.; Cunningham, B. "Updating United States Advanced Battery Consortium and Department of Energy Battery Technology Targets for Battery

Electric Vehicles," *Journal of Power Sources*, Volume 271, 20 December 2014, Pages 614–621. NREL Report No. JA-5400-62265

2. Neubauer, J; Wood, E. "Thru-life impacts of driver aggression, climate, cabin thermal management, and battery thermal management on battery electric vehicle utility," *Journal of Power Sources*, Volume 259, 1 August 2014, Pages 262–275. NREL Report No. JA-5400-61311.
3. Neubauer, J; Wood, E. "The impact of range anxiety and home, workplace, and public charging infrastructure on simulated battery electric vehicle lifetime utility," *Journal of Power Sources*, Volume 257, 1 July 2014, Pages 12–20. NREL Report No. JA 5400-61036

# PEV Battery Second Use

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### Subcontractors:

California for California for Sustainable Energy, UC San Diego, UC Davis, San Diego Gas and Electric

### Partners:

Southern California Edison and BMW USA

Start Date: FY2009

Projected End Date: FY2015

## Objectives

- Identify, assess, and verify sustainable applications for the second use of PEV lithium-ion traction batteries after their end of useful life in a vehicle
- Collaborate with industry and others through cost-share subcontracts to demonstrate and evaluate the potential and expected performance of used batteries in real applications

## Technical Barriers

- High cost of batteries hinders wide adoption of PEVs
- PEV end-of-service burdens (battery recycling, disposal) impedes PEV deployment; re-using PEV batteries in secondary applications and delaying recycling shifts burden from automotive industry
- Finding suitable second use applications for the large quantity of used PEV batteries that could become available from automotive markets
- Assessing the value of post-automotive applications for PEV batteries is challenged by uncertain electrical demands, complex and difficult-to-assess revenue streams, and prohibitive regulatory structures
- The processes of repurposing PEV batteries are yet to be identified and could have a major impact on the viability of second use strategies

- Uncertainty in the longevity of repurposed batteries in post-automotive applications
- Battery degradation in both automotive and post-automotive use is notoriously difficult to ascertain, yet has a strong impact on potential end-user acceptability and profitability of second use strategies

## Technical Targets

- Identify and demonstrate sustainable second use applications for PEV Li-ion traction batteries
- Conduct testing on aged PEV batteries to ascertain their longevity for second use applications
- Devise optimized use strategies for automotive traction batteries to facilitate their second use, maximizing their value and reducing cost to the automotive consumer and also preventing premature recycling of otherwise useable batteries

## Accomplishments

- Continued field testing of aged automotive batteries with California Center for Sustainable Energy (CCSE) to demonstrate viability of identified second use applications and quantify long term degradation; field testing expected to be complete in January 2015
- Continued laboratory testing of aged automotive batteries at NREL
- Developed a partnership with BMW and supported test planning for a large pre-commercial stage second use energy storage system
- Completed detailed analysis of behind-the-meter demand charge management (DCM) as a potential application for second use batteries



## Introduction

Accelerated market penetration of PEVs, as targeted by the DOE's EV Everywhere Grand Challenge, is presently limited by the high cost of Li-ion batteries. It has been estimated that a 50% reduction in battery cost may be necessary to equalize the current economics of owning PEVs and conventionally-fueled vehicles. Further, both vehicle manufacturers and consumers are concerned about end-of-service costs associated with proper handling of the battery.

One strategy that can positively affect both topics is battery second use – allocating a retired automotive battery for reuse in other applications where it may still have sufficient performance to be valuable. By extracting additional services and revenue from the battery in a post-

vehicle application, the total lifetime value of the battery is increased. This increase could be credited back to the automotive consumer, effectively decreasing automotive battery costs. Further, it transfers the cost of battery recycling or disposal from the automotive community to the second use industry.

There are several current and emerging applications where PEV battery technology may be beneficial. For example, the use of renewable solar and wind technologies to produce electricity is growing, and their increased market penetration can benefit from energy storage, mitigating the intermittency of wind and solar energy. New trends in utility peak load reduction, energy efficiency, and load management can also benefit from the addition of energy storage, as will smart grid, grid stabilization, low-energy buildings, and utility reliability. The prospect of extremely low-cost energy storage via second use batteries is attractive to these industries.

In past years, NREL has created a detailed framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications. The application of this framework to Li-Ion PEV batteries has highlighted the need for efficient repurposing strategies, and identified a promising market for repurposed batteries. It has also found that the most pressing remaining uncertainty is the longevity of repurposed batteries in post-automotive applications.

To address this uncertainty, NREL has acquired aged batteries, developed a long-term field test site and strategy, and initiated long-term testing via a subcontract with CCSE, leveraging a 50-50 cost share partnership with industry. NREL has also acquired additional aged batteries for on-site laboratory testing. Additionally, NREL worked with Southern California Edison to evaluate the potential of second use batteries in community energy storage applications, and BMW to demonstrate a pre-commercial second use battery system.

## Approach

Four aged automotive batteries have been deployed for field testing at UCSD, executed by CCSE. Two applications have been the focus of testing to date: regulation energy management (REM), and demand charge management (DCM). Though testing protocols for the latter have been developed specifically for a behind-the-meter scenario, it is more broadly applicable to generalized peak shaving applications as well. For both applications, we have developed both prescribed duty cycle and real-time testing modes. The objective of this testing is to characterize battery degradation in likely second use applications and begin demonstration of the feasibility of aged automotive batteries therein.

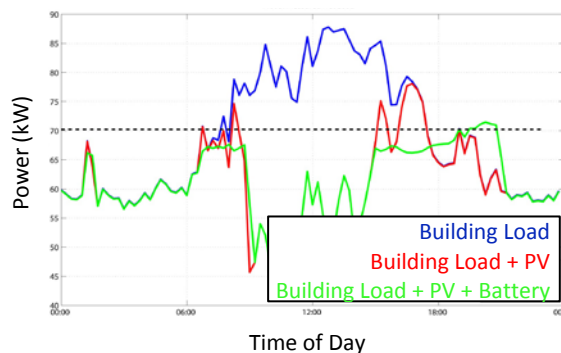
In parallel, NREL has initiated laboratory life tests to further characterize second use battery degradation. Included is a 10 kW pack that has been substantially

cycled to an automotive use duty cycle and disassembled to the cell level. Cells from this pack are being tested individually to provide insight into the variation in degradation across a single battery pack, as well as the response of cells to different duty cycles. Four ~4 kWh modules have also been acquired following extensive automotive cycling to the same state of health, albeit via different conditions (temperatures and number of cycles). A life test using a regulation energy management profile has been designed and initiated for these modules to answer the question of whether simple state data or full pack history data are necessary at the point of repurposing to quantify a battery's value.

In addition to application-specific duty cycles, all batteries underwent regular reference performance tests at defined intervals. The results will be used to track loss of capacity and growth of resistance within each battery.

## Results

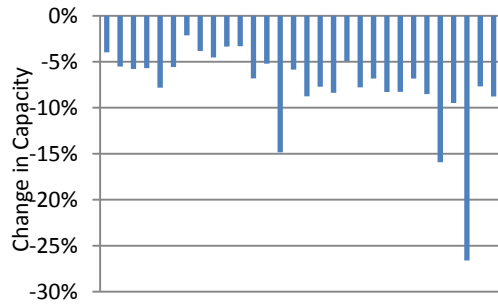
Figure 1 shows an example response of a battery in the field testing system at UCSD performing real-time DCM. It illustrates the complexity of operation of such an algorithm, requiring the inclusion of accurate solar power, building load, and battery performance prediction.



**Figure 1. Real-time DCM field test response**

As noted previously, both real-time and prescribed REM and DCM testing is being performed on multiple packs at the UCSD test site. A full analysis will be prepared on test results when testing completes in FY15.

Figure 2 shows the change in capacity of 30 cells under test at NREL taken from an aged 10 kW battery pack. The test conditions vary considerably across this data set, with DODs ranging from 40 to 80%, temperature ranging from 0 to 45 deg C, cycle frequency ranging from once to twice per day, and duty cycles including grid-specific, automotive-specific, and constant power profiles. The presented data represents the cells' states of health after one year of cycling at NREL. Initial results suggest that degradation rates for these conditions are relatively low. A full analysis of the data will be prepared in FY15 after additional cycling has been completed.



**Figure 2. Change in capacity of 30 cells under test at NREL taken from an aged 10 kW battery pack**

### Conclusions and Future Directions

NREL has performed comprehensive analyses and testing to assess the feasibility of PEV battery second use. The study has found that implementation of battery second use strategies will be a viable means to offset end-

of-service battery costs for PEV owners (e.g. battery removal, disposal, recycling), while offering secondary markets extremely large supplies of low cost energy storage. This could have drastic effects on the electricity grid, improving quality of service and reducing emissions. However, these efforts have also ascertained that the rate of battery degradation in second use applications is a large uncertainty that must be resolved to enable such a future. NREL is at present addressing these issues with multiple long term battery testing and analysis efforts.

In FY15, NREL will complete its battery life testing efforts, perform detailed analysis on results, and publish reports to disseminate their findings. NREL will also publish a comprehensive report on its second use analyses.

# Battery Life Trade-Off Studies

## Kandler Smith (NREL)

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Subcontractor:  
Texas A&M University, College Station, TX  
Prof. Partha Mukherjee

Start Date: October 2008  
Projected End Date: December 2014

## Objectives

- Develop physics-based battery life prediction models that quantify battery longevity over a range of real-world temperature and duty cycle conditions
- Extend cell life models to pack-level, capturing impacts of temperature non-uniformity, cell performance and aging variability on system lifetime
- Perform tradeoff studies to quantify potential battery lifetime extension and cost reduction achievable via advanced systems, controls, and operating strategies for electric drive vehicle battery packs

## Technical Barriers

- Multiplicity of degradation modes (10+) faced by Li-ion battery cells in automotive environment
- Lack of models and methods to accurately quantify battery lifetime
- Lifetime uncertainty leading to conservative, oversized batteries in order to reduce warranty risk

## Technical Targets

- 10-15 year battery life for electric drive vehicles in disparate geographic environments and duty cycles
- Battery lifetime predictive models validated against real-world data with less than 10% error
- Thermal and other control systems that reduce cell energy content while still meeting 10-15 year lifetime

## Accomplishments

- Integrated 10+ degradation mechanisms into a statistical framework for diagnosing degradation

mechanisms and predicting lifetime from cell experimental data

- Validated cell-level life models with pack-level life measurements using multi-cell pack-level electrical-thermal degradation model
- With Texas A&M, applied high order continuum physics transport/fracture models to develop reduced order models of electrode particle damage that can be used to interpret experimental data



## Introduction

Battery aging behavior directly impacts to what degree an EDV battery must be oversized to achieve desired service life across applications and environments. Eliminating extra cost associated with oversizing would positively benefit market acceptance of EDVs. Automotive batteries face large variability in thermal environment and duty cycle, with 10+ degradation factors that must be considered to predict lifetime. Worst-case cell aging conditions within a multi-cell battery pack drives the need to oversize battery cell energy content.

Physics-based models describing cell- and pack-level aging processes are needed to support engineering optimization of next generation batteries. Cell life models must capture a multiplicity of degradation modes experienced by Li-ion cells, such as interfacial film growth, loss of cycleable lithium, loss of active material, degradation of electronic and ionic pathways, with dependence on temperature, state-of-charge, depth-of-discharge, C-rate, and other duty cycle factors. In particular, the mechanical damage induced by high C-rate and depth-of-discharge electrochemical cycling is a poorly understood degradation mechanism which we seek to clarify with physical models. Pack-level life models must capture effects leading to non-uniform cell aging, including temperature imbalance, cell performance and aging variability, and interaction with balance of plant systems such as cell balancing.

## Approach

In FY14, NREL's existing life model framework developed for NCA, FeP, and NMC chemistries was extended to an additional NMC chemistry and validated at both the cell- and pack-level. The SEI microcracking model of Deshpande et al., *J. Electrochem. Soc.* (2012), was extended to capture mixed modes of cycling and calendar degradation. That model successfully describes



mid-life degradation for the FeP chemistry, to be described in a forthcoming journal article.

To describe resistance and capacity changes with lifetime for multiple Li-ion technologies, NREL's life modeling framework includes multiple degradation mechanisms:

- Side reactions forming electrode impedance films and consuming Li, such as at the negative electrode solid electrolyte interface (SEI) layer
- Lithium plating at low temperatures
- Binder degradation at high temperatures
- Electrolyte decomposition at high temperatures and voltages
- SEI microcracking and regrowth
- Particle and electrode fracture/fatigue/isolation due to electrochemical-thermal-mechanical cycling
- Separator pore closure due to viscoelastic creep caused by cycling
- Gas pressure buildup
- Break-in processes releasing excess Li and enhancing reaction/transport initially at beginning of life

During model development, multiple degradation hypotheses can be proposed, guided by knowledge of cell chemistry and cell teardown experiments when available. Mechanism hypotheses are confirmed/refuted based on regression statistics of model versus data.

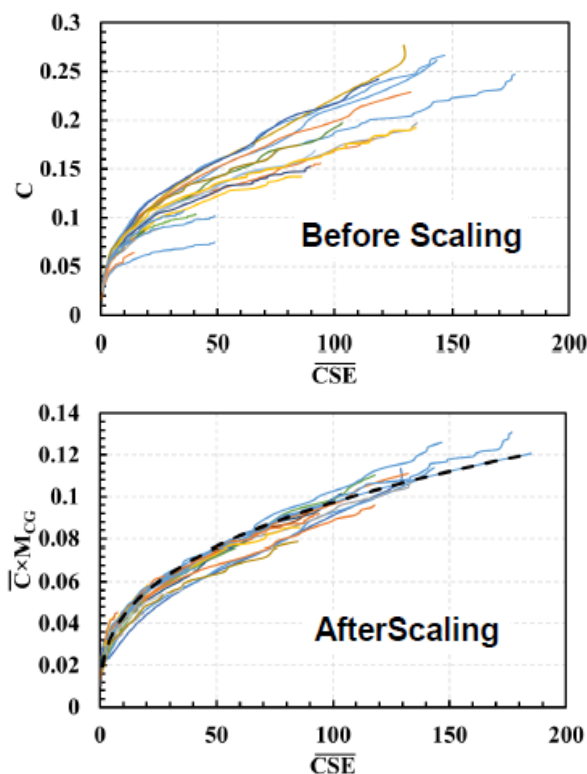
Of the above degradation mechanisms, the least understood mechanism is particle and electrode fracture/fatigue/isolation due to electrochemical-thermal-mechanical cycling. The model framework presently relies on empirical formulas to capture this degradation as a function of temperature, C-rate, and depth-of-discharge. To reduce this empiricism, NREL initiated a project with Texas A&M to explore a wide range of electrode particle fracture simulations using their physics-based lattice spring (or discrete element) model. From these computationally-expensive simulations, we extract low order fatigue models that can be applied to cell-level lifetime simulations and validated with experimental data.

## Results

### Particle Fracture Model

In previous work, Texas A&M developed an electrochemical/thermal model of an electrode active material particle coupled with solid mechanics (Barai, et al., *J. Electrochem. Soc.*, 2013). The model captures Li transport inside the particle, stress and fracture due to transport-limited concentration gradients, and impact of fracture on further limiting Li transport. The model is unique in that it predicts damage evolution dependent on charge/discharge condition and also captures the impact of that damage on subsequent performance of the battery. The model is too computationally-expensive,

however, to run large-scale cell or pack lifetime simulations. In FY14, NREL and Texas A&M ran a large matrix of simulation cases for various temperatures, constant currents, and drive cycles. We then tested various models from the fatigue literature to come up with low order models that describe the damage evolution across all operating conditions. Figure 1 shows the magnitude of concentration gradient,  $C$ , versus cumulative strain energy, CSE. By non-dimensionalizing independent and dependent variables and applying scaling laws, the 20 simulation cases reduce down to a single damage evolution path shown in the bottom panel of Figure 1. The scaling laws, derived from constant current charge/discharge simulations, are separately validated against more complex drive cycle charge/discharge simulations. This is significant, as the low order scaling model provides practical guidance as to what aspects of high rate current pulses cause the most damage during drive cycles. The results will be published in an upcoming paper.



**Figure 1. Damage evolution for 20 constant current discharge/charge simulations using particle fracture model, reduced to a single trend line using fatigue scaling laws**

### SEI Microcracking Model

In FY13, NREL developed a life predictive model for the graphite/FeP chemistry based on aging data for the A123 26650 2.2 Ah cell. A particular focus was to capture end-of-life effects, where capacity suddenly fades at a high rate due to cycling-related conditions. But the model required additional refinement in order to

more accurately capture mid-life capacity fade, where calendar fade has a weak coupling with cycling condition.

The SEI microcracking model of Deshpande et al., *J. Electrochem. Soc.* (2012), enhances the typical chemical degradation/SEI growth model by including mechanical damage to the SEI due to cycling. The damage is caused as high tensile stresses build in the SEI layer during delithiation, resulting in microcracks in the SEI. These microcracks expose fresh negative electrode sites for new SEI to form, consuming additional lithium from the system and degrading capacity.

Unlike the Deshpande model, which tracked capacity fade versus number of cycles, in FY14, we extended that model to capture mixed modes of cycling- and calendar- or time-driven degradation. That model successfully describes mid-life degradation for the FeP chemistry, to be described in a forthcoming journal article.

### Dissemination and Validation

To date, the NREL battery life model has been licensed to more than ten external companies, labs, and universities to apply in their own research studies. The life model is a critical component in NREL's electric vehicle techno-economic analysis model, Battery Lifetime Assessment Tool (BLAST) described elsewhere in this report. The BLAST model predicts the lifetime of batteries in electric vehicles for various driver behaviors, charge behaviors, climates, battery thermal management designs, and cell balancing systems. Two journal articles were published in FY14.

Under a cooperative research and development agreement (CRADA) with Eaton Corporation, the NREL life model is being integrated into Eaton's real-time hybrid electric vehicle (HEV) supervisory controller. By including the life prognostic model, the controller is able to maximize fuel economy and satisfy constraints on battery lifetime. The general method allows for increased vehicle performance even with a less expensive, downsized battery. For the CRADA project, NREL carried out life tests of Eaton's graphite/NMC cells under more than 20 aging conditions in order to develop a cell life model for that technology. Separately, NREL ran one-year aging tests on two Eaton HEV packs with substantially different duty cycles and at multiple environmental chamber temperatures representing different seasons of the year. The cell life model, together with a pack thermal model capturing temperature distributions in the packs, was able to predict the outcomes of these two packs within 3% and 5% of measured capacity and resistance, respectively, over the course of the one-year test. This validation provides further confidence in the approach

for physics-based modeling of battery lifetime at the cell- and pack-levels.

## Conclusions and Future Directions

A robust framework for modeling a multiplicity of degradation mechanisms in Li-ion cells has been developed. Models of multiple chemistries are now available and are being applied in multiple system and control design studies to lower the cost and extend the life of Li-ion battery systems. The parameterization of these life models remains a burden however, requiring 6-12 months of expensive testing for each new cell technology. As such, the models arrive too late in the design process to apply more directly in the cell design optimization process. Pending resources, future work will therefore focus on developing 3D multiphysics models of degradation processes consistent with the Computer-Aided Engineering of Batteries (CAEBAT) program at DOE. Goals of the models are to provide engineering feedback for cell design optimization, allow for accurate lifetime prediction with less test data, and help enable next generation Li-ion chemistries.

## FY 2014 Publications/Presentations

1. K. An, P. Barai, K. Smith, P.P. Mukherjee, "Probing the Thermal Implications in Mechanical Degradation of Lithium-Ion Battery Electrodes," *J. Electrochem Soc.* 161 (6) A1058-A1070, 2014. <http://dx.doi.org/10.1149/2.069406jes>
2. D.R. Diercks, M. Musselman, A. Morgenstern, T. Wilson, M. Kumar, K. Smith, M. Kawase, B.P. Gorman, M. Eberhart, C.E. Packard, "Evidence for Anisotropic Mechanical Behavior and Nanoscale Chemical Heterogeneity," *J. Electrochem. Soc.* 161 (11) F3039-F3045, 2014. <http://dx.doi.org/10.1149/2.0071411jes>
3. A. Hoke, A. Brisette, K. Smith, A. Pratt, D. Maksimovic, "Accounting for Lithium-Ion Battery Degradation in Electric Vehicle Charging Optimization," *IEEE J. Pwr. Electronics*, 2013. <http://dx.doi.org/10.1109/JESTPE.2014.2315961>
4. K. Smith, E. Wood, S. Santhanagopalan, G.-H. Kim, A. Pesaran, "Advanced Models and Controls for Prediction and Extension of Battery Lifetime," Large Lithium Ion Battery Technology & Application Symposia Advanced Automotive Battery Conference, Atlanta, GA, February 4-6, 2014. [NREL Report No. PR-5400-61037](#)
5. K. Smith, E. Wood, S. Santhanagopalan, G.-H. Kim, Y. Shi, A. Pesaran, "Predictive Models of Li-ion Battery Lifetime," IEEE Conference on Reliability Science for Advanced Materials and Devices, Golden, Colorado; September 7-9, 2014. [NREL Report No. PR-5400-62813](#)



# In-Vehicle Lower-Energy Energy Storage System (LEESS) Component Evaluation

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## Objectives

- Evaluate performance of lower-energy energy storage system (LEESS) devices to support power-assist or “full” hybrid electric vehicles (HEVs)
  - HEVs with lower cost or better performing energy storage systems could improve their cost-versus-benefit ratio, market penetration, and aggregate fuel savings
- Continue original equipment manufacturer (OEM) and supplier collaboration for conducting the project
  - Complete shake-down testing of the reusable HEV test bed
  - Install and test multiple LEESS devices relative to the performance of the production battery configuration

## Major Accomplishments

- Completed comparison testing between the converted Ford Fusion Hybrid test vehicle operating on its production battery pack and operating on lithium-ion capacitor (LIC) LEESS devices supplied by JSR Micro, Inc.
  - Comparisons included acceleration performance and fuel economy testing over multiple drive cycles; the evaluation also considered different LIC energy content scenarios
  - Several of the tested LIC configurations demonstrated equivalent fuel economy and acceleration performance as the production battery configuration across all tests conducted; the lowest energy LIC scenario demonstrated equivalent performance over

- most tests, though slightly higher fuel consumption on the US06 cycle
- The overall results indicate that as long as critical attributes such as engine start under worst case conditions can be retained, considerable energy storage system (ESS) downsizing may minimally impact HEV fuel savings
- Completed bench testing of the second set of LEESS devices to evaluate in the vehicle; ultracapacitor modules from Maxwell Technologies
- Removed and returned the JSR Micro LIC modules and installed the Maxwell ultracapacitor modules to prepare for in-vehicle comparison testing

## Future Achievements

- Complete in-vehicle comparison testing between the final LEESS devices under evaluation and the production vehicle battery pack
- Consider system optimization opportunities (such as different motor or engine size) around the particular performance capabilities of LEESS devices



## Background

Automakers have been mass-producing HEVs for more than a decade, and the technology has proven to be very effective at reducing per-vehicle fuel use. However, the cost of HEVs such as the Toyota Prius or Ford Fusion Hybrid remains several thousand dollars higher than the cost of comparable conventional vehicles, which has limited HEV market penetration. The battery energy storage device is typically the component with the greatest contribution toward this cost increment, so significant cost reductions and/or performance improvements to the ESS can correspondingly improve the vehicle-level cost-versus-benefit relationship. Such an improvement would, in turn, lead to larger HEV market penetration and greater aggregate fuel savings.

## Introduction

In recognition of these potential benefits, the United States Advanced Battery Consortium (USABC) asked NREL to collaborate with its workgroup and analyze the trade-offs between vehicle fuel economy and reducing the decade-old minimum energy requirement for power-

assist HEVs. NREL’s analysis showed that significant fuel savings could still be delivered from an ESS with much lower energy storage than the previous targets, which prompted USABC to issue a new set of lower-energy ESS (LEESS) targets and issue a request for proposals to support their development. To validate the fuel savings and performance of an HEV using such a LEESS device, this jointly-funded activity between the DOE VTO Energy Storage and Vehicle Systems Simulation and Testing programs has designed a test platform in which alternate energy storage devices can be installed and evaluated in an operating vehicle.

## Approach

The approach in previous fiscal years (FY12–FY13) included establishing a cooperative research and development agreement between NREL and Ford Motor Company to support the conversion of a Ford Fusion Hybrid into a test platform for evaluating LEESS devices. NREL subsequently acquired a 2012 Fusion Hybrid, designed the conversion, and entered into agreements with JSR Micro to provide (at JSR Micro’s expense) LIC modules as the first LEESS device to be evaluated in the vehicle. The LICs are asymmetric electrochemical energy storage devices possessing one electrode with battery-type characteristics (lithiated graphite) and one with ultracapacitor-type characteristics (carbon). In FY13, NREL completed bench testing on the LIC replacement pack compared to the production nickel metal hydride (NiMH) battery pack from the 2012 Fusion Hybrid and integrated the modules into the Fusion Hybrid test platform.

The approach in FY14 included troubleshooting and shakedown testing to get the vehicle fully operational with the alternative LEESS modules. Subsequently, on-road and chassis dynamometer testing were used to perform back-to-back comparisons of operation using the LIC replacement pack relative to the production NiMH configuration. While this testing was being completed (using multiple energy storage configurations of the LIC modules), NREL established agreements with Maxwell Technologies to provide ultracapacitor modules as the second LEESS device to evaluate in the vehicle (again at the supplier’s expense). In the second half of FY14, NREL completed bench testing on the Maxwell ultracapacitor modules, removed and returned the JSR Micro LIC modules, and integrated the Maxwell ultracapacitor modules into the vehicle test platform. The remainder of the planned in-vehicle testing will be completed in FY15.

## Results

Figure 1 shows a photograph of the production high-voltage traction battery (HVTB) unit, which is mounted between the rear seat and the trunk area in the Fusion

Hybrid. Important components of the HVTB include the high-voltage bussed electrical center (BEC), the battery pack sensor module (BPSM), and the battery energy control module (BECM). The BEC acts as an interface between the high-voltage output of the HVTB and the vehicle’s electric motor, air-conditioning compressor, and DC/DC converter. The BPSM measures the voltage and temperature of the NiMH cells and communicates with the BECM, which manages the charge/discharge of the battery and also communicates with the other vehicle control modules via the high-speed controller area network (CAN) bus.



Figure 1. Photo of Fusion Hybrid HVTB. Image by John Ireland, NREL

To implement the vehicle conversion, NREL kept the production HVTB installed in its original position so that direct comparison testing could be conducted by switching back and forth between the production battery and the alternative LEESS under test. Figure 2 shows a schematic of this configuration, in which parts from a second HVTB acquired by NREL (including the BECM, BEC, BPSM, module sense leads, and various wiring harnesses) were reconfigured to work with the alternative LEESS under test. The dSpace component represented in the schematic is a dSpace MicroAutoBox (MABx), which is used to intercept certain CAN signals pertaining to the BECM’s calculations for the production NiMH battery (state of charge, power capability, etc.) and to replace them with corresponding calculations for the alternate LEESS under test. The MABx also records data and handles safety controls during the testing.

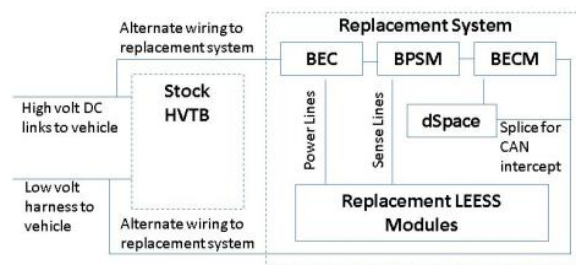


Figure 2. Schematic of connections among replacement components and the vehicle

Prior to actually integrating the JSR LIC modules into the test vehicle, NREL first performed bench testing with the modules mounted in an environmental chamber (see Figure 3). The purposes of the bench testing included confirming expected LIC performance,

comparing the LIC pack's operation to that of the production battery over a representative driving profile, and generating test data for calibrating the custom state estimator model to implement in the dSpace MABx. Results from the LIC module hybrid pulse power characterization (HPPC) bench testing are presented later alongside the results from the comparable testing of the Maxwell ultracapacitor modules.



**Figure 3. JSR LIC modules in environmental chamber during bench testing, with production 2012 Fusion Hybrid NiMH modules in the background. Image by John Ireland, NREL**

Following bench testing, the LIC modules were integrated into the Fusion Hybrid test platform to enable the in-vehicle comparison testing. Figure 4 shows a picture of the fully-integrated conversion system, including LIC modules, mounted in the trunk of the Fusion Hybrid. The LIC modules and the replacement BEC are shown in the large box with the clear lid; to the side, the picture shows the MABx mounted on top of an electronics box containing a voltage divider circuit and related components.



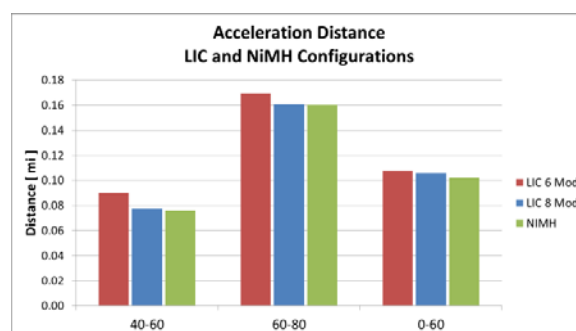
**Figure 4. Fully-integrated conversion system mounted in the trunk of the Fusion Hybrid test platform. Image by Jon Cosgrove, NREL**

In addition to the physical components shown in Figure 4, completing the vehicle integration involved validating the custom state estimator code (for calculating the LEES state of charge and charge/discharge capability at any moment in time) against the bench test data. This code was incorporated into the MABx and included temperature dependence functionality calibrated against the various temperature conditions from the bench testing (-20°C, 25°C, and 45°C).

Initial driving tests focused on confirming proper operation of the converted vehicle. This included making sure the vehicle could operate while intercepting and rebroadcasting modified signals via the vehicle CAN bus. Further shakedown tests verified proper functioning of the safety controls and the state estimator model for the alternate LEES device. After this was confirmed, NREL conducted closed-course performance testing on the vehicle in both the LIC and production configurations (see Figure 5 and Figure 6).



**Figure 5. Closed-road acceleration performance testing. Image by Petr Sindler, NREL**



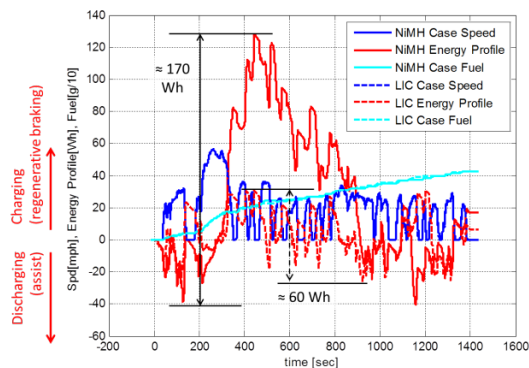
**Figure 6. Acceleration distance for NiMH, eight-module LIC, and six-module LIC configurations while performing 0-60, 40-60, and 60-80 accelerations**

Figure 6 shows the standing and passing acceleration performance from six- and eight-module configurations of the LIC replacement pack compared to the production NiMH system. NREL evaluated different configurations of the LIC storage system to examine trade-offs between size/energy content (which would ultimately influence component cost) and measured in-vehicle performance. As Figure 6 indicates, the eight-module configuration achieved similar performance to the production system in all three of the evaluated acceleration categories. Although the six-module configuration demonstrated a slight performance penalty, it is very possible that more extensive controls calibration than was possible as part of this investigation could eliminate this difference. NREL therefore concluded that the LEES LIC configurations can support comparable level-road acceleration performance to the production configuration, but that the smallest LIC scenario evaluated may be on the edge of some small acceleration performance degradation.



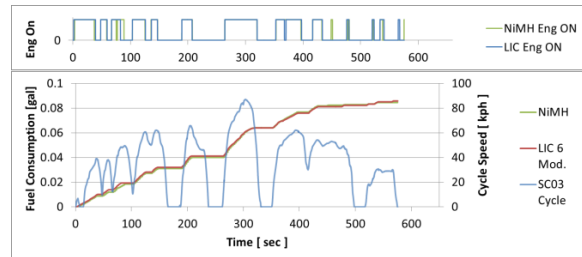
For HEV fuel economy evaluation, NREL utilized chassis dynamometer testing facilities at SGS Environmental Testing Corporation in Aurora, Colorado. Tests included standard certification cycles such as the Federal Test Procedure (FTP) and its constituent Urban Dynamometer Driving Schedule (UDDS), the Highway Fuel Economy Test (HWFET), the aggressive US06, and the hot SC03 cycle (including air-conditioning). These tests allowed NREL to evaluate in-vehicle ESS performance under a variety of conditions, including moderate (24°C), hot (35°C), and cold (-7°C) temperatures.

Figure 7 shows test results on the stop-and-go UDDS driving profile for both the production NiMH configuration and for a low-energy LIC scenario. The ESS energy profile for both storage system configurations showed oscillations in energy usage aligned with the individual microtrips in the driving profile—i.e., when the vehicle accelerated from a stop to some nominal driving speed, then later decelerated back to a stop, the ESS profile showed some amount of discharge to support accessories while stopped as well as to assist the acceleration, and then later recaptured energy through regenerative braking during the deceleration. For the low-energy LIC scenario, these oscillations remained within a 60 Wh window; whereas the production NiMH configuration showed a bulk energy swing in addition to the microtrip-scale oscillations that spanned one 70 Wh window. Comparing the cumulative fuel consumption curves for the two configurations, the NiMH case showed slightly more fuel use during the period when bulk ESS charging occurred and slightly less during the bulk discharging period, but by the end of the test cycle, the fuel use between the two cases was essentially equal.



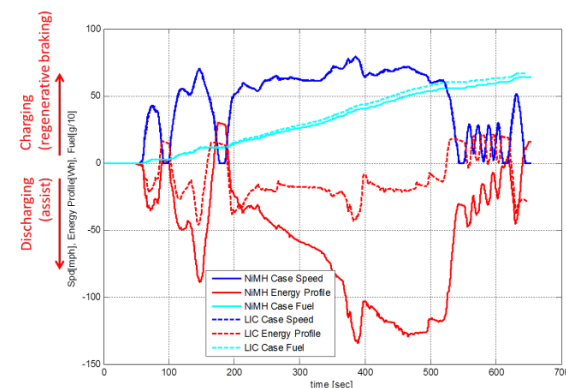
**Figure 7. ESS energy profile and fuel use for 24°C UDDS tests of production NiMH and low-energy LIC configurations**

Figure 8 shows similar results for a low-energy six-module LIC configuration compared to the production NiMH case during the 35°C SC03 cycle. This figure shows equivalent cumulative fuel use between the two scenarios, along with similar engine on/off behavior during the test cycle.



**Figure 8. Fuel consumption and engine on/off cycling during hot (35°C) SC03 testing with air-conditioning**

Figure 9 shows the ESS energy profile and cumulative fuel consumption results for the aggressive US06 cycle, which was the one test profile in which the low-energy LIC configuration showed higher cumulative fuel consumption (by approximately 4%) than the production NiMH configuration. The energy window sizes for each configuration are approximately the same as for the UDDS test shown in Figure 7, but in the US06 test, the bulk depletion of the NiMH in the middle of the cycle helped to measurably reduce cumulative fuel consumption during that high-speed driving section. The NiMH ESS was then able to recapture regenerative braking energy during the decelerations at the end of the cycle to remain charge-neutral during the test; whereas, the low-energy LIC scenario did not have enough available capacity to capture as much energy during those braking events.



**Figure 9. ESS energy profile and fuel use for 24°C UDDS tests of production NiMH and low-energy LIC configurations**

Figure 10 summarizes the fuel consumption and energy window comparisons among multiple ESS configurations during five different test cycles. Note that the test matrix included intermediate LIC energy scenarios as well as the low-energy scenarios discussed in the previous plots. These intermediate energy scenarios still fall under the LEESS category for power-assist HEV ESS, because they possess much lower nominal energy content than the roughly 1.4 kWh

production NiMH ESS.<sup>3</sup> Several of the relatively higher energy content LIC scenarios tested achieved energy window sizes and fuel consumption comparable to the NiMH reference case—including during the US06 cycle. For all cycles except for the US06 (including the -7°C FTP and the HWFET in addition to those already discussed), even the lowest energy LIC configurations were able to match the fuel consumption of the reference NiMH test (using roughly 60 Wh energy windows compared to energy windows closer to 200 Wh for many of the NiMH tests).

The final set of FY14 results involved the ultracapacitor or electrochemical double-layer capacitor (EDLC) modules provided by Maxwell Technologies. These 48 V modules underwent a similar suite of bench tests as the JSR LIC modules. Figure 11 shows a comparison of the 2 second and 0.5 second pack-level resistance for the indicated LIC and EDLC configurations. These calculations were derived from the HPPC test results and depend on the timescale during which the measurement is taken because of the combined influence of impedance and changing energy content when measuring voltage rise/drop following each pulse. These results indicated roughly three times lower internal resistance for the LEESS devices than for the production NiMH ESS.

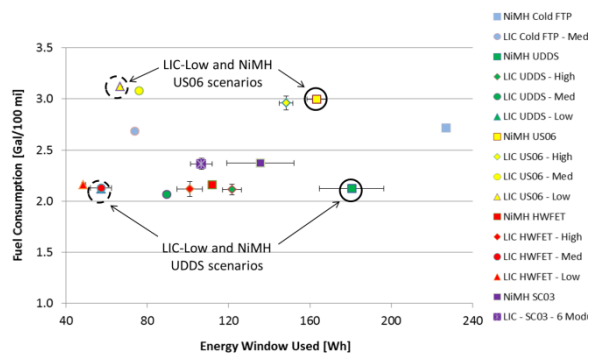
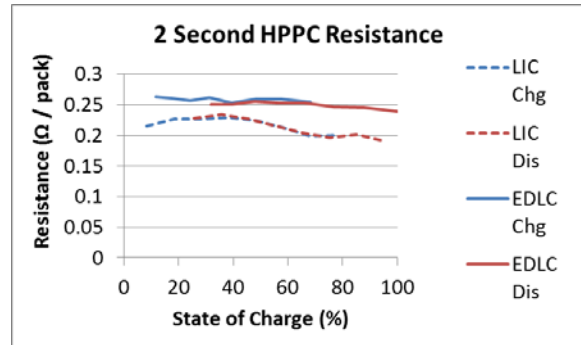


Figure 10. Summary of fuel consumption and energy window results for multiple test cycles and vehicle configurations



<sup>3</sup> Based on a fact sheet published by Idaho National Laboratory: [www1.eere.energy.gov/vehiclesandfuels/avta/pdfs/hev/batteryfusion4699.pdf](http://www1.eere.energy.gov/vehiclesandfuels/avta/pdfs/hev/batteryfusion4699.pdf)

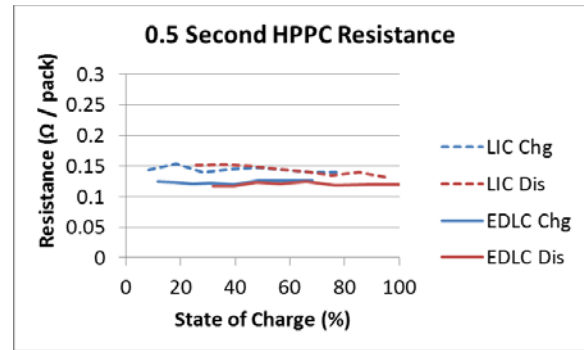


Figure 11. Pack level 2 second and 0.5 second resistance for the (“high-energy”) eight-module LIC and the seven-module EDLC configurations

The EDLC modules were also characterized for drive cycle performance and power capabilities. This data was used to calibrate the models running on the MABx in a similar manner as was used for the LIC configuration. As shown in Figure 12, the EDLC modules have been installed in the test vehicle. In addition to conducting many of the same tests that were completed for the LIC configurations, NREL hopes to assess any operating advantage the modules may see at very cold temperatures (as low as -20°C). This testing had been planned for the LIC configurations, but the test facility was not able to maintain such a low chamber temperature during summer testing; whereas the facility expects to be able to maintain lower temperatures during winter testing.



Figure 12. Installed Maxwell EDLC seven-module configuration. Image by Jon Cosgrove, NREL

## Conclusions

Alternate HEV storage systems such as the LIC and EDLC modules described in this report have the potential for improved life, superior cold temperature performance, and lower long-term cost projections relative to traditional battery storage systems. If such LEESS devices can also be shown to maintain high HEV fuel savings, then future HEVs designed with these devices could have an increased value proposition relative to conventional vehicles, thus resulting in greater HEV market penetration and aggregate fuel

savings. This jointly-funded activity between the DOE VTO Energy Storage and Vehicle Systems Simulation and Testing programs developed a vehicle test platform to help validate the in-vehicle performance capability of alternative LEESS devices and identify unforeseen issues.

This report describes the successful creation of the Ford Fusion Hybrid test platform for in-vehicle evaluation of such alternative LEESS devices, bench testing of the initial LIC pack provided by JSR Micro, integration and testing of the LIC pack in the test vehicle, and the bench testing and installation of a second LEESS pack from Maxwell Technologies (consisting of EDLC modules). The in-vehicle LIC testing results suggest technical viability of LEESS devices to support HEV operation. Several of the tested LIC configurations demonstrated equivalent fuel economy and acceleration performance as the production NiMH ESS configuration across all tests conducted. The lowest energy LIC scenario demonstrated equivalent performance during several tests, although slightly higher fuel consumption on the US06 cycle and slightly slower acceleration performance. However, more extensive vehicle-level calibration than was possible for this conversion project may be able to reduce or eliminate these performance differences. The overall results indicate that as long as critical attributes such as engine start under worst-case conditions can be retained, considerable ESS downsizing may minimally impact HEV fuel savings.

Ongoing work into FY15 will include completion of in-vehicle comparison testing between the EDLC pack and the production NiMH ESS. Other possible future work topics include evaluating the potential offered by LEESS devices with more extensive vehicle modification, such as by better matching the size of the motor in the vehicle to the LEESS power capabilities.

This project has helped demonstrate the technical viability of nontraditional technologies to compete with typical battery systems for HEV energy storage. However, some combination of systems optimization to

best leverage LEESS capabilities and cost reductions on the part of suppliers will be necessary to move LEESS technology from mere technical viability to having a compelling business case for broad use in HEV energy storage.

## Publications

6. Cosgrove, J.; Gonder, J.; Pesaran, A. "Performance Evaluation of Lower-Energy Energy Storage Alternatives for Full-Hybrid Vehicles." Presentation at the Supercapacitors USA International Conference and Tradeshow, November 2013.
7. Gonder, J.; Cosgrove, J.; Pesaran, A. "Performance Evaluation of Lower-Energy Energy Storage Alternatives for Full-Hybrid Vehicles." Proceedings of the SAE 2014 Hybrid and Electric Vehicle Technology Symposium, February 2014.
8. Gonder, J.; Cosgrove, J.; Pesaran, A.; Keyser, M. "In-Vehicle Evaluation of Lower-Energy Energy Storage System (LEESS) Devices." DOE Vehicle Technologies Annual Merit Review – Project ID#: VSS129, June 2014.
9. Gonder, J.; Cosgrove, J.; Shi, Y.; Saxon, A.; Pesaran, A. "Lower-Energy Energy Storage System (LEESS) Component Evaluation." NREL Milestone Report MP-5400-62853, September 2014.

## Tools and Data

1. The converted Ford Fusion Hybrid test vehicle serves as a reusable tool for evaluating multiple alternative LEESS devices
2. Data collected from bench and in-vehicle LEESS device testing is detailed in the publications listed above

# Battery Thermal Analysis and Characterization Activities

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Ahmad Pesaran - National Renewable Energy  
Laboratory; GM, Ford, Chrysler

Partners: USABC, JCI, LG CPI, SK Innovations,  
Leyden, Saft, Envia, and Farasis

Start Date: October 1, 2009

Projected End Date: September 2015

## Objectives

- Thermally characterize battery cells and evaluate thermal performance of battery packs provided by USABC developers
- Provide technical assistance and modeling support to USDRIVE/USABC and developers to improve thermal design and performance of energy storage systems
- Quantify the impact of temperature and duty cycle on energy storage system life and cost

## Technical Barriers

- Decreased battery life at high temperatures
- High cost due to oversized thermal management system
- Cost, size, complexity, and energy consumption of thermal management system
- Decreased performance at low temperatures
- Insufficient cycle life stability to achieve 3,000 to 5,000 “charge-depleting” deep discharge cycles

## Technical Targets

- Battery operating temperature from -30°C to 52°C without degradation in performance or life
- Develop a high-power battery technology exceeding 300,000 cycles
- 15-year calendar life at 30°C

## Accomplishments

- Obtained cells from various USABC battery partners including Johnson Controls Incorporated (JCI), LG Chem Power, Inc. (LGCPI), SK Innovations, Leyden, and Farasis
- Obtained infrared thermal images of cells provided by USABC battery developers and identified areas of thermal concern
- Used NREL's unique calorimeters to measure heat generation from cells and modules under various charge/discharge profiles in order to design the appropriate thermal management system
- Obtained thermal and electrical performance data of cells under HEV, plug-in hybrid electric vehicle (PHEV), and EV power profiles
- Determined that the energy efficiency of most lithium ion cells is above 93%
- Evaluated thermal performance of a PHEV pack
- Presented results of cell thermal characterization and pack thermal evaluation at USABC/battery developer review meetings



## Introduction

Operating temperature is critical in achieving the right balance between performance, cost, and life for both Li-ion batteries and ultracapacitors. At NREL, we have developed unique capabilities to measure the thermal properties of cells and evaluate thermal performance of battery packs (air or liquid cooled). We also use our electro-thermal finite element models to analyze thermal performance of battery systems in order to aid battery developers with improved thermal designs.

## Approach

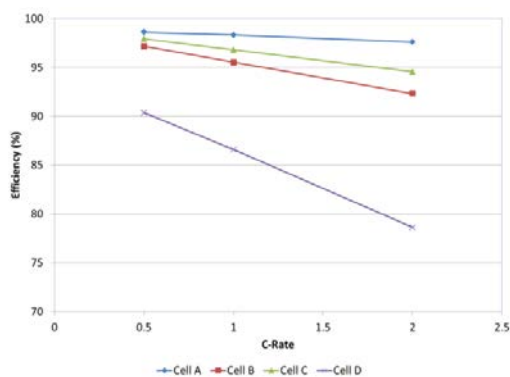
Using NREL's unique R&D 100 Award-winning calorimeters and infrared thermal imaging equipment, we obtain thermal characteristics (heat generation, heat capacity, and thermal images) of batteries and ultracapacitors developed by USABC battery developers and other industry partners. NREL supports the Energy Storage Technical Team by participating in various workgroups such as the JCI, LG CPI, SK Innovations, Leyden, Saft, Envia, and Farasis USABC Working Groups.



## Results

### Calorimeter Testing

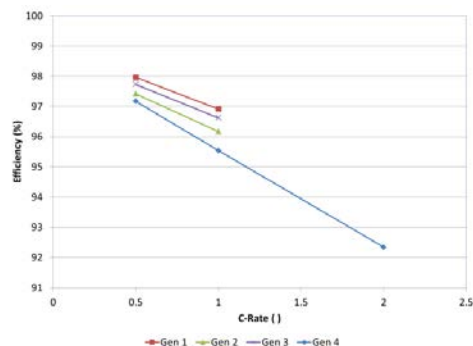
Figure 1 shows the efficiency of cells tested in FY14 at NREL at a calorimeter temperature of 30°C. The lithium-ion cells were fully discharged from 100% SOC to 0% SOC under C/2, C/1, and 2C currents. It should be noted that the cells in the figure are for both power and energy cells, and have been developed for the HEV, PHEV, EV, or LEES programs with USABC. The figure shows that most of the lithium-ion cells, A-C, are very efficient over this cycling regime – typically greater than 93%. The range of efficiencies at a 2C discharge rate is between 93% and 97%. A 4% difference in efficiency may not appear to be of concern; however, if you consider a 50 kW pulse from the battery in an electrified advanced vehicle, then a 1% difference in efficiency results in an additional 500 Watts of heat for the pulse duration – taking the example further, a 4% difference results in 2000 Watts of additional heat. The efficiency differences between the cells will require the thermal management system to be tailored to the cell thermal characteristics so as not to affect the cycle life of the cells. Finally, Cell D shows a fairly low efficiency, as compared to many of the other cells tested in FY14, and could benefit from design improvements to the cell. NREL's calorimeter can identify these outliers but can also help determine if the inefficiency is due to chemistry or cell design.



**Figure 1. Efficiency of cells tested at 30°C in NREL's calorimeter during FY14**

Figure 2 compares the efficiency of multiple generations of a cell from the same manufacturer. The cells were all discharged under a constant C-rate current from 100% to 0% SOC. The efficiency of the first generation cell is the highest, whereas the fourth generation cell has the lowest efficiency. The efficiency differences between successive generations of cells are due to many different factors – different material suppliers, different additives, cathode or anode thickness changes, or the cell is tweaked to be an energy cell versus a power cell. The NREL calorimeters help the battery manufacturers to understand how their design changes and improvements affect the efficiency and

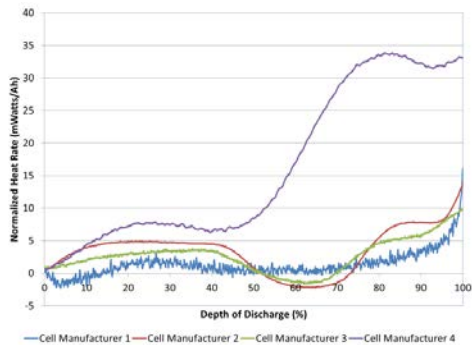
heat generation of their cells. Battery manufacturers use the data from the calorimeter to ensure that the cell has the desired efficiency over the usage range while making tradeoffs on other aspects of the cell design, such as low temperature operation, safety, cost, and ease of manufacturing.



**Figure 2. Efficiency of four generations of cells tested at 30°C under a constant current discharge from 100% to 0% SOC**

NREL's calorimeters are designed to be accurate enough to measure the electrochemical response from batteries under test. As car manufacturers progress from HEVs to PHEVs and EVs, the design of the battery pack will also change. For instance, an HEV battery pack is cycled within a very narrow band – typically within a window encompassing 10% of the overall energy window of the pack. In contrast, a PHEV or EV battery is typically cycled over a much wider range – typically, 80-90% of the battery's capacity. Figure 3 shows normalized heat rates of four different cells tested during FY14. The batteries in this figure were cycled from 0% to 100% depth of discharge (DOD) at a very low current. As shown in the figure, the battery undergoes endothermic and exothermic heat generation over the cycling range. The figure also shows how the battery chemistry affects the entropic signature of the battery. Cell 1 is endothermic at the beginning of the discharge as compared to cells 2 and 3, which are exothermic. The fourth cell is the most inefficient cell of the group tested – some of this inefficiency is due to the design of the electrical paths in the cell. The figure also shows where a cell is most inefficient – below 80% DOD for Cells 1-3 and below 50% DOD for Cell 4. The data from this graph helps manufacturers and OEMs to understand where to cycle their battery and which areas to avoid, thereby increasing the cycle life of the battery.



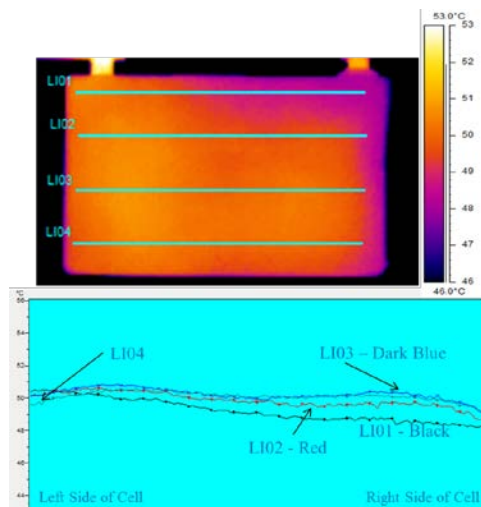


**Figure 3. Normalized heat rate at 30°C for cells discharged from 0% to 100% DOD**

### Infrared Imaging

NREL performs infrared (IR) thermal imaging of battery manufacturers' cells to determine areas of thermal concern. We conduct imaging under a set of prescribed procedures and environments to minimize error from different sources such as reflective cell surfaces, radiation from surrounding surfaces, and cooling from power cables attached to the cell. NREL combines IR imaging equipment with a battery cycler to test under various drive cycles, such as a US06 charge-depleting cycle for PHEVs, and understand temperature differences within the cell. We then recommend thermal design improvements to battery manufacturers and USABC to increase cycle life and safety.

Figure 4 shows the thermal image of a PHEV cell under a constant current discharge. The figure contains a thermal image of the cell at the end of discharge as well as a plot indicating horizontal contour lines across the face of the cell – L01, L02, L03, and L04. A hot spot appears in the upper left corner of the thermal image, corresponding to the positive (aluminum) terminal of the cell. The positive terminal will typically be warmer due to the electrical conductivity difference between the aluminum and the negative terminal, which is usually nickel-coated copper. When following a contour line from left to right, the temperature generally decreases, as we would expect. One interesting phenomenon associated with the thermal image is the temperature increase from top to bottom under the negative terminal (right side). The current density is highest near and between the two terminals; thus, we expected the LI01 contour line to be hotter than the LI04 contour line. The cell was imaged under an aggressive constant current discharge and shows good temperature uniformity across its face, with a difference of only 3°C. With uniform and consistent temperature, all areas within the cell age at the same rate, leading to better cycle life. NREL is working with battery developers to understand how temperature non-uniformities affect the efficiency and cost of the cell over its lifetime.



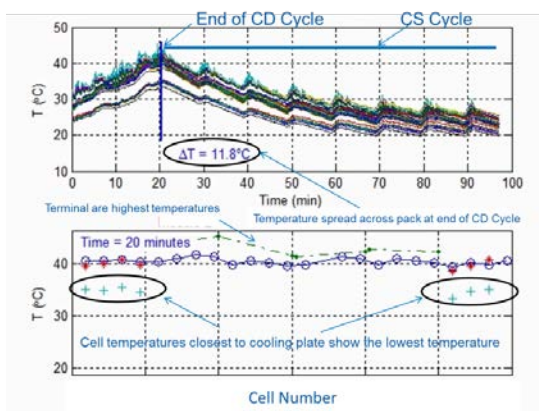
**Figure 4. Thermal image of lithium-ion cell at the end of constant current discharge from 100% to 0% SOC**

### Pack Thermal Studies

In FY14, NREL evaluated air, liquid, and vapor compression cooled packs for USABC battery developers, measuring the temperature rise and difference between corresponding cells, as well as the voltage of each cell within the pack. Testing is performed at temperatures between -20°C and 30°C with drive cycles pertinent for the battery under test – PHEV or EV. It has been shown that a 2-3% difference in cell temperature can have a 2-3% effect on fuel economy. Also, the higher temperature cells within a pack are typically more efficient and therefore work harder than the cells at lower temperatures – higher temperature cells typically provide more power. When different cells within the pack provide different amounts of energy over time, the cells age differently and may cause pack imbalances, resulting in potential warranty issues.

The pack shown in Figure 5 was tested under a US06 charge-depletion (CD) cycle followed by a US06 charge-sustaining (CS) cycle. Figure 5 is divided into two graphs. The top graph shows measured cell temperatures of the pack as a function of time. The bottom graph shows cell temperatures at one point in time, which, for this graph, is at the end of the CD portion of the US06 cycle, 20 minutes into the test. At the end of the charge depletion cycle, a number of interesting conclusions can be drawn. The temperature difference across all cells in the pack is around 11.8°C. As noted previously, temperature differences between cells cause the cells to age differently, which affects the longevity of the pack. We typically recommend a cell temperature difference across the pack of only 3°C and no higher than 5°C. Figure 5 also shows that terminal temperatures are the highest in the pack and that cell temperatures closest to the cooling plate are the lowest. In this pack, we are not only creating cycle life age differences between individual cells, but we are also aging portions of a single cell differently – top versus

the bottom of the cell. As we get the thermal data, we work with battery developers and OEMs to improve the temperature uniformity of cells within a pack and the effectiveness of the thermal management system.



**Figure 5. Average cell temperature in a pack with and without cooling; the pack underwent a US06 CD cycle followed by a US06 CS cycle**

### Conclusions and Future Directions

NREL has thermally tested cells, modules, and/or packs from JCI, LG CPI, SK Innovations, Leyden, and Farasis. We've provided critical data to the battery manufacturers and OEMs that can be used to improve thermal design of cells, modules, packs, and their respective thermal management systems. The data included heat generation of cells under typical profiles

for HEV, PHEV, and EV applications, which is essential for designing the appropriate sized battery thermal management system. We found that the majority of the cells tested had a thermal efficiency greater than 94% when cycled under a 2C constant current discharge. During the thermal imaging of the cells, we identified areas of thermal concern and helped battery developers improve the thermal design of their cells. Finally, we evaluated multiple packs during FY14 and determined that all aspects of the design need to be evaluated for the best thermal performance of the pack and the longest life.

In FY15, NREL will continue to thermally characterize cells, modules, and packs for USABC, DOE, and USDRIVE.

### FY 2014 Publications/Presentations

1. 2010 DOE Annual Peer Review Meeting Presentation
2. Quarterly meeting presentations to battery working groups and manufacturers
3. "The NREL Large-Volume Battery Calorimeter – A Crucial Tool for the Development of Batteries for Electric-Drive Vehicles", CALCON 2014, New Mexico, July, 2014.
4. "Using the NREL Large-Volume Battery Calorimeter for the Thermal Development of Battery Technologies for Advanced Vehicles" SAE Thermal Management Systems Symposium, Denver, September, 2014.

# Battery Multiscale Multidomain Framework & Modeling

## Gi-Heon Kim

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Collaborators:  
Peter Graf - National Renewable Energy Laboratory

## Objectives

- Continue updating the NREL multi-scale multi-domain (MSMD) battery performance model to run faster
- Develop code from NREL's baseline (MSMD) battery model in an open-source programming language to provide wider portability and accessibility to public

## Technical Barriers

Battery cost, performance, life, and safety are barriers to wide adoption of plug-in electric vehicles. Fast, accurate multiphysics battery models and computer tools would accelerate development of batteries, addressing these barriers.

NREL developed the multi-scale multiphysics battery model framework that became a cornerstone for the initiation of the Computer-Aided Engineering of Automotive Batteries (CAEBAT) program. The code realization of the model was mostly done in a commercial scripting language, MATLAB. This has limited the computational speed of the model simulations and the portability of the codes to existing software in different programming platforms. Utilization of high performance computing (HPC) resources was also restricted.

## Technical Targets

- Restructure MSMD MATLAB codes
- Port baseline MSMD model codes into open source programming language platform (such as C or C++)
- Enhance expandability of new developments
- Accelerate collaboration with external industry experts
- Support battery community in reduced amount of time, helping with advanced modeling capability to address daily engineering problems

## Accomplishments

- Standardized model input-output and data structure for particle domain (PD), electrode domain (ED), and cell domain (CD) models in MSMD platform
- Restructured the MATLAB code structure of baseline MSMD model codes
- Completed porting of particle domain model (PDM) and electrode domain model (EDM) in C++
- Completed prototype porting of cell domain model (CDM) to C++
- Verified newly-developed C++ model code performance against corresponding MATLAB codes



## Introduction

### Expandable Multi-scale Multiphysics Modular Framework – MSMD

Physicochemical processes in Li batteries occur in intricate geometries over a wide range of time and length scales. As the size of the battery increases to meet the system demands of high-energy and high-power energy storage in electric vehicle applications, macroscopic design factors in combination with highly dynamic environmental conditions significantly influence the electrical, thermal, electrochemical, and mechanical responses of a battery system. Without better knowledge of the interplay among interdisciplinary multiphysics occurring across varied scales in battery systems, it is costly to design long-lasting, high-performing, safe, large battery systems.

NREL pioneered the multi-scale multi-domain model, overcoming challenges in modeling the highly nonlinear multi-scale response of battery systems (see Figure 1). The model resolves battery geometry into three coupled computational domains and provides high extent flexibility and multiphysics expandability through its modularized architecture, as well as computational efficiency, enabling it to run on standard desktop PCs by providing selective, finer meshes for low hierarchical subdomains. Model domain separation for the interplay between physicochemical processes is carried out where the characteristic time or length scale is segregated. The MSMD PDMs solve the collective response of electrically- and ionically-connected particle batteries, which are co-located in the electrode domain. The EDMs solve the collective behavior of PD batteries, considering polarization through electrolyte and composite matrices. The CDMs of the MSMD solve single- or multi-cell battery responses by resolving the collective behavior of

paired plate batteries, considering polarization caused by non-uniform temperature and electric potential fields across cell volume.

### MSMD – Bridging Scales

Extending scales, higher fidelity, fully integrated system

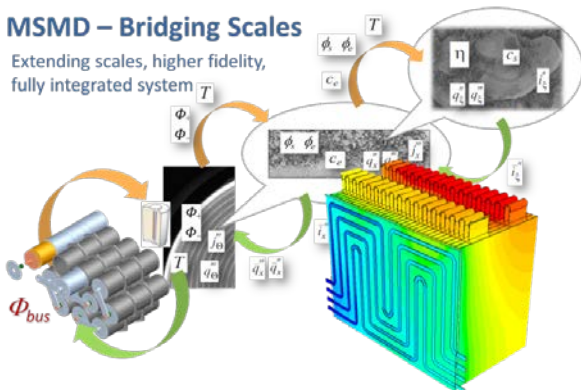


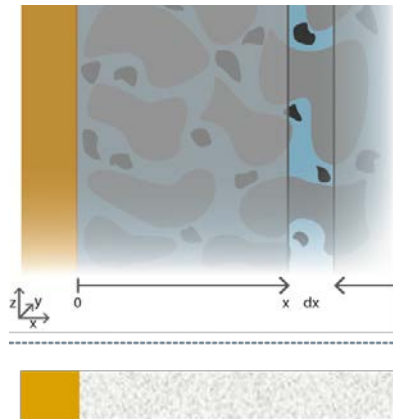
Figure 2. NREL’s MSMD provides modular architecture, facilitating flexible integration of multiphysics submodels

## Approach

### MSMD Baseline Submodels

The MSMD baseline submodels are identified and ported into C++. Here are summarized the descriptions of the submodels in each scale domain.

The PDM resolves lithium transport in solid electrode particles, interfacial reaction kinetics, and charge conservation at the interfaces. NREL has developed the discrete diffusion particle model (DDPM) as a baseline PDM for the MSMD to better address the impacts of particulate morphology, size distribution, surface modification, contact resistance, and mixture composition of active particles (see Figure 2). A system of particles is considered electronically continuous, but ionically discrete. An arbitrary number of quantized discrete particles is given as user input, and thermodynamic, kinetic, transport, electric, and geometric model parameters of each particle is independently determined.



DDPM



Figure 3. DDPM, a baseline PDM for MSMD, for better representation of complex dynamic particulate behaviors

EDM solves electronic and ionic charge conservation in composite electrodes and electrolyte, and species conservation in electrolyte. Assuming the existence of a local in-plane ensemble average in a finite volume of the cell domain, a one-dimensional porous electrode model is chosen for a baseline EDM.

The CDM solves for temperature and electronic current in current collectors and other passive pathways across cell dimensions. An orthotropic cell composite model is a baseline CDM for the MSMD. Battery cell composite has intricate stratified structures, and the assembly units of paired electrode layers are stacked or wound to build prismatic or cylindrical cells. Macroscopic designs for electrically and thermally configuring cell components greatly affect the physicochemical processes occurring in a battery. Treating the cell composite as a homogeneous orthotropic continuum can significantly reduce numerical complexity of a model. For example, the single potential-pair continuum (SPPC) model treats the stratified cell composite as a homogeneous continuum with orthotropic transport properties, and resolves temperature and a pair of current collector phase potentials in the continuum volume with distinguished in-plane and transverse conductivities for heat diffusion and electrical current conduction.

## Results

### Standalone Models and Standard Input Files

In the MSMD hierarchical architecture, PDMs become a subscale domain model to EDMs, and, in turn, EDMs to CDMs. However, PDMs or EDMs can also be run in standalone mode without being integrated into their upper hierarchical parent models. Standard input files define batteries (via physicochemical properties and design parameters) in each scale, define the usage, and provide

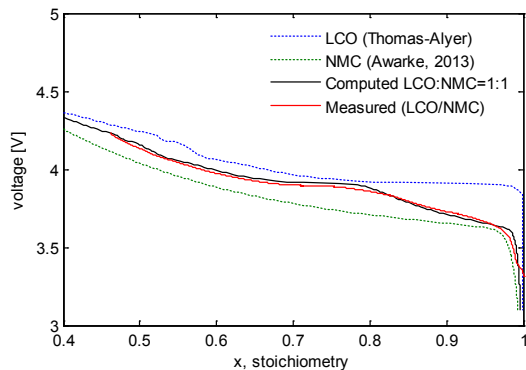
the required numerical setup for the models. This input file structure sustains the MSMD's modularity. Each input file can be independently modified or replaced for corresponding changes in materials or system design (see Table 1).

**Table 1. Comparison of model input file lists for standalone PDM, EDM and CDM**

	PDM	EDM	CDM
<b>Define Batteries</b>			
posptcltbl.inp, negptcltbl.inp	0	0	0
edparm.inp		0	0
cdparm.inp			0
<b>Define Usage (Load Profile)</b>			
ELprfl.inp	0	0	0
<b>Define Model</b>			
setup.inp	0	0	0

### Model Application

The ED model captures the impact of application characteristics on inhomogeneous use of electrode materials for a mixed chemistry battery. Figure 3 compares the experimentally-measured open circuit potential (OCP) curve from a 1:1 mixed lithium cobalt oxide (LCO) and nickel manganese cobalt (NMC) cathode and the computed OCP from the component materials.



**Figure 3. Comparison of measured and computed open circuit potential curves for 1:1 LCO-NMC cathode**

Utilization of LCO and NMC particles in a 1:1 mixed cathode during 20-minutes of a US06 drive profile for a midsize sedan is presented below in Figure 4, with results for a PHEV10 (left) and HEV (right). When the mixed cathode battery is used in a PHEV application, the battery is operated over a wide range of SOC in charge depletion mode. Local thermodynamic equilibria among the mixture components substantially vary, and so does the usage of the materials. Lithium content difference between LCO and NMC grows during the drive. In charge sustaining mode (after ~ 800 sec), the battery is cycled with LCO nearly saturated. Overall, charge transfer current throughput is larger with LCO particles, especially discharge throughput, but NMC particles take more current in charging events. However, the usage pattern among the mixed material components changes greatly with application characteristics. In HEVs, while discharge and charge throughputs are balanced for both components, LCO is used more than NMC by about 17% in terms of charge throughput.

### Conclusions and Future Directions

NREL's baseline MSMD model codes developed in MATLAB have been successfully restructured and ported into C++, and the ported codes were verified against the corresponding MATLAB codes. Standard experimental and computational procedure to identify the MSMD model inputs will be developed and documented. This code is now available to the battery community for use in any platform that accepts compiled versions of C++.

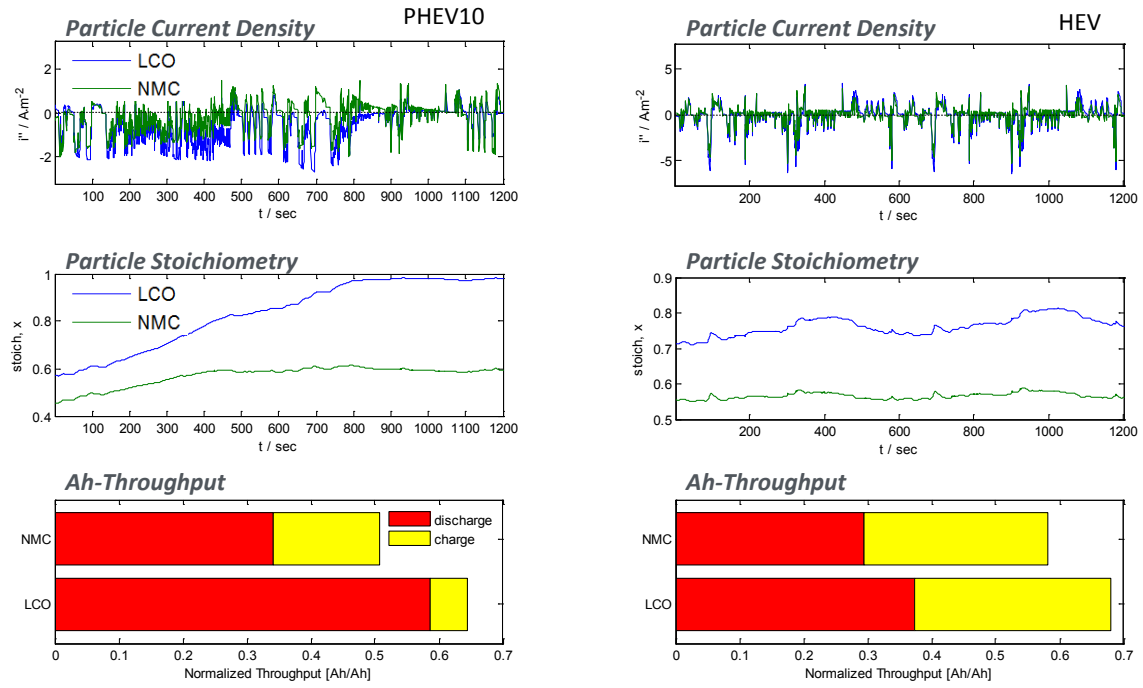


Figure 4. Utilization of LCO and NMC particles in 1:1 mixed cathode during 20-minute US06 profile drive with midsize sedan in PHEV10 (left) and HEV (right) applications



# Computer-Aided Engineering of Batteries (NREL)

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### Subcontractors:

General Motors, ANSYS, and ESim  
EC Power, Ford, JCI, and PSU  
CD-adapco, Battery Design, A123Systems, and JCI

Start Date: April 2010

Projected End Date: September 2015

## Objectives

The overall objective of the Computer-Aided Engineering of Electric Drive Vehicle Batteries (CAEBAT) project is to develop electrochemical-thermal software tools to accelerate design and simulate the performance, life, and safety of electric drive vehicle batteries. As part of this effort, the NREL objectives are:

- Coordinate the activities of CAEBAT for DOE
- Develop battery modeling tools to enhance understanding of battery performance, life, and safety to enable development of cost-effective batteries for electric drive vehicles
- Support the U.S. vehicle battery industry with cost-shared subcontracts to develop battery modeling tools to simulate and design cells and battery packs in order to accelerate development of improved batteries for hybrid, plug-in hybrid, and electric vehicles
- Technically manage the performance of the three subcontract teams led by General Motors, CD-adapco, and EC Power
- Collaborate with Oak Ridge National Laboratory (ORNL) in their development of Open Architecture Software (OAS) to link various battery models developed under the DOE Energy Storage R&D program

## Technical Barriers

- Cost, life (calendar and cycle), high performance at all temperatures, and safety are barriers for widespread adoption of lithium-ion batteries in electric drive vehicles (EDVs)
- Large investments and long lead times in cell and pack research, design, prototyping, and testing—and then repeating the design-build-test-break cycle many times—increase production costs
- There is a lack of advanced computer-aided engineering tools to optimize cost-effective electrical-thermal-chemical-mechanical solutions for battery packs in EDVs under various conditions

## Technical Targets

- Develop suites of software tools that enable automobile manufacturers, battery developers, pack integrators, and other end-users to design and simulate the electrochemical and thermal performance of cells and battery packs in order to accelerate development of energy storage systems that meet the requirements of electric drive vehicles

## Accomplishments

- NREL enhanced its battery multiphysics, multi-scale, multi-domain (MSMD) platform for CAEBAT and developed a stand-alone version of the MSMD in open-source C++ for ease of use by any party
- Three subcontract teams (CD-adapco, EC Power, and General Motors) continued developing and validating CAEBAT software tools
- NREL continued monitoring the technical performance of the three subcontract teams through monthly progress conference calls, quarterly review meetings, and annual reporting with DOE
- Each subcontract team has been successful in delivering CAEBAT software tools to the public and their many clients
- The following are major accomplishments from each subcontract team in FY14:
  - CD-adapco completed the framework for electrochemical and thermal modeling of spirally-wound prismatic and cylindrical cells in its widely-used commercial simulation platform STAR-CCM+; the model was validated with experimental data from JCI
  - EC Power completed the final version of its commercial software tool AutoLion, developed based on CAEBAT versions of the Electrochemical-Thermal Coupled 3-Dimensional

Li-ion Battery Model (ECT3D) model; PSU provided data for validation; more than 30 licensees are using these software tools, including Ford

- General Motors supported ANSYS to release the CAEBAT software tool in the leading simulation platform Fluent-15



## Introduction

In April 2010, DOE announced a new program activity called Computer-Aided Engineering of Electric Drive Vehicle Batteries (CAEBAT) to develop software tools for battery design, R&D, and manufacturing. The objective of CAEBAT is to incorporate existing and new models into battery design suites/tools with the goal of shortening design cycles and optimizing batteries (cells and packs) for improved performance, safety, long life, and low cost. The goal is to address the existing practices with which battery and pack developers operate: tediously experimenting with many different cell chemistries and geometries in an attempt to produce greater cell capacity, power, battery life, thermal performance, safety, and lower cost. By introducing battery simulation and design automation at an early stage in the battery design life cycle, it is possible to significantly reduce the product cycle time and cost, and thus significantly reduce the cost of the battery. When the project started three years ago, NREL had already developed an electrochemical-thermal model of lithium-ion cells with three-dimensional geometries. However, those tools were not integrated into a 3D computer-aided engineering platform, which automotive engineers routinely use for other components. In many industries, including automotive and combustion engine development, computer-aided engineering (CAE) tools have been proven pathways to:

- Improve performance by resolving relevant physics in complex systems;
- Shorten product development design cycles, thus reducing cost; and
- Provide an efficient manner for evaluating parameters for robust design.

DOE initiated the CAEBAT project to provide battery CAE tools to the industry. The CAEBAT project is broken down into four elements, as shown in Figure 1.

- Material- and component-level models
- Cell-level models
- Pack-level models
- Open architecture software for interfacing and linking all models

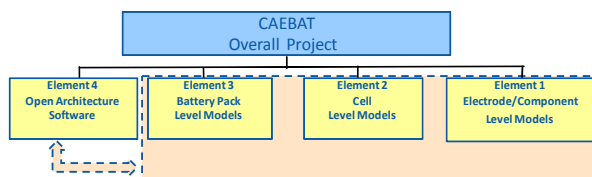


Figure 1. The four elements of CAEBAT activity

The goal of the CAEBAT activity is to “develop suites of software tools that enable automobile manufacturers, battery developers, pack integrators, and other end-users to simulate and design cells and battery packs in order to accelerate the development of energy storage systems that meet the requirements of the electric drive vehicle.” So, the involvement of industry (automakers, battery developers, and software producers) in the CAEBAT activity, particularly for Elements 2 and 3 (Development of Cell and Pack Models) was essential. In 2010, DOE’s major strategy was to solicit active participation of the industry in developing cell and pack software suites for the design of batteries.

To oversee the successful execution of the CAEBAT program, NREL was assigned to coordinate the industry and academic activities on Cell-Level Modeling and Pack-Level Modeling. The Open Architecture Software element was assigned to ORNL. In order to engage serious involvement of industry, NREL, with guidance from DOE, issued a Request for Proposals (RFP) in FY10 to seek development of cell and pack battery design tools for a period of three years with 50-50% cost sharing. The CD-adapco, General Motors (GM), and EC Power teams were awarded in the middle of 2011. The three subcontract teams started technical work in July 2011, made steady progress, and have either met their milestones or are on track to complete them in early FY15 after no-cost extensions.

In addition, NREL continued working on developing and further improving its 3D electrochemical-thermal models. NREL also collaborated with ORNL in their development of the Open Architecture Software as part of Element 4.

## Results

### Subcontracts with Industry

In FY14, NREL continued to monitor the technical performance of the three subcontract teams through monthly progress conference calls, quarterly review meetings, and annual reporting with DOE. Quarterly review meetings took place at subcontractor sites, NREL, and near DOE.

Significant progress has been reported by each subcontractor, according to each team’s statement of work. CD-adapco completed its project, according to plan, at the end of July 2014, and delivered the final version of the battery electrochemical-thermal models for spirally-wound cells in its Star-CCM+ flagship simulation



platform to various clients. EC Power, although finished with all deliverables, including the commercial version of their CAEBAT tool, requested a no-cost extension to deliver all final reports by the end of December 2014. The General Motors team has released the latest version of their CAEBAT tool in ANSYS Fluent-15 and will complete their subcontract in December 2014. A summary of the major accomplishments for each subcontractor is provided below.

### CD-adapco

- Project successfully delivered overall modeling framework into computer-aided engineering tool STAR-CCM+, produced by CD-adapco
- Enhanced electrochemistry model created; original model is based on the work of Newman, et al.; model has been significantly extended to include effect of concentration dependence of solid phase diffusion coefficient and also multiple active materials
- Electrochemical and thermal datasets have been created and validated within the project for spiral cells; these have been created after the provision of cell-specific data from JCI (see Figure 2); a process to extract unknown electrochemical properties from specific test work has been developed
- Dataset of contemporary electrolytes has been added to simulation environment; dataset contains molarity, conductivity, diffusion coefficient, transport number, activity coefficient, density, and viscosity for 12 electrolytes; all values are concentration- and temperature-dependent within appropriate ranges
- Approach to simulating aging within lithium-ion cells has been formulated which considers solid electrolyte interphase (SEI) layer growth and associated capacity reduction driven by lithium loss; model is based on the work of H. Ploehn
- Star-CCM+ flagship commercial software was released with battery modeling modules developed under CAEBAT project; (see Figure 3)

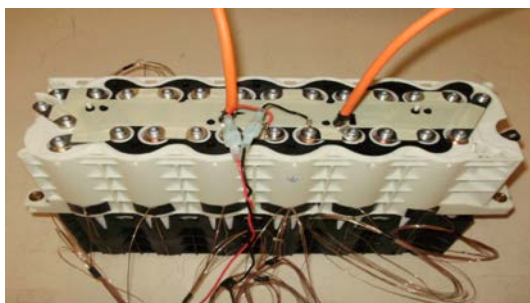


Figure 2. Johnson Controls' 12-cell module, used for validating the Star-CCM+ Battery Model

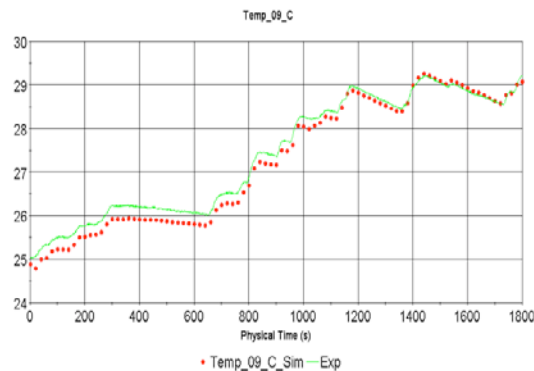


Figure 3. Thermal result for cell within VL6P module using standard drive cycle (red dots are simulation, green line is experiment)

### EC Power

- Delivered final version of the large-format software tool “Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model” (ECT3D) to partners during FY14; recent updates to the software included additional technical features, enhanced robustness and execution speed, and upgrades based on Ford, JCI, and NREL user feedback
- Completed property characterization for materials database
- Completed final validation (see Figure 4)
- Demonstrated advanced coupling of ECT3D with third party software via OAS developed by ORNL
- Delivered eighteen high-impact publications and presentations across the team over the course of the project
- The AutoLion™ commercial software developed, in part, under this project has been well received, with approximately 30 licensees employing the software
- AutoLion™ software is now being applied in markets beyond automotive, including batteries designed for personal and wearable electronic devices and large-scale energy storage

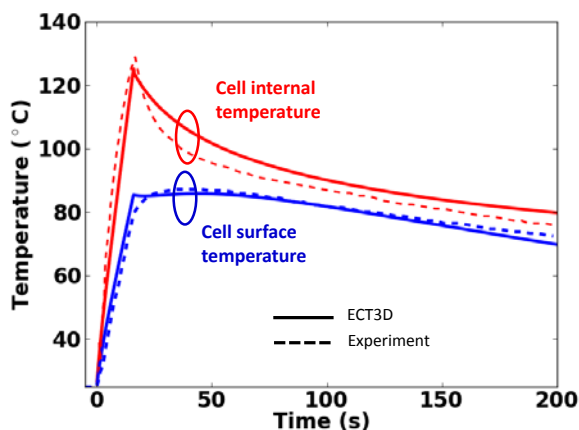
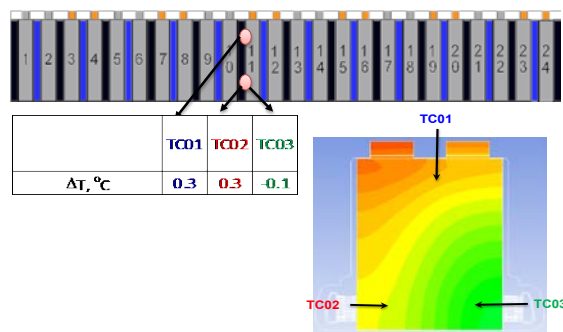


Figure 4. Validation of externally-short-circuited 1.6 Ah NMC/graphite 18650 cell; experimental data acquired using reaction temperature sensor (RTS)

### General Motors

- Continued implementation of NREL’s MSMD framework in FLUENT with three electrochemistry sub-models
- Released official public version of ANSYS battery tools in Fluent - Release15
- Developed ANSYS Battery Design Tool (ABDT) utilizing the ANSYS Workbench framework
- Completed reduced-order models (linear time invariant [LTI]/linear parameter varying [LPV]) for system-level simulations and performed demonstration on an entire pack
- Developed cycle life model for LG CPI cell based on continuous fading equivalent circuit model by adding SEI side reaction
- Included newly-developed NREL user-defined function for multiple particle/multiple active material models
- Validated full 3D electrochemical and thermal model with a 24-cell liquid-cooled module with satisfactory results in comparison with test data (see Figure 5)



**Figure 5. Temperature difference between simulation and test data at three thermocouple locations**

### Collaboration with ORNL on Open Architecture Software

NREL and ORNL held meetings to discuss the best approach and strategy for OAS. This included collaboration on battery input, battery state, wrappers, and translators. CAEBAT subcontractors were engaged with ORNL for interfacing with OAS.

### Development of Multi-Physics Battery Models at NREL

NREL standardized the model input-output, and the data structure for particle domain (PD), electrode domain (ED), and cell domain (CD) models in the MSMD platform, and restructured the MATLAB code structure of the baseline MSMD model codes. The porting of PDM and EDM in C++ and prototype porting of the CDM was

completed. The newly-developed C++ model code performance was verified against the corresponding MATLAB codes.

### Conclusions and Future Directions

- The three CAEBAT subcontract teams lead by CD-adapco, EC Power, and General Motors made significant progress toward achieving their project objectives
- Experimental data are being collected by each team to validate the models; simulation results of CAEBAT tools show good agreement with the experimental data
- Each subcontractor released a mature version of their CAEBAT software tools to the public—CD-adapco in Star-CCM+, EC Power with AutoLion™, and General Motors in ANSYS Fluent-15
- NREL enhanced its battery MSMD platform for CAEBAT and developed a stand-alone version of MSMD in C++ for ease of use by any party
- NREL collaborated with ORNL on development of the OAS to link developed and existing models
- CD-adapco completed its project and subcontract in July 2014
- EC Power has completed its project and will finalize reporting in December 2014
- General Motors has completed its project and will finalize reporting in December 2014
- The original CAEBAT project will be complete in early FY15; this project has been successful in delivering three stand-alone computer-aided battery engineering tools for accelerating the electrochemical and thermal design of electric drive vehicle batteries
- The second phase of CAEBAT activity, called CAEBAT-2, will be coordinated directly by DOE with competitive procurements through Funding Opportunity Announcements; the focus will be on understating the behavior of batteries under abuse conditions such as crash-induced crush, thermal ramp, and sharp object penetration

### FY 2014 Publications/Presentation

- Ahmad Pesaran, Gi-Heon Kim, Kandler Smith, Shriram Santhanagopalan, “Multi-physics Computational Models for Accelerated Design of Batteries,” Conference Proceedings, Batteries 2014, September 24-September 26, 2014, Nice, France

# Development of Computer-Aided Design Tools for Automotive Batteries (General Motors)

## Gi-Heon Kim (NREL Technical Monitor)

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Partners: ANSYS Inc. and ESIM, LLC

Start Date: June 2011  
Projected End Date: Dec 2014

## Objectives

- As one of the subcontract teams, support the DOE/NREL CAEBAT activity to shorten the product development cycle for EDVs and reduce the cost associated with current hardware build and test design iterations
- Provide simulation tools that expand the inclusion of advanced lithium-ion battery systems into ground transportation; validate advanced lithium-ion battery systems using GM's six-step model verification and validation approach
- Participate in the OAS program led by ORNL to develop a flexible and scalable computational framework to integrate multiple battery physics sub-models produced by different teams

## Technical Barriers

- Existing design tools are not practical for realistic battery pack design and optimization
- Various cell physics sub-models exist, but they have not been integrated in a single framework in commercial code
- Current engineering workstations do not have the computational power required to simulate pack-level thermal response coupled with electrochemistry; system-level analysis or Reduced Order Modeling (ROM) is required to simulate integrated pack-level physics; however, ROM approaches for battery packs are not well established
- Collaboration to date has been difficult since software developer's commercial code, automaker's electrification strategies, and battery developer's cell designs and chemistry are all well-guarded intellectual property

## Technical Targets

To be useful to automotive engineers, battery cell and pack design tools should have the following analytical capabilities:

1. Evaluate battery pack thermal management strategies by predicting max intra/inter-cell temperature difference under various drive-cycles
2. System simulations with ROM that allow tradeoff studies between the cooling cost and the battery pack warranty cost in the early stage of vehicle development
3. Real-time system simulation speed that can support battery management system (BMS) development and enhancement

## Accomplishments

- First version of the battery software was officially released to public with Release 15 of FLUENT in winter of 2014
- Software development:
  - The ANSYS Battery Design Tool (ABDT) has been developed by utilizing the ANSYS Workbench framework
  - Linear time invariant (LTI)/linear parameter varying (LPV) system-level model was completed and demonstrated for the entire pack
  - Cycle life model has been developed for an LG cell based on a continuous fading equivalent circuit model by adding a SEI side reaction
  - NREL has developed a user-defined function for multiple particle/multiple active material models
- Cycle life test:
  - Cycle life test at an elevated temperature was completed
  - Physics-based cycle life model has been developed
- Pack level validation:
  - Field simulation has been validated with satisfactory results in comparison with test data
  - System-level model was completed and validated compared to the full field simulation and the test data; comparisons are satisfactory
  - LTI system-level ROM model approach has been validated in comparison with full field simulation results
  - Thermal abuse and runaway model has been implemented and demonstrated for thermal propagation in a pack



## Introduction

The principal objective of the GM team is to produce an efficient and flexible simulation tool that predicts multiphysics responses for battery pack thermal management and optimum cell energy capacity in terms of electrical performance, cooling requirements, life, safety, and cost. GM has assembled a CAEBAT project team composed of GM researchers and engineers, ANSYS software developers, and Prof. R.E. White of the University of South Carolina and his ESim staff. In partnership with DOE/NREL, the project team has interacted with CAEBAT working groups to integrate and enhance existing submodels, develop cell- and pack-level design tools, and perform experimental testing to validate simulation tools. The GM team has also created interfaces to enable these new tools to interact with current and future battery models developed by others. NREL has provided technical consultation and monitored the overall progress. ORNL has provided the standard for OAS. With rapid deployment to industry, these project results will contribute to accelerating the pace of battery innovation and development for future EDVs.

## Approach

The project objective is to develop an open, flexible, efficient software tool for multi-scale, multiphysics battery simulation based on the ANSYS Workbench framework. ANSYS is leveraging and enhancing existing commercial products to provide both field-level (Fluent) and system-level (Simplorer) capabilities, including novel ROM methods and other battery tools through the OAS interface. Figure 1 shows a conceptual view of the ABDT architecture which is the basis for ANSYS software development. The essential role of the ABDT is to automate, integrate, and enhance ANSYS simulation tools to tailor various components for cell and pack capabilities.

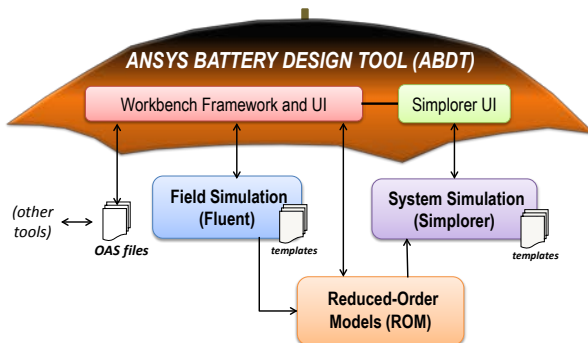


Figure 1. Conceptual view of the ANSYS Battery Design Tool

GM engineers and ESim tested submodels, evaluated ABDT tools, and provided further enhancements. The GM team also built prototypes for a battery module and a pack and performed experimental testing to validate these tools. At the pack level, the tools significantly advanced through

the development of innovative reduced-order models, derived and calibrated from the cell-level models and carefully validated through experimentation.

## Results

New features were added to the ANSYS Fluent battery model that offer additional functionality and flexibility to the user. The electric load profile can now be provided as a *time-scheduled* or as an *event-scheduled* function according to the user's choice (see Figures 2 and 3). Both methods allow the user to change the electric load type and electric load value during the simulation.

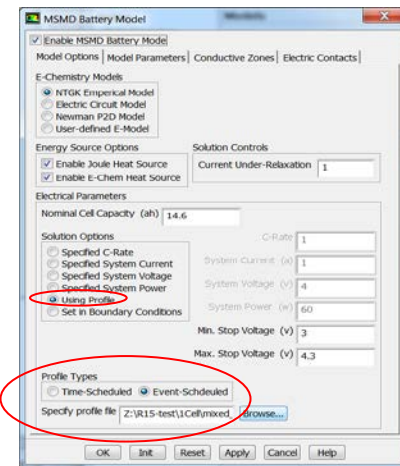


Figure 2. Profile Type Selection

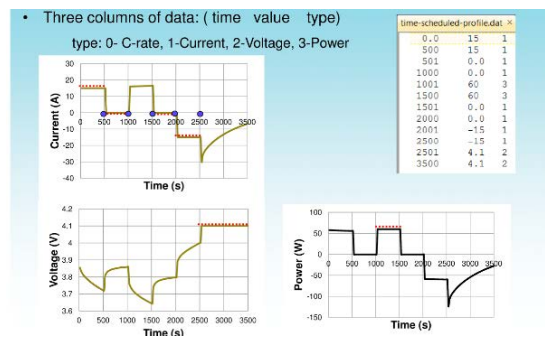


Figure 3. Time-Scheduled Profile

The team has also developed a model parameter estimation tool (see Figure 4) for the Newman, Tiedemann, Gu, Kim (NTGK) and equivalent circuit model (ECM) electrochemistry submodels. These model parameters are battery specific and users estimate them by curve fitting data points from experimental measurements of the battery's electric behavior.



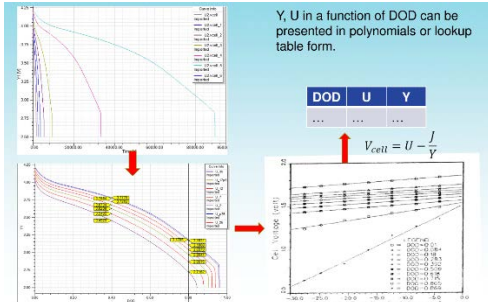


Figure 4. NTGK Model Parameter Estimation Procedure

Typically, battery cells are connected either in parallel or series in a module or pack, and highly conductive busbars are used to connect cell tabs accordingly. However, a busbar is usually very thin and meshing becomes a challenging task, especially in large and complex arrangements. A simpler battery connection technique (see Figure 5) has been researched and ANSYS has developed a virtual battery connection that avoids physically modeling the connectors. The Fluent solver sets up the connections accordingly by automatically associating conductive zones with each cell.

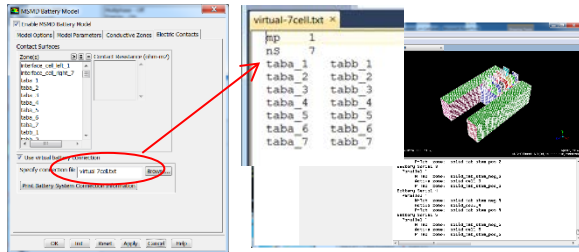


Figure 5. Virtual Battery Connection

Occasionally, battery cells are abused due to accident or extreme conditions. The associated chemical side reactions and potential for thermal runaway are important safety considerations. To evaluate the tolerance of battery packs for such abuse conditions, a thermal abuse model has been developed in the Fluent solver through a user-defined function and corresponding interface (see Figure 6) for editing model parameters.

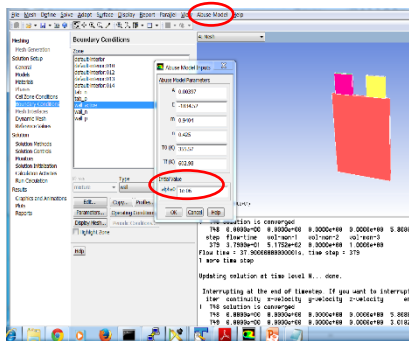


Figure 6. Thermal Abuse Model in Fluent

The team continued making progress on simulating battery packs with ROMs. The LTI ROM algorithm has been automated within the ABDT environment. In

parallel, the development of a robust LPV macro-model has been continued with the algorithm being validated on a 20-cell module with time-varying coolant flow rate. ANSYS has also continued to explore the use of Proper Orthogonal Decomposition (POD) ROMs for simulating battery packs in a more direct method. This method extracts thermal, electrical, and electrochemical matrix information, based on the finite-volume mesh and the representative solution and builds a high-quality ROM. The method has been applied to a large test case and will be extended to include variable coolant flow rates.

Regarding the battery life model, Deshpande's model has been evaluated with LG cell OCAP data (every 500 cycles) by ESim. However, Deshpande's model has three limitations: first, the model does not work for cells with varied cycling protocols; second, the model only predicts capacity for full charge/discharge and cannot be used for incomplete charge/discharge cycles; third, the model cannot be used to predict the power fade of a cell. Due to the above-mentioned limitations, ESim developed a continuous fading ECM by adding an SEI side reaction branch, as shown in Figure 7.

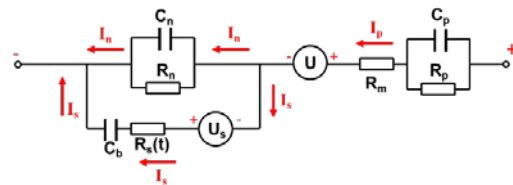


Figure 7. The ECM with an SEI formation branch

In the SEI formation branch,  $U_s$  denotes the open-circuit potential for the deposition reaction,  $R_s$  stands for the sum of the ohmic and kinetic resistances, and  $C_b$  is a balancing capacitor. Due to the deposition reaction, the resistance of the SEI increases with time through the following correlation:

$$\frac{dR_s}{dt} = K_u I_s \quad (\text{for } I_s > 0) \quad \frac{dR_s}{dt} = 0 \quad (\text{for } I_s \leq 0) \quad (1)$$

where  $K_u$  ( $\Omega \text{ m}^4/\text{C}$ ) is a parameter that relates side reaction current density,  $I_s$ , to film resistance,  $R_s$ , ( $\Omega \text{ m}^2$ ), with  $R_s(t=0)$  as a parameter. Initial values for the circuit components ( $C_p$ ,  $R_p$ ,  $C_n$ ,  $R_n$ , and  $R_m$ ) were obtained by validating the model with discharge data at different rates for fresh cells at 25°C. Initial fitting results are presented in Figure 8. Equivalent circuit components ( $C_p$ ,  $R_p$ ,  $C_n$ ,  $R_n$ ) take the following expression:

$$\Psi = \left( \frac{1}{a \cdot \text{DoD}^2 + b \cdot \text{DoD} + c} \right)^2 \quad (\text{where } \Psi = R_n, C_n, R_p, C_p) \quad (2)$$

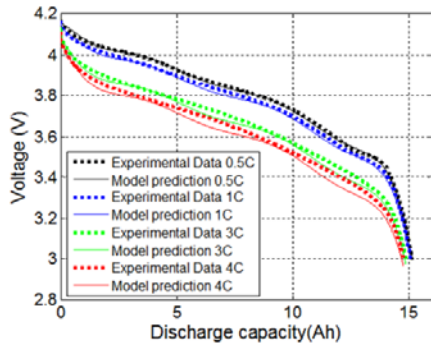


Figure 8. Fit of ECM life model at the beginning of life

Comparison of the simulated and experimental capacity values during the first 500 cycles was used to determine the fade parameters ( $R_s(t=0)$ ,  $C_b$ ,  $U_s$ , and  $K_u$ ), and the results are presented in Figure 9. In each cycle, the cell was charged at 30 A (2C) to 4.091 V followed a CV charge to 0.75 A (0.05 C), then discharged at 45 A (3C) to 3.513 V. Continuous SEI formation on the anode of a Li-ion cell can be represented as a circuit branch in an ECM. The continuous ECM life model shows good agreement with experimental data.

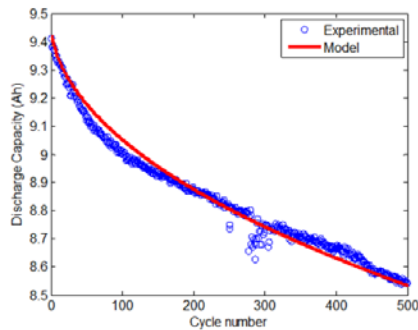


Figure 9. Comparison between ECM life model and experimental cycling data

GM has built a 24-cell module with a liquid-fin cooling system (see Figure 10). Thermocouples were located at various places in the module to validate full field computational fluid dynamics (CFD) simulations, with a CFD model constructed by GM engineers and validated to compare simulation results with test data for a 1 sec charge/discharge pulse case at a 3.5 C-rate and SOC at a constant value of 50%. This is a simple test case with a constant heat generation rate to validate the model. The battery surface temperature predictions are within 0.5°C accuracy at a steady state (see Figures 11 and 12).

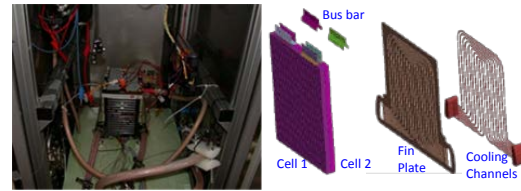


Figure 10. 24-cell module validation test setup for full field simulation against test data for high-frequency charge/discharge pulse case

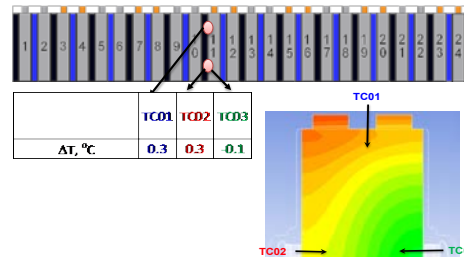


Figure 11. Temperature difference between simulation and test data at three thermocouple locations

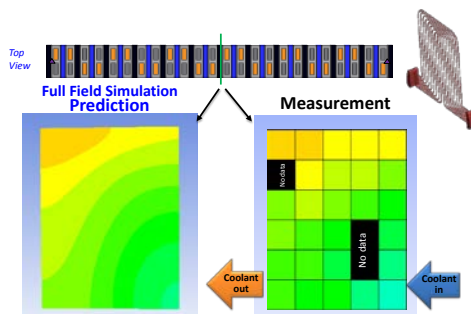


Figure 12. Comparison of temperature distribution on battery surface located in the middle of the module

In 2014, the GM team continued making progress on simulating battery packs and system-level development with and without ROM. In order to validate the system-level model without a ROM approach, GM engineers constructed it from an automated ABDT user interface, as shown in Figure 13. For the high frequency charge/discharge pulse case shown in Figures 11 and 12, system simulation (see Figure 14) required total CPU time of less than 1 minute (Dell Z800 PC), compared to 4-5 days of full field simulation on a 64-processor HPC cluster.

The team has also developed a procedure to obtain empirical parameters from HPPC test data to accurately predict load voltage, and hence heat generation, in cells under various drive cycles. GM engineers also validated the system-level approach for a realistic US06 driving cycle, as shown in Figure 15. Validation of system simulations for the 24-cell module was completed and predicted temperatures were within 0.5°C as compared to test data, as shown in Figure 15. Simulation of five back-to-back US06 drive cycles for a total of 30 minutes of driving simulation took less than a few seconds of computational time with the system model.

Agreement for pack total heat generation is satisfactory compared with measured coolant total heat rejection rate and temperature difference between the inlet and outlet, as shown in Figure 15. System simulation accurately characterizes cell thermal behavior in the 24-cell module. Activity was also initiated to leverage existing battery pack CAE models and test data sets for further validation of the new tools.

Finally, as the team continues to develop new simulation tools to comply with OAS, ANSYS has issued a related product license for ORNL, which is now assisting to ensure compatibility for ANSYS tools.

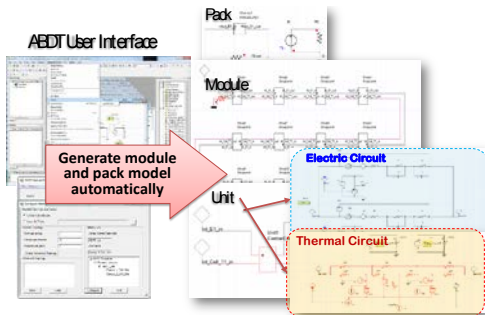


Figure 13. Automatic system model construction for 24-cell module from ABDT interface

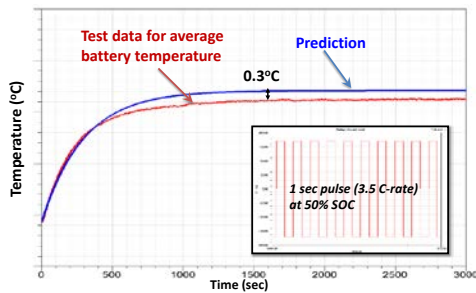


Figure 14. Prediction of battery temperature due to internal heat generation by 1 sec charge/discharge pulses at 3.5 C-rate

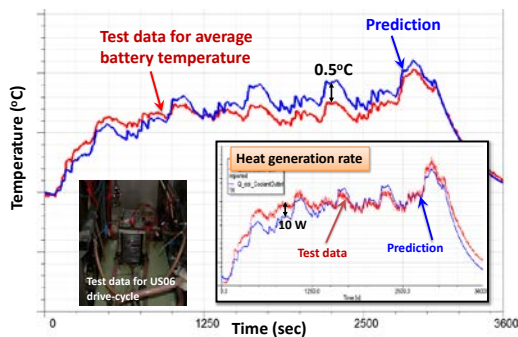


Figure 15. Comparison of cell temperatures during US06 drive cycle and heat generation comparison

## Conclusions and Future Directions

Overall, the project is on track and technical progress is consistent with the project plan. The first version of battery software was officially released to the public with Release 15 of FLUENT in 2014.

We have two remaining tasks to be completed by the end of 2014:

1. Complete the battery life model based on an equivalent circuit model by adding an SEI side reaction branch
2. Complete pack-level validation for production battery packs to meet future capability matrix for pack-level CAE

## Acknowledgement

Supported by the U.S. Department of Energy, specifically Dave Howell and Brian Cunningham.

## FY 2014 Publications/Presentations

1. M. Guo and R. E. White, "Mathematical Model for a Spirally-Wound Lithium-Ion Cell," Journal of Power Sources 250 (2014), also presented at the ECS meeting, spring 2014, Orlando, FL.
2. R. Rebba, J. McDade, S. Kaushik, J. Wang, T. Han, "Verification and Validation of Semi-Empirical Thermal Models for Lithium Ion Batteries," 2014 SAE World Congress, Detroit, MI.
3. G. Li, S. Li, "Physics-Based CFD Simulation of Lithium-Ion Battery under a Real Driving Cycle," Presentation at 2014 ECS and SMEQ Joint International Meeting, Oct 5-9, 2014, Cancun, Mexico.
4. G. Li, S. Li and J. Cao, "Application of the MSMD Framework in the Simulation of Battery Packs", Paper IMECE2014-39882, Proceedings of ASME 2014 International Mechanical Engineering Congress & Exposition, IMECM 2014, Nov 14-20, 2014, Montreal, Canada.
5. Y. Dai, L. Cai, and R. E. White, "Simulation and Analysis of Inhomogeneous Degradation in Large Format LiMn2O4/Carbon Cells," Journal of The Electrochemical Society, 161 (8), 2014
6. T. Han, G. Kim, R. White, D. Tselepidakis, "Development of Computer Aided Design Tools for Automotive Batteries," ANSYS Convergence conference, Detroit, MI, June 5, 2014.
7. T. Han, M. Fortier, L. Collins, "Accelerating Electric-Vehicle Battery Development with Advanced Simulation," Aug 21, 2014, Webcast seminar organized by SAE International, <http://www.sae.org/magazines/webcasts>.

# Development of Computer-Aided Design Tools for Automotive Batteries (CD-adapco)

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Partners: Johnson Control Inc. and A123 Systems

Start Date: August 2011  
End Date: July 2014

## Objectives

- As one of the subcontract teams, support the DOE/NREL Computer Aided Engineering for Batteries (CAEBAT) activity
- Develop battery CAE software that reduces design cycle time, reduces the cost and enhances the performance, life and safety of large format automotive cells and packs
- Specifically develop a numerical simulation model which can resolve the appropriate phenomena required to create a coupled thermal and electrochemical response model
- Apply advanced numerical techniques to expedite the solution of the governing fundamental equations within lithium ion battery cells.
- In partnership with commercial battery suppliers, validate the accuracy of the numerical models for multiple automotive cell designs and module thermal configurations

## Technical Barriers

One of the major challenges of this project is to include the important aspects of the rapidly maturing lithium ion battery simulation field in to an easy to use, widely accepted computer aided engineering tool. This implementation should be flexible and extensible to

ensure the methods can move forward as the level of understanding in the fundamental physics evolves.

Another significant challenge is the creation of a modeling concept for spirally wound cells and their underlying architecture. Spiral cells can be grouped in to several categories and hence flexible templates were created, the user then provides appropriate data to populate such templates creating a complete electrochemical and thermal cell model. The creation of such electrochemical and thermal templates and overall method is a significant part of this project.

It should also be stated that obtaining some of the modeling parameters used within such electrochemical models has proved a challenge. Part of proliferating the use of such a coupled thermal-electrochemical tool is to present a process to obtain such parameters to users so there is confidence in results obtained from such models.

## Technical Targets

- Create a spiral cell analysis framework which includes the two electrodes wound together to create the spiral jellyroll. This method should resolve the planar electrical/thermal gradients along the length and height of the electrodes as well as the overall performance of the electrode pair.
- Validate the created cell simulation models against test work provided by sub-contractors including both cylindrical and prismatic forms of spiral cells
- Use the validated methods within a larger framework to create simulations of battery modules including such cells. These methods will be validated against electrical and thermal results from appropriate battery modules

## Accomplishments

- The project has successfully delivered the overall modeling framework, both electrochemical and thermal, as described above in to the computer aided engineering tool STAR-CCM+, produced by CD-adapco.
- An enhanced electrochemistry model has now been created. The original model is based on the work of Newman et al<sup>4</sup>. This model has been significantly extended to include the effect of concentration

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<sup>4</sup> Simulation and Optimization of the Dual Lithium Ion Insertion Cell, T. Fuller, M. Doyle, J. Newman, J. Electrochem. Soc. 141 (1994) 1-10



dependence of the solid phase diffusion coefficient<sup>5</sup> and also multiple active materials as often found in contemporary lithium ion cell design.

- Electrochemical and thermal datasets have been created and validated within the project for the spiral cells listed below. These have been created after the provision of cell specific data from Johnson Controls Inc. A process to extract the unknown electrochemical properties from specific test work has been developed
- A dataset of contemporary electrolytes has been added to the simulation environment. The dataset contains molarity, conductivity, diffusion coefficient, transport number, activity coefficient, density, and viscosity for 12 electrolytes. All values are concentration and temperature dependent within appropriate ranges.
- An approach to simulating aging within lithium ion cells has been formulated which considers SEI layer growth and associated capacity reduction driven by lithium loss. This model is based on the work of H. Ploehn<sup>6</sup>.
- The Star-CCM+, flagship commercial software of CD-adapco was released with battery modeling module developed under this CAEBAT project. Many around the world use this tool for accelerating battery design.



## Introduction

Department of Energy established the Computer Aided Engineering for Electric Drive Vehicle Batteries (CAEBAT) activity to develop multi-physic design tools. NREL, with guidance from DOE, co-funded three subcontractors including CD-adapco, to develop software tools for CAEBAT. CD-adapco has extended its class leading computer aided engineering code, STAR-CCM+, to analyze the flow, thermal and electrochemical phenomena occurring within spirally wound lithium ion battery modules and packs. This coding has been developed in collaboration with Battery Design LLC who is a sub-contractor to CD-adapco and has considerable experience in the field of electrochemistry modeling. As well as resolving the electrochemically active regions in a spiral cell the model accounts for the tabbing of the electrode in the overall performance.

<sup>5</sup> Concentration dependence of lithium diffusion coefficient in LiCoO<sub>2</sub>, Young-Il Jang, Bernd J. Neudecker, and Nancy J. Dudney, *Electrochemical and Solid-State Letters*, 4 (6) A74-A77 (2001)

<sup>6</sup> Solvent diffusion model for aging of lithium-Ion battery cells, Ploehn, P Ramadass & R. White J. *Electrochem. Soc* A456-A462(2004).

The created electrochemical model has now been applied to the lithium ion cells listed below, excluding the pouch cell where an empirical model has been used.

Manufacturer	Format	Capacity
JCI	Cylindrical	7Ah (HP)
JCI	Cylindrical	40Ah (HE)
JCI	Prismatic	6Ah (HP)
JCI	Prismatic	27Ah (HE)
A123	Pouch	20Ah

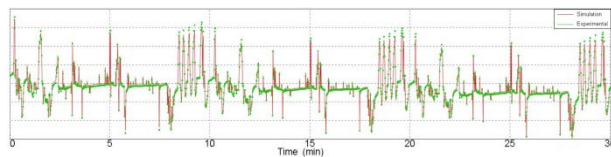
## Approach

Detailed design information was obtained from Johnson Controls Inc. to describe the dimensions of the electrode, the details of the can and finally details of the electrode chemistry used in each of the designs. These cell models also used the appropriate electrolyte formulation from the newly integrated dataset provided by K. Gering at Idaho National Laboratory (INL) (also part of this project). Tightly controlled cell level test work was specified to enable the remaining modelling parameters to be extracted. This has now been done for all 4 spiral cells. The project now has a high level of confidence in the overall process, including cell test work specification and parameter extraction. This is borne out by the validation results presented below.

## Results

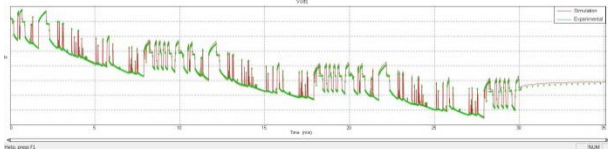
### Electrochemistry

A validation of the voltage response from the created models was completed. This validation used either a charge-sustaining or charge-depleting load as appropriate for the cell in question and compared with experimentally obtained voltage curves. Validation results are shown below.

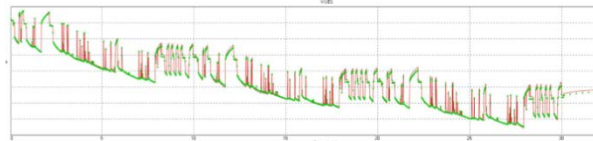


**Figure 4. Voltage response from the created electrochemical model for the JCI VL6P cell over a 30min drive cycle compared to test work (Voltage scale removed)**

The mean squared error for the VL6P simulation model (Figure 2) over the 30 minute drive cycle is 9mv. Similar error levels are seen in the other models.



**Figure 5. Voltage response using the electrochemistry model for the JCI VL41M high energy cell over a 30min drive cycle compared to test work (Voltage scale removed)**



**Figure 6. Voltage response using the electrochemistry model for the PL27M cell over a 30min drive cycle compared to test work (Voltage scale removed)**

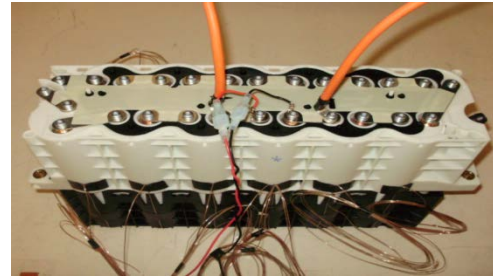
The above validation work was completed using a ‘lumped’ electrochemistry model. This essentially means a single temperature for the whole cell is assumed. The cell representations were then transferred in to STAR-CCM+ and complex three dimensional models of the cell were created. This model now accounts for the internal anisotropic thermal conductivity of the jelly roll as well as the jelly roll’s thermal interfaces with neighbor components such as mandrels and external cans. The electric conductivity of the current collectors is also included in the model. The figure below compares the simulation results for the VL6P electrochemistry model using the lumped model and the 3D model. The mean difference is 8mV over the 30 minute drive cycle. Differences are expected within the results due to the 3D model having a distribution of temperature within the jelly roll, hence a differing response. Overall we can conclude that the voltage response of the cell is well captured within both lumped and 3D modelling domains hence engineers can use the same cell data within either modeling framework, lumped or detailed 3D.



**Figure 7. Comparison of lumped electrochemistry model vs three dimensional electrochemistry model over a 30min drive cycle (Voltage scale removed)**

### Thermal

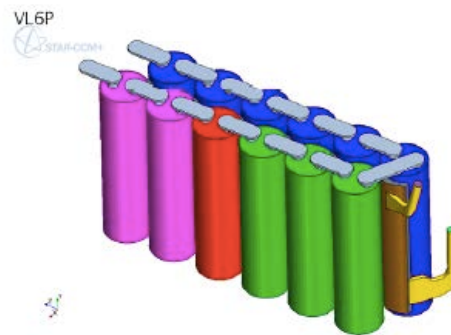
The thermal validation was completed using the 3D model within STAR-CCM+. Module test work for all the cells has now been complete. The image below shows the VL6P 12 module that is used within the module tests. This arrangement is liquid cooled.



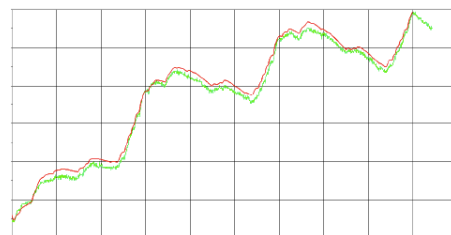
**Figure 8. Johnson Controls 12 cell module ready for testing**

The main thermal validation test used the same drive cycle input condition as used in the lumped model and cell can surface temperatures were monitored.

A high fidelity finite volume model was created within STAR-CCM+ including all cell components (jelly rolls, current collection designs, outer cans) as well as current carrying straps and coolant system.



A number of thermocouples were located on the cell of interest and the graph below shows one result compared to the appropriate test result. These thermocouples were located on the outer surface of the cells can. The scales have been removed as this is sensitive data.



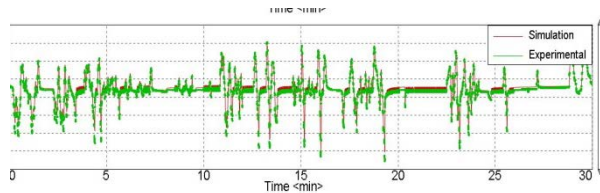
**Figure 9. Thermal result for a cell within the VL6P module (red line is simulation, green line is experiment)**

The spatial distribution around the cell is considered by having a number of thermocouples and this was used to validate the simulation model. Due to the confidential nature of the commercial cells and modules used for validation more extensive plots cannot be shown within this report.

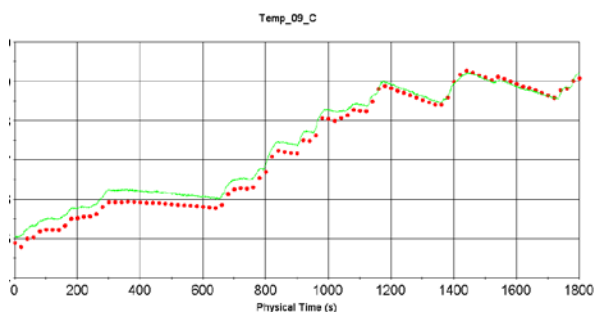
### Blind Test

As well as the original US06 drive cycle experiments towards the end of the project it was decided to expand

the scope and do some blind tests on a different drive cycle. This tested the flexibility and general applicability of the model. The second drive cycle chosen was a worldwide harmonized light vehicles test procedure (abbreviated to WLTP) and this was performed on the VL6P also. The figures below show both electrical and thermal performance of the model.



**Figure 10. Voltage prediction for WLTP drive cycle as a blind test (Voltage scale removed)**



**Figure 11. Thermal result for a cell within the VL6P module using WLTP drive cycle (red dots are simulation, green line is experiment)**

## Conclusions and Future Directions

The breadth of lithium ion cells covered by this work and the addition of the WLTP drive cycle demonstrate that coupled electrochemical and thermal highly resolved 3D simulations are now possible within a mainstream CAE framework. Although a significant proportion of the cell specific details remained confidential the learning and method development covering how to conduct studies and the critical points to focus on is now openly available from CD-adapco and its project partners. Star-CCM+ with battery modeling methods developed under the DOE CAEBAT activity can be licensed from CD-adapco. These methods are already being used outside of this project to add value to other lithium ion applications.

The project is now complete (July 2014) and final reports have been issued. A dedicated team at CD-adapco continues to move these methods forward and expand the coverage of the tool to address other lithium ion applications.

## Acknowledgments

The subcontractors would like to acknowledge the contribution and input that the National Renewable Energy Laboratory has made, particularly Kandler Smith and the support of the Department of Energy, specifically Dave Howell and Brian Cunningham. The authors would like to acknowledge the subcontractors, namely JCI and A123 Systems, support in sharing some of the results from this work.

# Development of Computer-Aided Design Tools for Automotive Batteries (EC Power)

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Partners:  
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Johnson Controls, Inc.  
Pennsylvania State University

Start Date: June 2011  
End Date: December 2014

## Objectives

The objectives of this work, in support of the DOE/NREL CAEBAT activity, are:

- Develop a commercial electrochemical-thermal coupled model and associated computer code for large-format, automotive Li-ion cells and packs
- Create a novel computational framework that allows for rapid and accurate performance/safety simulations; algorithms will span across several length scales, ranging from particle size, to an electrochemical unit cell, to a 3D battery, and finally to an entire battery pack; this computational framework will be able to model both wound and stacked cell geometries
- Develop a comprehensive materials database that is critical for accurate modeling and simulation of large-format Li-ion batteries
- Test and validate the developed cell and pack models against a wide range of operating conditions relevant to automotive use, such as extreme temperature operation, complex power profiles, etc.

## Technical Barriers

The large format nature of automotive Li-ion batteries presents a unique set of challenges that sets them apart from batteries used in cell phones, laptops, and other consumer goods. For example, high rates of charge and discharge, in combination with the large surface area of the cell, lead to widely-varied temperature distributions on the cell and throughout the packs. This non-uniformity

causes a number of serious issues, including poor battery performance, increased degradation effects, potential safety concerns, and the inability to fully utilize the active material inside the battery. Creating actual cells and packs is time consuming and extremely expensive, which makes an efficient, high fidelity simulation tool very desirable.

However, the strongly coupled nature of electrochemical and thermal physics, the relevant scales of a battery cell or pack (ranging from sub-microns to meters), and the need for a comprehensive materials database, makes the creation and development of a Li-ion battery model a unique and challenging task.

## Technical Targets

- Development of an extensive database of material properties for accurate model input
- Creation of a multi-dimensional, electrochemical-thermal coupled model, complete with an easy to use, intuitive graphical user interface (GUI)
- Development of fast, scalable numerical algorithms enabling near real-time simulation of batteries on a single PC, and packs with thermal management systems on a small computer cluster
- Experimental validation of the model and corresponding software

## Accomplishments

- Delivered final version of our large-format software tool, “Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model” (ECT3D) to partners during FY2014; recent updates to software included additional technical features, enhanced robustness and execution speed, and upgrades based on Ford, JCI, and NREL user feedback
- Property characterization for materials database complete
- Final validation complete
- Demonstrated advanced coupling of ECT3D with third party software via OAS developed by ORNL
- Eighteen high-impact publications and presentations from the team over the course of the project
- AutoLion™ commercial software developed in part under this project has been well received, with approximately 30 licensees employing the software
- AutoLion™ software is now being applied in markets beyond automotive, including batteries designed for personal and wearable electronics devices and large-scale energy storage





## Introduction

In order to reduce greenhouse gas emissions and reduce U.S. dependence on foreign oil, the development of hybrid electric, electric, and plug-in electric vehicles is extremely important. The Li-ion chemistry used in automotive batteries can store large amounts of energy, while maintaining a low weight (relative to other battery chemistries).

The design, build, and testing process for batteries and packs is extremely time consuming and expensive. The CAEBAT activity was initiated by DOE and monitored by NREL to develop software tools to accelerate the development and design of batteries.

EC Power's code, ECT3D, directly addresses the issues related to the design and engineering of these cells. Many technical characteristics of batteries and packs that are critical to battery performance and safety are impossible to measure experimentally.

However, these same characteristics are easily analyzed using ECT3D in a virtual environment. The use of advanced software such as ECT3D allows design engineers to gain unique insights into system performance that would be inaccessible via experimental measurements. Furthermore, the analysis is done completely in a virtual environment, eliminating the need for any physical production of test cells.

## Approach

EC Power has developed the large-format, li-ion battery simulation software ECT3D to analyze battery cells and packs for electrified vehicles (EV, PHEV, HEV). Team member Pennsylvania State University was primarily responsible for performing materials characterization experiments and diagnostic experiments for multi-dimensional validation. The materials characterization experiments supplied data for the extensive materials database incorporated into ECT3D.

Industrial partners Ford Motor Company and Johnson Controls, Inc. are currently testing and validating ECT3D to ensure its utility for industrial use. The overarching goal of the project is to produce a world-class, large-format lithium-ion cell and pack design tool that drives innovation and accelerates the design process for electric vehicles and their power systems.

## Results

Figure 1 highlights the validation of the external shorting safety model developed during the course of the project. In addition to external shorting, we also developed models to simulate internal shorting and nail penetration. Specifically in these figures, we note an overall good agreement for simulated and experimental voltage, current, and local temperature over the entire shorting process. A maximum error of approximately 2%

was observed for voltage, 10% for current, and ~4% error for local temperatures at the peak time (~16s). The internal cell temperature measurement was made using a novel reaction temperature sensor (RTS). These results emphasize the importance of measuring or predicting the local internal cell temperature as an appropriate metric for safety. As observed below, a difference in peak temperature of 45°C was observed. A local (surface) temperature of 85°C does not indicate safety concerns, but a temperature of 130°C (internally) may be on the verge of thermal runaway.

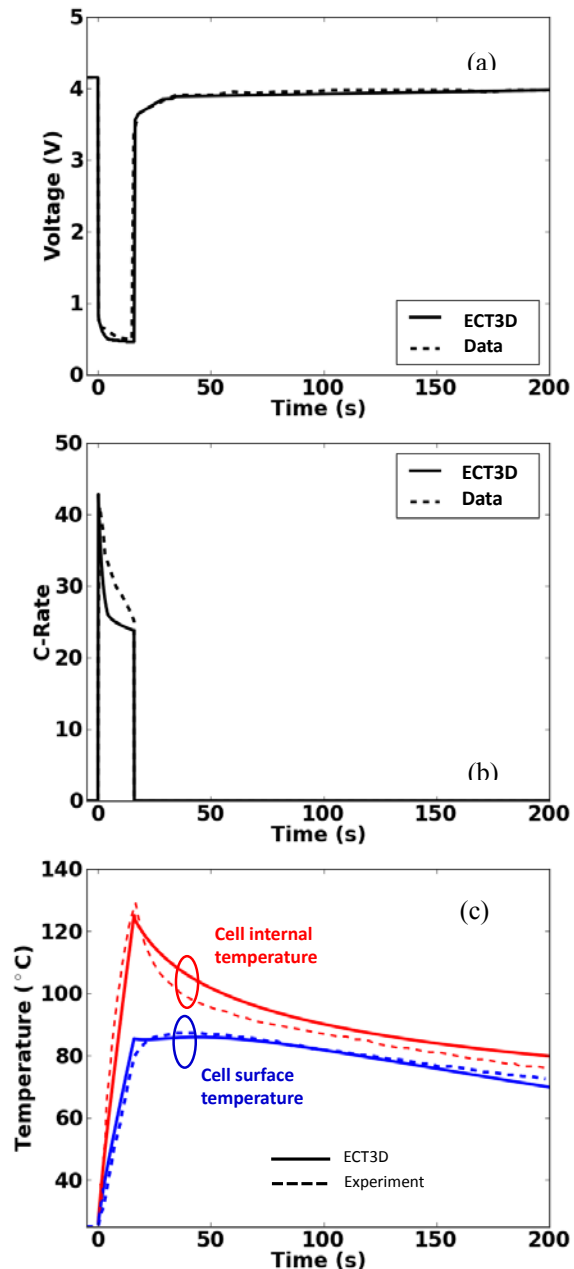


Figure 1. Validation of externally shorted 1.6 Ah NMC/graphite 18650 cell; experimental data acquired using RTS sensor [14, 16, 17]; (a) voltage, (b) current (C-rate), and (c) cell-internal and surface temperatures

Figure 2 illustrates a good example of how the software can be applied to enhance cell design efficiency and materials utilization. The cell's normalized energy is shown on the y axis, and the x axis gives the cell time-averaged current density non-uniformity factor (CDNUF). Details can be found in reference [15], but the CDNUF is generally a metric used to measure how non-uniform the current density is within a large-format cell; typically the larger this value, the poorer the active materials utilization and the less energy can be usefully extracted from the same amount of active material. Specifically, figure 2 shows the results of simulated cells with various numbers of tabs in both symmetric and asymmetric format, along with experimental data from 2.4Ah cells with various tab designs. Clearly, the results show that a larger number of tabs can increase the energy efficiency of the cell by more than 50%. Note that while continuous tabs are widely used to reduce the CDNUF, they can also add substantial weight to the cell; this multi-tab design is an example of lean engineering. Further, this highlights one example of how to increase a large format cell's energy density not through material innovations, but rather by *cell engineering*.

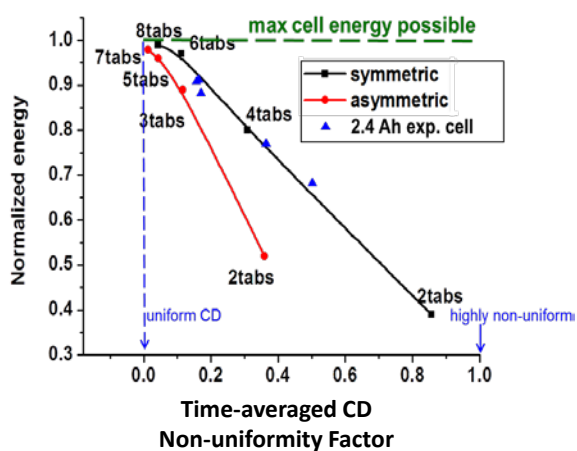


Figure 2. Cell normalized energy vs. time-averaged current density non-uniformity factor for cells with various tab designs (experiment and simulation results shown) [15]

## Conclusions and Future Directions

EC Power has completed the project successfully, accomplishing all goals set forth at the outset. The final version of the ECT3D software contains an extensive materials database, including NMC, LFP, LMO, and LCO cathode materials, along with graphite and LTO anode materials characterized between  $-30^{\circ}\text{C} < T < 60^{\circ}\text{C}$ . The validated software accurately predicts the coupled thermal and electrochemical response of large-format batteries, and has been used to investigate enhanced cell design for reduced weight, volume, and cost, enhanced safety, and life prediction under real-world driving conditions. The pack model has likewise been used in the design of advanced thermal management strategies. The

AutoLion™ commercial version of ECT3D software has been offered to the public and 30 licensees are employing the software to design battery cells and packs for various applications.

## Project Term Publications/Presentations

1. Wei Zhao, C.Y. Wang, Gang Luo, Christian E. Shaffer, "New Findings on Large Li-ion Battery Safety through Computer Simulation", Battery Safety 2011- Advancements in System Design, Integration, & Testing for Safety & Reliability, November 9-10, 2011, Las Vegas, NV.
2. G. Luo and C.Y. Wang, A Multi-dimensional, Electrochemical-Thermal Coupled Li-ion Battery Model, Chap.6 in Lithium-Ion Batteries: Advanced Materials and Technologies, CRC Press, 2012.
3. Yang, Xiao Guang, Miller, Ted and Yu, Paul, Ford Motor Company, "Li-Ion Electrochemical Model," 2012 Automotive Simulation World Congress, October 30-31, 2012, Detroit, MI
4. Shaffer, C.E., Wang, C.Y., Luo, G. and Zhao, W., "Safety Analysis Design of Lithium-ion Battery EV Pack through Computer Simulation," Battery Safety 2012, Knowledge Foundation Conference, December 6-7, 2012, Las Vegas, NV
5. Shaffer, C.E. and Wang, C.Y., "Thermal Management for Start-up of Li-Ion Batteries," 222nd Meeting of The Electrochemical Society (PRiME 2012), Honolulu, HI, October 7-12, 2012
6. Luo, Gang, Shaffer, C.E. and Wang C.Y., "Electrochemical-thermal Coupled Modeling for Battery Pack Design," 222nd Meeting of The Electrochemical Society (PRiME 2012), Honolulu, HI, October 7-12, 2012
7. G.S. Zhang, L. Cao, S. Ge, C.Y. Wang, C. E. Shaffer, C. D. Rahn, In Situ Measurement of Li-Ion Battery Internal Temperature, 224th ECS Meeting, Abstract #538, San Francisco, CA, USA, Oct. 27 - Nov. 01, 2013
8. Kalupson, J., Luo, G. and Shaffer, C., "AutoLion™: A Thermally Coupled Simulation Tool for Automotive Li-ion Batteries," SAE Technical Paper 2013-01-1522, 2013, doi: 10.4271/2013-01-1522. SAE International World Congress and Exhibition, April 16, 2013, Detroit, MI
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11. Ji, Y., Wang, C.Y. (2013). "Heating strategies for Li-ion batteries operated from subzero temperatures," Electrochimica Acta, 107, 664-674



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13. W. Zhao, G. Luo and CY Wang, "Modeling Nail Penetration Process in Large-Format Li-ion Cells," submitted to *J power sources* (2014)
14. Zhang, G., Cao, L., Ge, S., Wang, C.Y., Shaffer, C.E. and Rahn, C.D. (2014). "In Situ Measurement of Radial Temperature Distributions in Cylindrical Li-Ion Cells," *Journal of the Electrochemical Society*, 161, A1499-A1507
15. W. Zhao, G. Luo, and C.Y. Wang, "Effect of Tab Design on Large-format Li-ion Cell Performance," *Journal of Power Sources* 257 70-79 (2014)
16. G. Zhang, L. Cao, S. Ge, C. Y. Wang, C.E. Shaffer, and C.D. Rahn, "In Situ Measurement of Temperature Distribution in Cylindrical Li-Ion Cells," 226th ECS Meeting, Cancun, Mexico, October 9, 2014
17. Guangsheng Zhang, Lei Cao, Shanhai Ge, Chao-Yang Wang, Christian E. Shaffer, and Christopher D. Rahn, "Reaction temperature sensing (RTS)-based control for Li-ion battery safety," submitted for publication in *Nature Communications* (2014)
18. Qing Wang, Christian Shaffer, and Puneet Sinha, "Implications of Cell Design on Safety of Large-format Li-ion Batteries Undergoing Nail Penetration," submitted for publication in *Journal of Power Sources* (2014)

# Coupling of Mechanical Behavior of Cell Components to Electrochemical-Thermal Models

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### Subcontractors:

Massachusetts Institute of Technology; ANSYS, Inc.

Start Date: October 2013

Projected End Date: September 2015

## Objectives

- Develop a model to couple the electrochemical-thermal (ECT) behavior of a lithium-ion cell to its structural behavior after rapid mechanical deformation
- Develop a model to predict the thermal response of cells to thermal ramp
- Make models compatible with CAEBAT-1 tools and OAS for wider proliferation of use

## Technical Barriers

- Unavailability of a standard experimental approach that is widely accepted by industry to characterize the mechanical response of a lithium-ion cell, and resulting implications for battery safety
- Limited understanding of physical phenomena that take place within a lithium-ion cell just before and after introduction of a short circuit
- Inability of simplified safety models to identify the mechanism behind a variety of short circuit responses observed following mechanical crush of a lithium-ion cell

## Technical Targets

The major technical targets for this effort include:

- Creation of an experimentally validated mechanical deformation model for a lithium-ion cell

- Development of a mechanism to understand the interaction between the mechanical effects and runaway reactions that occur within the cell
- Implementation of the coupling between mechanical and electrochemical-thermal models on the ANSYS software platform

## Accomplishments

- Built two types of material models for electrode assemblies—*isotropic* and *anisotropic*— to simulate local battery deformation and damage
- Used experimental results to calibrate new anisotropic model
- Developed coupled modeling methodology encompassing mechanical, thermal, and electrical response for predicting short circuit mechanism of a cell under external load



## Introduction

During the first phase of CAEBAT, performance models simulating the electrochemical and thermal performance of lithium-ion batteries were developed and incorporated into commercially-available software tools, and efforts toward modeling abuse response were initiated. Existing models in literature, as well as those developed under the previous phase of CAEBAT, assume a predetermined value for the short circuit resistance when calculating the heat generation rate during thermal runaway events. Depending on the value of contact resistance chosen for a particular simulation case, the outcome of the cell response can be varied arbitrarily. Thus, the existing models are limited in their ability to predict the outcome of an internal short circuit or mechanical crush.

In the current effort, we develop a methodology to couple the mechanical response of different cell components (anode, cathode, separator, etc.) with NREL's electrochemical-thermal models. This will provide a comprehensive set of tools to compute properties such as the nature of the short circuit or evolution of short resistance as a function of chemical composition, thermal, and electrical properties, as well as the mechanical constraints on the material, thereby accounting for experimental observations using realistic modeling tools.

## Approach

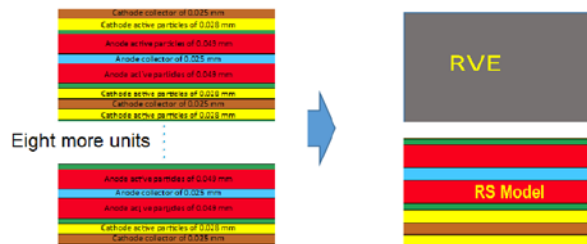
Simulating simultaneous mechanical, thermal, and electrochemical response of a cell during a crush event is very complex and requires modeling simplification. Our approach is to assume that the crush is rapid (the cell is damaged in less than a fraction of a second) and that the electrochemical and thermal response of a cell takes longer than a few seconds. This allows us to couple the mechanical aspect with the thermal aspect in a sequential, unidirectional fashion.

- In order to identify the location of cracks originating within the cell during a compression test, two mechanical models—one isotropic and another anisotropic—were developed by MIT
- Comparisons to experimentally measured load versus displacement curves, as well as CT scans, were used to verify the validity of the models
- Comparison will be performed between thermal/electrochemical model solutions on deformed geometry versus the use of effective resistance to characterize mechanical damage
- Additional tests required to calibrate new material properties associated with the anisotropic model will be performed in FY15

## Results

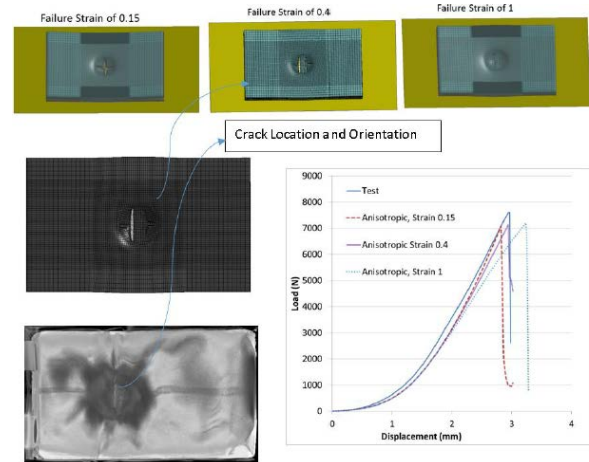
### Mechanical Simulations

Figure 1 shows the different simplifications to the mechanical representation of a lithium-ion cell. The representative volume element (RVE) approach uses one effective layer with equivalent mechanical properties to represent the composite stack of active material, current collectors, and separator. The representative sandwich (RS) modeling approach retains the properties of the individual layers but uses one sandwich, with thickness values scaled, to represent the repeat units of the different components within the cell.



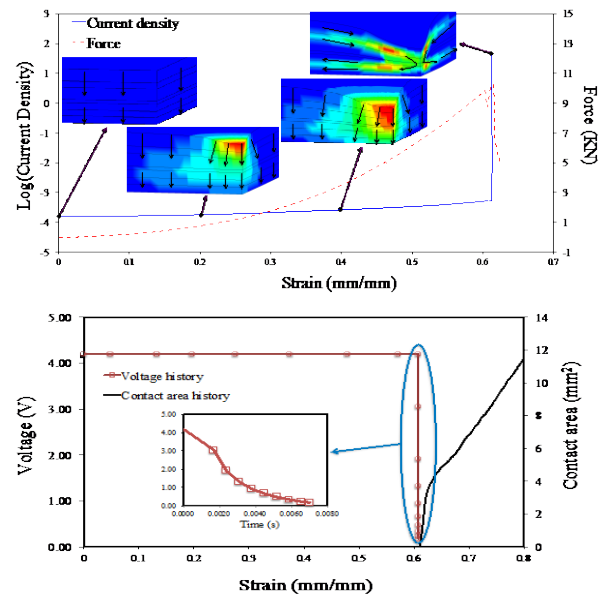
**Figure 1. Simplified representations of lithium-ion cell used in mechanical/electrical simulations: RVE approach is efficient in calibrating cell response to measured values of mechanical response of individual layers; RS model is useful for simulating electrical short circuit across different components in deformed geometry**

Figure 2 shows crack orientations for a small pouch cell under hemispherical loading, assuming three trial failure strains for the RVE. The load versus displacement calibration shows good agreement with the test results.



**Figure 2. Location of crack and comparison of load-displacement curves; simulations were performed with anisotropic pouch cell model using RVE at assumed failure strains of 0.15, 0.4, and 1.0**

Figure 3 shows current density and voltage with the progression of the short circuit and evolution of the short circuit area across different layers as a function of time, predicted based on the electrical and mechanical properties of the different layers.



**Figure 3. Current density across active material before and after a short circuit at different levels of total strain and corresponding plot of current vectors during indentation of prismatic cell similar to test shown in Figure 2; RS model was used to calculate voltage history and evolution of short circuit area during crush**

## Conclusions and Future Directions

Two different representations for the cell geometry—the layer-by-layer model and the representative sandwich model, were developed in FY14. Comparisons with experimental data from MIT indicate that the representative sandwich model adequately captures the mechanics of deformation of a cell. This approach expedites the mechanical simulations considerably. Different approaches to couple mechanical response of the cell to thermal/electrical response were also developed. Results from the first implementation, which involves performing electrical simulations on the deformed mesh in LS-DYNA, were discussed in this report. Future work will involve building a robust coupling methodology between existing thermal-electrochemical models for lithium-ion cell abuse, with the origin and evolution of a short circuit, as shown in this report.

## FY 2014 Publications/Presentations

1. T. Wierzbicki and E. Sahraei, “Homogenized mechanical properties for the jellyroll of cylindrical

Lithium-ion cells,” *J. Power Sources*, Vol. 241, pp. 467-476, 2013.

2. E. Sahraei E., J. Meier, T. Wierzbicki, “Characterizing mechanical properties and onset of short circuit for three types of lithium-ion pouch cells,” *J. Power Sources*, Vol. 247, pp. 503–516, 2014.
3. C. Yang, G.-H. Kim, S. Santhanagopalan, A. Pesaran, “Multiphysics Modeling of Thermal Runaway in a Li-Ion Battery,” Presented at the 225<sup>th</sup> ECS Meeting, May 2014, Orlando FL.
4. S. Santhanagopalan, “Mathematical Modeling of Battery Safety under Crush”, Presented at the Discussion of Issues Related to Safety of Batteries in Hybrid and Electric Vehicles by the International Energy Agency, January 2014, Washington, D.C.
5. C. Zhang, S. Santhanagopalan, M. Sprague, A. Pesaran, “Coupled Mechanical-Electrical-Thermal Modeling for Lithium-ion Batteries,” *J. Power Sources*, Under Review.

# Significant Enhancement of Computational Efficiency in Nonlinear Multiscale Battery Model for Computer-Aided Engineering

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Subcontractor:  
ANSYS Inc. (Genong Li, Amit Hotchman, Dimitrios Tselepidakis)

## Objectives

- Improve computation speed of CAEBAT-1 tools
- Develop computational methodology for a significant enhancement in computation speed of nonlinear multi-scale battery modeling while maintaining or improving the solution accuracy from the most advanced state-of-the-art models

## Technical Barriers

- Inevitable nested iteration, ensuring self-consistency in state-of-the-art multi-scale multiphysics (MSMD) battery modeling, is a limiting factor in the further improvement of computation speed
- The traditional multiphysics approach—collapsing scales into a single, large, differential algebraic equation system—renders the system impractically large and stiff, sacrificing modularity
- As soon as reduced order model (ROM) basis is acquired in reduced-dimension space, physical interpretations are easily lost
- ROM basis is restricted to reuse in systems where characteristics are evolving, such as battery aging
- ROM build process is computationally costly, especially with an increased number of parameters
- Most state-of-the-art, efficient battery models address coupling battery physics only within limited scales
- State-of-the-art ROMs suggested for battery models lose validity when severe nonlinearities arise
- Model applicability can be limited for varied design, environment, and operation conditions

## Technical Targets

- Develop innovative multi-scale coupling method using time-scale separation and variable decomposition to eliminate several layers of nested iteration, while still keeping modular framework architecture critical to battery behavior simulations
- Establish new technique to identify low order State Variable Model (SVM) that is adaptive to system evolution, such as during aging
- Design new ROM that does not fail under severe nonlinear conditions and achieves speeds compatible with state-of-the-art ROMs for battery models
- Construct multiple options of modular component models for various subsystems

## Accomplishments

- Increased computational speed of running electrode domain model by factor of 100 without any loss in accuracy
- Reformulated model equations using time-scale separation and partial linearization
- Prototyped ED-GHMSMD and CD-GHMSMD on MATLAB
- Completed evaluating promising methods for adaptive-SVM
- Implemented VECTFIT open-source software to improve stability and speed of look-up table identification
- Developed method using interconnection-of-systems approach for time-domain realization of nested transfer functions
- Performed full look-up table identification of all transfer functions associated with Newman model electrode potentials and concentrations
- Developed API to use NREL's SVM and LPD library in ANSYS/FLUENT's CAEBAT module
- Completed GH-PDM and GH-EDM implementation
- Demonstrated stack cell model in new model framework
- Carried out EDM benchmark tests; x100 speed-up was achieved with new model framework
- Performed testing a-SVM prototype code in MATLAB to evaluate tradeoffs in computational efficiency, memory vs. full order model



## Introduction

DOE's CAEBAT program has focused on developing innovative modeling capabilities to help the battery industry accelerate mass market adoption of electric drive vehicles (EDVs). NREL pioneered the multi-scale multi-domain (MSMD) model, overcoming challenges in modeling the highly nonlinear multi-scale response of battery systems. The MSMD provides high extent flexibility and multiphysics expandability through its modularized architecture, as well as computational efficiency (see Figure 1). NREL also served as a technical advisor/coordinator in transforming the MSMD for industrial use in the first phase of CAEBAT.

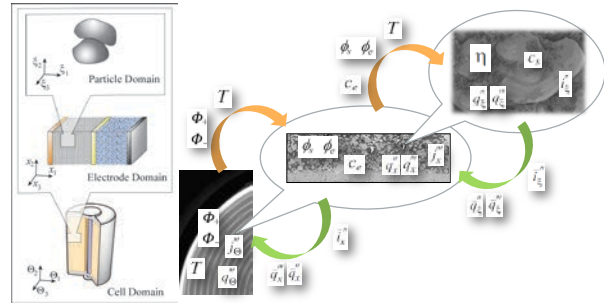
However, there are still remaining challenges. Significant efforts continue being invested to improve energy-power capability and reliability of batteries through engineering at the material level by controlling particulate morphology and size, modifying the particle surface, or redesigning thermodynamics. Due to the complex nonlinear interactions across a wide range and scale of physics, computational cost becomes excessively high to quantify such improvements for the benefits in device-level response even with the state-of-the-art models. The CAEBAT program has resulted in software packages providing 3D battery pack simulation modeling capability. Because of the system's extreme complexity, the computational cost of simulating a battery pack response is still very high.

Therefore, further improvement of computational efficiency is needed, and the intrinsic nonlinearity of battery physics must be resolved properly. This would enable the use of models in design and management tradeoff studies of performance/life in large vehicle battery systems, which are typically composed of several hundred large-format individual cells.

In this project, we develop a computational methodology for a significant improvement in computational efficiency of nonlinear multi-scale battery modeling while maintaining or enhancing the solution accuracy from the most advanced state-of-the-art models. The project objectives are to:

1. Significantly improve the computation speed and stability of multi-scale model framework by eliminating several layers of nested iteration through innovative multi-scale coupling methodology, while still keeping the modular framework architecture
2. Provide a new ROM that is adaptive to system evolution and identifiable with fewer compound parameters, which is critically needed to improve non-uniformly evolving large battery system life predictions
3. Provide a new ROM that will not fail under severe nonlinear conditions and can achieve compatible speed-up against the state-of-the-art ROMs for battery models

4. Provide multiple options for efficient submodules to improve overall simulation speed while accommodating high-fidelity physics models



**Figure 1. Diagram of intra- and inter-domain coupling protocols used in NREL's MSMD framework, integrating widely-varied scale battery physics in a computationally-efficient manner with hierarchical modular architecture (particle, electrode, and cell domains)**

## Approach

The project target will be achieved through complementary parallel efforts in framework efficiency improvement and component efficiency improvement. The team applies an innovative multi-scale coupling methodology (so called, GH-MSMD) using time-scale separation, elimination of several layers of nested iteration, significantly improving the speed and stability of the original MSMD, and retaining the modular framework architecture that is critical to battery behavior simulations. We also develop advanced ROMs for the component models. Computational time is often invested in advance to find reduced-order basis in a much lower dimension than that of the full ordinary differential equation systems derived from spatial discretization of the partial differential equation systems. NREL researchers pioneered a reduced-order state space representation of the one-dimensional porous electrochemical model, the State Variable Model (SVM), already having improved the computational speed of the present MSMD model. The ROM basis is typically restricted to reuse in the system where its characteristics are evolving, such as the battery aging process. In this project, the team develops a new ROM that adapts to system evolution and is identifiable with fewer compound parameters. The state-of-the-art ROMs for battery modeling lose validity when severe nonlinearities arise in the system. In a parallel effort, the team also explores a new ROM that does not fail under severe nonlinear condition. The project team plans to have the models available to industrial users on a commercial software platform by implementing them in the ANSYS CAEBAT-1 software.

## Results

In order to improve the computation speed and stability of the multi-scale model framework by



eliminating several layers of nested iteration through innovative multi-scale coupling methodology, the original MSMD model-governing equations were reformulated using time-scale separation, and variable decomposition. In addition, we established a new technique to identify a low-order SVM that is adaptive to system evolution, such as during aging.

### Framework Efficiency Improvement

An innovative new framework, GH-MSMD, has been developed and implemented up to the electrode domain model (EDM) for FY14. Recent benchmark testing performed at the EDM level demonstrates that the new GH-MSMD framework could achieve 100 times speed-up while maintaining model accuracy and modular architecture. The results from the EDM benchmark test are presented in Figure 2.

### Adaptive ROM Development

In this task, we extended previous ROM development in the SVM form by fitting the frequency response of transfer functions representing distributed electrochemical dynamics and using numerical and/or analytical approaches to eliminate the cumbersome pre-processing required to fit frequency responses and compile results into look-up tables usable only for one battery design at one state of health. Full look-up table identification of all transfer functions associated with the Newman model of electrode potentials & concentrations has been performed. Adaptive-SVM code has been prototyped in MATLAB to evaluate tradeoffs in computational efficiency and memory versus the full order model.

### API Development Integrating New Models in CAEBAT Platform

An API has been established to integrate NREL's newly developed, computationally efficient physics-based electrochemical model in the ANSYS CAEBAT-1 software. This opens the possibility for industry users to access the most updated NREL models while using commercially-available CAE software suites.

### Conclusions and Future Directions

As part of the CAEBAT-2 activity, a new quasi-explicit nonlinear multi-scale model framework GH-MSMD has been developed and implemented up to the EDM level demonstrating x100 speed-up while maintaining model accuracy. In FY15, the model framework will be further refined and extended to cell domain models (CDMs). We will also identify further order reduction opportunities, while developing an algorithm to utilize non-dimensional form and scaling to circumvent frequent lookup table searches or reduce computation upon changes in the parameters.

### FY 2014 Publications/Presentations

1. 2014 DOE Annual Peer Review Meeting Presentation
2. M. Jun, K. Smith, P. Graf, "State-space Representation of Li-ion Battery Porous Electrode Impedance Model with Balanced Model Reduction." J. Power Sources

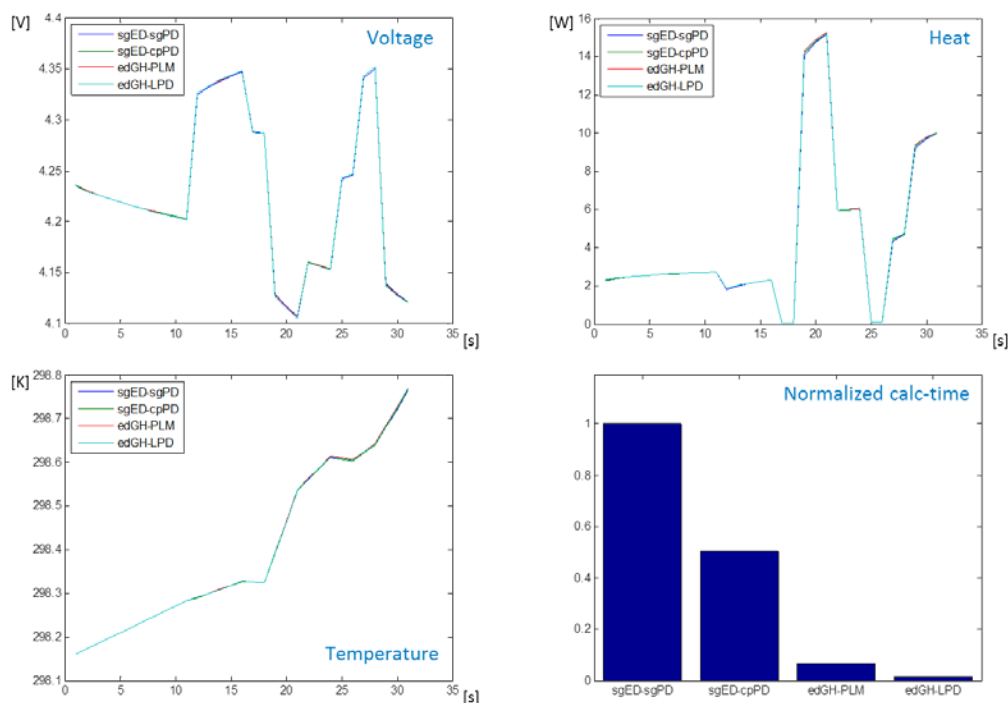


Figure 2. EDM benchmark results show that, without losing accuracy, x100 speed-up is achieved with the new GH-MSMD framework when the most efficient PDM and EDM submodel combination is chosen

# Crash Propagation Simulation and Validation

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Renewable Energy Laboratory

Subcontractor:  
Ford Motor Company

Start Date: December 2013  
Projected End Date: December 2015

## Objective

Simulate the electrical, thermal, and mechanical responses of a lithium-ion battery subjected to a sudden mechanical impact, such as a crash, focusing largely on the module- to pack-level phenomena

## Technical Barriers

- PEV battery safety during abuse conditions
- Lack of experimental data and analytical models for understanding battery response during crash-induced crush

One of the most commonly encountered field safety events for PHEV batteries is related to mechanical failure. However, the abuse response of batteries to mechanical failure is not very well understood.

The lack of reliable test procedures to characterize the short circuit response of an individual cell during a crash event is a major barrier for cell developers and pack integrators to assess the safe threshold the batteries can withstand. Limited experimental studies on the modes of propagation, as well as the arbitrary nature of the test conditions, also limit the understanding of how failure at the individual cell level translates to implications for the safety of the module or the pack.

The computational intensity of coupled simulations due to the inherently non-linear nature of the physics, as well as the need for explicit solvers for high-speed mechanical crush, has traditionally prevented battery simulation in commonly available software.

## Technical Targets

This effort aims to develop mechanical models that can be coupled with thermal and electrochemical aspects of failure propagation in lithium-ion batteries. The emphasis is on single-cell to multi-cell propagation.

The technical target is to develop simulation capability in this area for individual cells and cell strings that shows good agreement with experimental data for the coordinates of the origin of failure.

## Accomplishments

- Established the approach to import computer-aided design (CAD) geometries for individual cells to modules into LS-DYNA, to generate a mesh to perform calculations in a reasonable time frame and export the results back to CFD software (e.g., ANSYS)
- Performed crash simulations on different cell formats (prismatic versus cylindrical, stacked versus wound cell designs) under various impact conditions (slow crush versus impact load) to demonstrate the versatility of the approach; some case studies involving multi-cell simulations were also performed to demonstrate scalability of these models
- Built an approach to calculate short circuit area from the deformed geometries
- Initiated comparison with experimental results; the validation task is underway



## Introduction

NREL has actively participated in building mathematical models to simulate performance and life of lithium-ion batteries as part of the DOE/VTO CAEBAT activity. These models accommodate a wide variety of physics, including thermal and electrochemical aspects. In FY13, simulations showing the effect of different chemical species on the overcharge response of these cells were carried out. These models assumed that the contributions from the mechanical constraints imposed on the cells were limited. Physical deformation of the cells due to thermal/electrochemical events was not considered.

Existing thermal/electrochemical models in the literature assume a short circuit resistance when calculating the heat generation rate and temperature evolution during thermal runaway events, and are thus limited in their ability to predict the outcome of mechanical crash. On the other hand, existing mechanical simulations of vehicle batteries treat the batteries as passive components and do not include the energetics that

ensues from mechanical failure of a battery. Thus, design of structural components based on these calculations is not straightforward.

In the current effort, we are developing a modeling approach that incorporates the effects of mechanical failure (e.g., during a crash) on the energetics that follow the event.

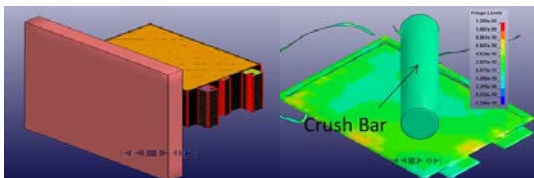
## Approach

- The dynamic impact response of structures typically has a short time constant, on the order of microseconds to milliseconds; however, the full battery discharge/thermal event can continue over much longer time scales; taking advantage of this wide disparity in the time scales for these processes, we simulate the mechanical changes following an impact as a step process, which happens instantaneously
- Secondly, the simulation of individual layers within a cell is computationally expensive; so, we have built cell-level and multi-cell simulations using a representative sandwich model, which lumps the mechanical response of the multiple layers within the cell to one electrode pair with an equivalent set of properties
- The subsequent development of the electrical and thermal pathways is treated as a separate set of events that take place under a quasi-steady state

## Results

### Cell-Level Simulations

The response of individual cells subjected to mechanical crush was simulated using LS-DYNA, a software package commonly utilized by the automotive industry to perform explicit dynamics simulations. We have established the ability to simulate mechanical events at the single cell level: these models are versatile in simulating different form factors of cells - prismatic can versus pouch, stacked versus wound, etc. (See Figure 1). These simulations can be performed on CAD geometries imported into LS-DYNA in a reasonable time frame. The deformed geometries can be exported to CFD software (e.g., ANSYS) for use in short-resistance calculations. Simplifications to the thermal/electrochemical calculations after impact are currently being validated.

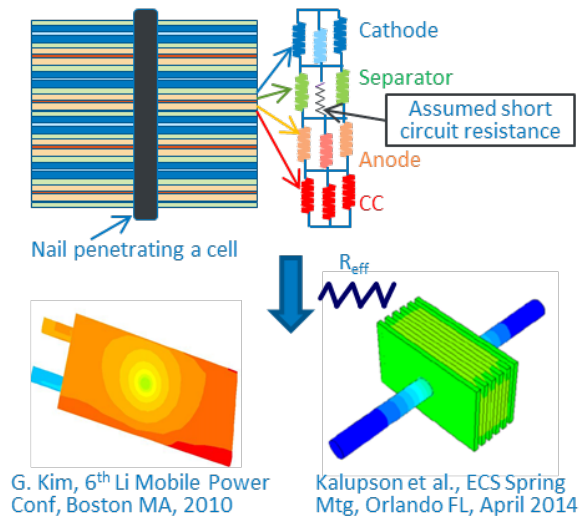


**Figure 1. Model versatility - crush response of different types of cells under various load conditions can be studied using the tools developed under this effort; left, a prismatic cell crush on a wall; right, deformed pouch cell geometry after crush**

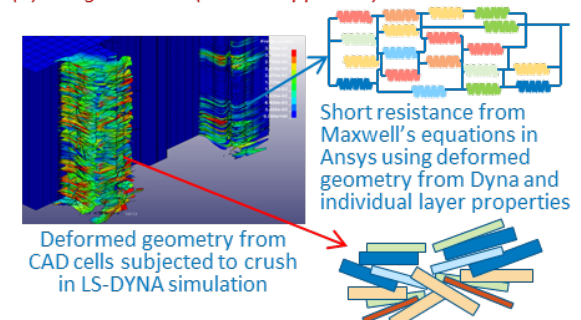
### Short-Circuit Characterization

Traditional short circuit simulations assume a short area and compute the resultant thermal response of the cells. Under the current effort, the electrical simulations are performed on the deformed geometry, resulting in calculation of the short circuit contact area. A simple schematic comparing the two approaches using a circuit analogy is shown in Figure 2.

**(a). Regular Short (Previously Reported Approach):**



**(b). Irregular Short (Current Approach):**



**Figure 2. Short circuit propagation under crash - the conventional approach (a) does not consider the impact of mechanical deformation; so, crash simulations must consider (b) the evolution of geometry along with the thermal/electrical effects that ensue following a crash event**

### Multi-Cell Simulations

The lumped modeling approach enables us to simulate crush in a multi-cell module. These results can then be used to assess the extent of deformation across the different cells for a given impact scenario. Some results are shown in Figures 3 and 4.

One example is the thermal response of the module when heat exchange fins of different designs are used for thermal management of cells. In the second case study, two load scenarios on the first fin design (lateral and normal impact) are considered.

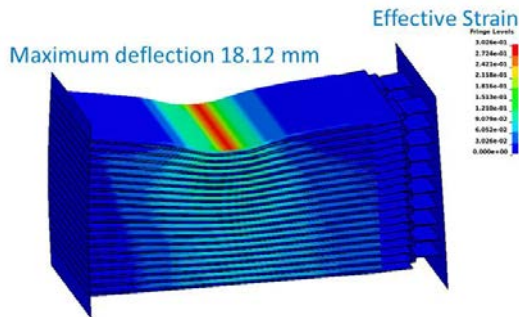


Figure 3. Propagation of mechanical failure across multiple cells in a module containing 20 prismatic stacked cells (15 Ah each) of the NMC chemistry

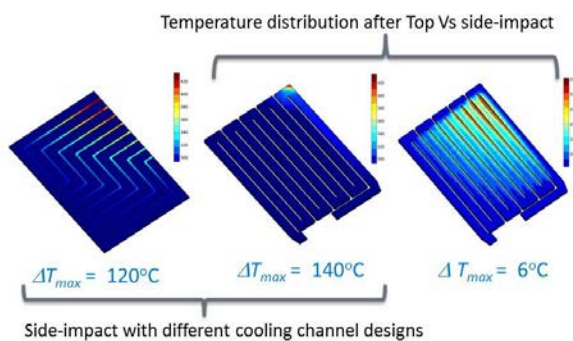


Figure 4. Demonstration of the utility of multi-cell crash-response simulations - two case studies are shown, the first comparing the effect of different locations of impact on temperature rise, and the second comparing two different cooling-fin designs

## Conclusions and Future Directions

Simulation tools that couple mechanical response of a battery subjected to crash with the thermal/electrical response of the cells were developed. Several case studies to demonstrate the versatility and scalability of these models were performed. We are in the process of validating the model results against experimental data. This effort will continue through FY15, together with some module-level simulations. The effect of the evolution of short-circuit with time on the propagation of failure from individual cells to other areas within the pack will be studied. Approaches to integrate these simulations within the CAEBAT framework will be proposed.

## FY 2014 Publications/Presentations

1. S. Santhanagopalan, C. Yang, G.H. Kim, M. Keyser and A. Pesaran, "Impact Response of Lithium Ion Batteries," Presented at the 224<sup>th</sup> ECS Meeting, November 2013, San Francisco, CA.
2. S. Santhanagopalan, "Mathematical Modeling of Battery Safety under Crush", Presented at the Discussion of Issues Related to Safety of Batteries in Hybrid and Electric Vehicles by the International Energy Agency, January 2014, Washington, D.C.
3. S. Santhanagopalan, "Pushing the Envelope on Battery Safety - Some Simulation Tools," Presented at the Battery Show, September 2014, Novi, MI.
4. C. Zhang, S. Santhanagopalan, M. Sprague, A. Pesaran, "Coupled Mechanical-Electrical-Thermal Modeling for Lithium-ion Batteries," *J. Power Sources*, Under Review.

# Development of Industrially Viable ALD Electrode Coatings

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Subcontractor: University of Colorado at Boulder

Start Date: October 2012  
End Date: September 2014

## Accomplishments

- Constructed an in-line ALD reactor system for flexible substrates compatible with existing commercial battery electrode coating facilities
- Demonstrated controlled deposition of aluminum oxide on a flexible substrate at an effective processing line speed of >400 ft/min, nearly an order of magnitude higher than current industrial processes
- While further experimentation is warranted with additional funding, these results indicate that integration of in-line ALD coating within current industrial processes is feasible



## Objectives

- The overall objective of the Applied Battery Research (ABR) program is to improve cycle life and abuse tolerance and reduce the cost of advanced lithium-ion battery technologies for PEVs
- Previous laboratory work conducted by NREL and the University of Colorado at Boulder (CU) has demonstrated that thin, conformal coatings of aluminum oxide on lithium-ion battery electrodes formed by atomic layer deposition (ALD) can dramatically improve abuse tolerance and cycle life, which, in turn, reduces ultimate cost
- Current technology for performing ALD is not amenable to high-throughput manufacturing methods and thus represents a high priced bottleneck in the implementation of ultrathin electrode coatings at a commercial scale
- The objective of this current work is the development of a system for deposition of thin protective electrode coatings using a novel “in-line” atmospheric pressure atomic layer deposition (AP-ALD) reactor design that can be integrated into manufacturing to address needs for improvement in rate capability, cycle life, and abuse tolerance in a cost effective manner

## Technical Barriers

- Lithium-ion limited calendar and cycle life
- Poor abuse tolerance of lithium-ion batteries
- High cost of lithium-ion batteries

## Technical Targets

- Design and construct a prototype in-line ALD coater for deposition on porous substrates characteristic of cathode materials

## Introduction

In previous work, NREL, in partnership with the University of Colorado, has shown that extremely thin, conformal coatings of aluminum oxide deposited with the ALD technique are capable of dramatically improving cycleability of lithium-ion cells. This project seeks to convert the common ALD processing format into a new reactor geometry that is compatible with battery electrode manufacturing.

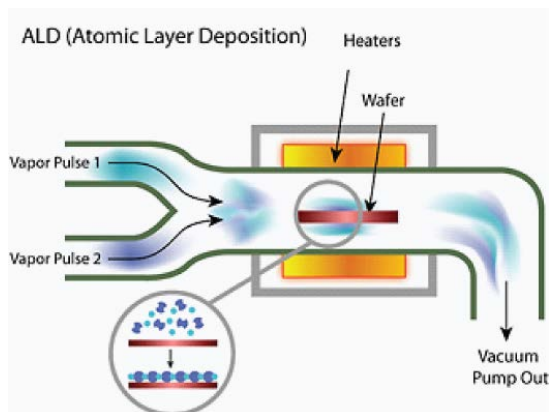
As part of this effort for FY14, NREL and the CU-Boulder team, working with limited carryover funding, has successfully completed the design and construction of a new in-line ALD reactor. Work in this area has focused on the modification of previous reactor designs to build a system capable of assessing the ability to obtain ALD-type coating processes in an in-line format and under acceptable battery manufacturing conditions. Earlier reactors were constructed to conduct initial feasibility testing of the ALD process when converted to an in-line format and with deposition occurring at atmospheric pressure; however, these early designs focused on planar substrates. More recent work has focused on creating a system that is capable of deposition onto moving coated battery electrode foils, as used in present manufacturing. Special emphasis was placed on designing a system to understand the impact of coating on porous substrates.

## Approach

ALD coating methods are conducted by sequential and separate exposure of a sample substrate surface to gas phase precursors that react to form a film. Deposition is typically performed in a closed reactor system at mild vacuum as shown in Figure 1. Precursor exposure steps are conducted in a single chamber and are separated in time.

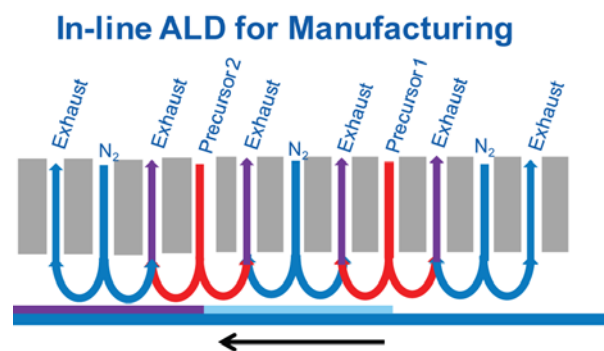


In a typical exposure “cycle,” a sample is exposed to one precursor and then the chamber is purged with inert gas prior to exposure to the second precursor, which completes the coating reaction. The “cycle” ends with another extensive inert gas purging step before the process can be started again. Film growth takes place by repeating this cycling precursor exposure process multiple times. The sequential and separate exposures are key to achieving the excellent conformal film deposition on highly-textured substrates, for which the ALD technique is known. ALD coatings have become common in the semiconductor industry for integration in microelectronics.



**Figure 1. A typical ALD chamber with sequentially separated precursor exposures that draws out overall processing time**

As an alternative to the temporal separation of precursor exposure in the same reaction chamber, our work proposes a spatial separation of precursor exposure steps that is more consistent with “in-line” processing techniques. Figure 2 shows a simplified conceptual schematic of our proposed apparatus.



**Electrode slurry coated foil translates under multiport “AP-ALD” deposition head**

**Figure 2. A simplified schematic demonstrating the in-line spatial ALD concept**

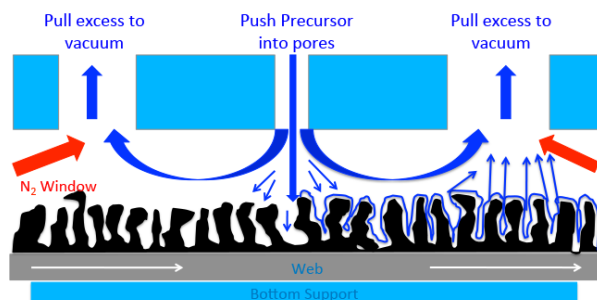
Our “spatial” ALD approach employs a multichannel gas manifold deposition “head” that performs sequential exposure of precursor materials as an electrode foil translates beneath it. It is important to note that similarly-designed deposition heads are currently employed by glass manufacturers for production of a variety of coated glass

products using high-volume, in-line atmospheric pressure chemical vapor deposition (AP-CVD). Our approach leverages this existing knowledge base as well as our ALD expertise in order to enable in-line ALD coating that will allow the transfer of our previously demonstrated ALD-based performance improvements to larger format devices.

## Results

### Push-Pull Reactor Design

Current Li-ion battery electrodes are porous. A crucial factor for the successful coating of these electrodes using the in-line ALD technique is the ability to coat porous substrates. Coating of a porous substrate presents a specific technical challenge, as precursor materials must be able to fully penetrate as well as be removed from the porous film as rapidly as possible to enable high processing line speeds. This requires that the porous film be exposed to alternating high and low gas pressure regimes at different stages of the deposition process. At high local pressures (viscous flow conditions), a high number of gas phase collisions drive the penetration of precursor gases into the film, while low local pressures (molecular flow conditions) allow the rapid removal of unreacted precursor prior to the next precursor exposure step. We have termed the rapid progression through alternating high and low local pressure regimes the “push-pull” reactor design. A fundamental schematic of the “push-pull” reactor concept is shown in Figure 3. In addition to precursor introduction and exhaust channels, the system is also designed with a nitrogen gas window that is more highly pressurized than the dosing precursors in between the precursor ports. This nitrogen gas purge will ensure that there is no cross talk between the different reactants that would lead to bulk film deposition.



**Figure 3. A simple schematic demonstrating alternate high and low pressure regimes present in “push-pull” reactor concept**

### Digital Modular Roll-to-Roll System Design

As shown schematically earlier, a linear translational roll-to-roll design was initially considered for our “push-pull” deposition system. However, it was determined through earlier results and discussions with additional roll to roll (R2R) processing experts that a linear design would not be capable of maintaining adequate tension on the web substrate during the “push-pull” deposition process. An improved format is a rotating drum-in-drum design, as



shown in Figure 4. In the drum-in-drum system, a rotating inner drum, on which substrates are mounted, is set inside a fixed outer drum that contains all gas sources as well as purge and exhaust lines. The inner drum rotates the web radially while maintaining sufficient tension on the line to ensure accurate gas head to substrate spacing.

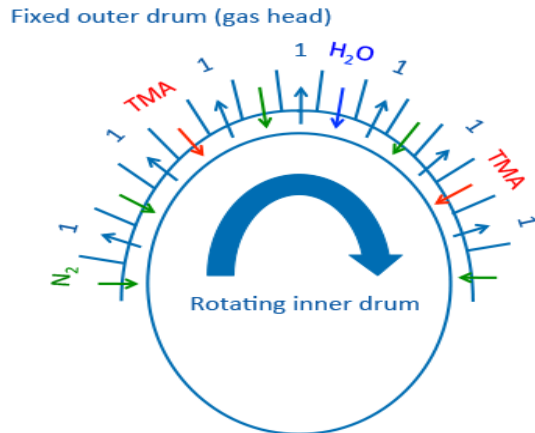


Figure 4. Schematic representation of the "digital modular" design concept

In order to maximize reactor flexibility and enable extensive deposition condition optimization work, we have adopted what we term a "digital modular" system design. Figure 5 shows a more detailed schematic of the drum-in-drum reactor design and demonstrates the digital modular design. To implement the digital modular design, the fixed outer drum of the reactor is faceted and has slots drilled every 2.5 cm. Precursor introduction, as well as reactant exhaust, occurs through the attachment of specific "modules" to these slots. Precursor dosing and vacuum exhaust modules have been fabricated that are able to fit to any of the slots in the external drum. This design will allow the modules to be moved interchangeably on the external drum to allow the maximum amount of variability in dosing and vacuum module spacing. This enables extensive experimentation across a broad range of deposition conditions in order to optimize performance.

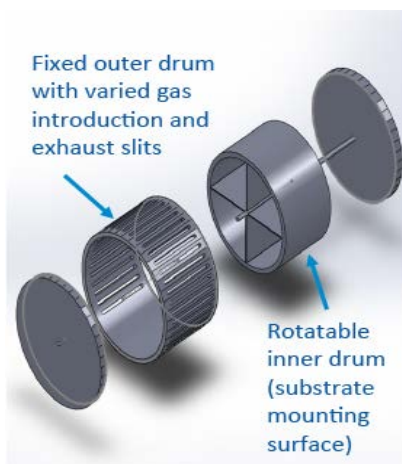


Figure 5. Diagram of drum-in-drum reactor format

## Module Design

CFD simulations were conducted to optimize the precursor introduction module design in order to ensure uniform precursor exposure to the moving substrate across the sample surface. As an example, Figure 6 shows output from CFD calculations, as well as the final constructed precursor introduction module. Our simulations showed that under expected deposition conditions, a minimum height of 2" was required for the precursor concentration to become uniform across the entire width of the module. Modules were constructed at a height of 5" in order to allow sufficient time and space for the precursor concentration to become uniform.

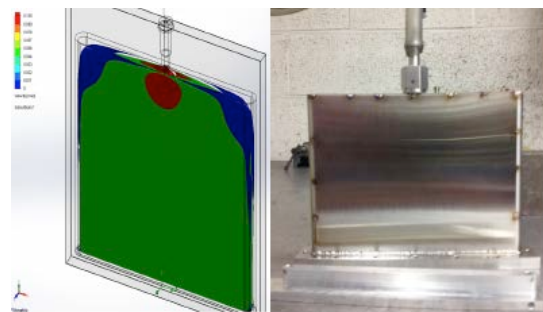


Figure 6. CFD simulation of gas flow through precursor introduction module and final construction

As discussed previously, another benefit of using the modular slot design is that blank modules can be added to modify channel spacing, furthermore, new modules can be added in the future without having to modify the main deposition head. As an example, additional modules are being designed that will allow for the use of in-situ diagnostics including pressure sensing and mass spectrometry as well as a module that will enable in-line plasma-assisted deposition.

## Reactor Construction and Assembly

Following the design phase, reactor parts were fabricated, assembled, and tested. Figure 7 shows the final assembled reactor before and after sample loading. Initial demonstration of reactor functionality was conducted through deposition of aluminum oxide onto flexible plastic films. While these films do not necessarily mimic the high porosity desired for a battery electrode, they were chosen as an initial candidate sample to allow initial deposition properties to be determined, which could later be refined for porous substrate deposition.

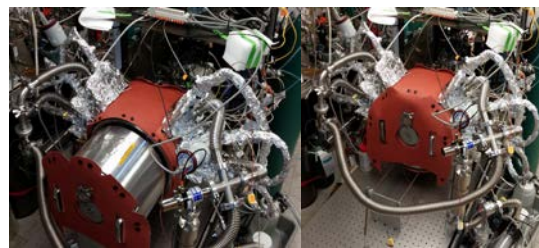
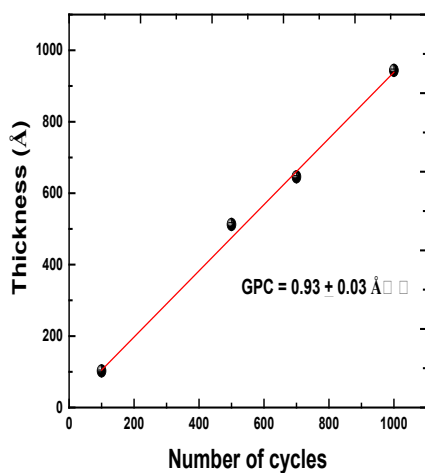


Figure 7. Final construction and sample loading of in-line ALD reactor

Initial reactor setup included only two separate “channels” for precursor introduction to the sample. One channel for trimethyl aluminum and a second for ozone as the secondary reactant. Ozone was chosen as a precursor to help minimize the introduction of water to eventual battery electrode substrates, as well as for the ability to ramp deposition rates to higher speeds, which should enable coating at high processing line speeds. Figure 8 shows the measured thickness of aluminum oxide grown under fixed deposition conditions for a specific number of reactor rotations (or ALD cycles; 1 cycle per rotation). Note that film thickness increases linearly with the number of ALD cycles. This data has been fit to show film growth on a per reaction cycle basis (GPC, “growth per cycle”). The data in Figure 8 achieved deposition rates per cycle typical with those observed on flat silicon substrates. It is important to note that the data shown in Figure 8 was collected at a reactor rotation rate of 100 revolutions per minute that translates to an effective processing line speed of 400 ft per minute. Typical processing line speeds for state-of-the-art battery manufacturing is near 50 ft per minute. These results prove that ALD coating can be conducted in a well-controlled fashion at line speeds well above traditional battery electrode coating processes and thereby are not likely to present significant bottlenecks when integrated with existing commercial lines. Further demonstrations need to be conducted to assess the impact of film porosity on the ability to effectively deposit coatings at high effective line speeds. Work of this nature is planned using typical porous substrates as well as battery electrodes upon availability of sufficient funds.



**Figure 8. Measured thickness of aluminum oxide deposited using in-line ALD, showing linear film growth at ~400 ft/min line speed**

## Conclusions and Future Directions

In FY14, the NREL/CU team designed and completed construction of a new in-line ALD-based electrode coating reactor. Testing of the unit indicated that thin layers of aluminum oxide could be deposited on flexible substrates in a well-controlled fashion and at effective processing line speeds in excess of 400 ft per minute without loss in coating performance. This result indicated that practical integration of in-line ALD coating with state-of-the-art commercial electrode coating facilities is reasonable. Additional work needs to be conducted to assess the impact of sample porosity on the ability to coat electrodes effectively. If additional funding can be obtained for a continuation of this effort into FY15, experiments will be conducted to determine optimal parameters for conformal coating on porous substrates. This work will entail detailed design of experiment methods used to determine optimal conditions to ensure conformal coating of a moving porous substrate. The output from this work will identify acceptable conditions for conformal coating of materials in an in-line format. Experiments will initially be conducted with model porous substrates with well-known geometries that will enable detailed measurements of coating quality. Following this initial optimization work, the NREL/CU team will partner with other ABR collaborators to coat larger format battery electrodes. Larger format electrodes will be fabricated into cells for testing at the NREL/CU laboratories as well as within collaborating labs.

It is anticipated that in a later stage, the NREL/CU team will partner with electrode and battery manufacturers and other organizations to integrate the new reactor design into a battery electrode coating process. Toward that end, the existing reactor was intentionally designed to enable integration with further R2R processing capabilities.

## FY 2014 Publications/Presentations

- Manuscript entitled “Spatial Atomic Layer Deposition on Flexible Substrates Using a Modular Rotating Cylinder Reactor”, submitted to the Journal of Vacuum Science and Technology, A, currently under review

# Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

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Start Date: October 2010  
Projected End Date: September 2015

## Objectives

- Develop a low-cost, thick, high-capacity silicon anode with sustainable cycling performance via advanced surface modification
- Synthesize novel stable and elastic coatings for silicon (Si) anodes using Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD)
- Demonstrate durable cycling performance of thick Si anodes by using new ALD/MLD coatings and electrode designs
- Investigate coating mechanism on electrochemical cycling performance via:
  - Studying mechanical properties of MLD coating materials
  - Researching morphology and structural evolution during lithiation/delithiation
- Explore the importance and mechanism of various coatings via the Batteries for Advanced Transportation Technologies (BATT) Coating Group
- Collaborate within the BATT program with the aim of developing high-rate PHEV-compatible electrodes (both anodes and cathodes)

## Technical Barriers

Major barriers include battery cost, performance, life, and safety. We addressed the following in this project:

- Cost: inexpensive processing techniques are employed to fabricate conventional thick electrodes
- High Capacity: silicon is predominantly being explored as a high capacity anode material; there is also a collaborative emphasis to enable high capacity cathode materials
- High Rate: both ALD and MLD coatings are being developed such that high-rate capability is demonstrated for emerging materials
- Safety: ALD/MLD coatings are targeted to improve safety for a variety of electrode materials

## Technical Targets

- Stabilize high-capacity silicon anodes by employing advanced ALD and MLD surface coating techniques
- Demonstrate stable high-rate cycling performance of Si anodes
- Relevant to USABC goals: 200Wh/kg (EV requirement), 96Wh/kg, 316W/kg, 3000 cycles (PHEV 40 miles requirement); calendar life of 15 years; improved abuse tolerance

## Accomplishments

- Developed new aluminum alkoxide polymer (alucone) film using sequential reactions of trimethylaluminum (TMA) and hydroquinone (HQ)
- Achieved sustainable cycling behavior with 2000 mAh g<sup>-1</sup> at 50 cycles and enhanced rate performance for new MLD-engineered thick Si anodes
- Characterized morphology and structure evolution of both uncoated and MLD-coated silicon anodes during cycling
- Investigated effect of coatings on properties of additives and current collectors, in order to further mitigate irreversible capacity loss



## Introduction

Significant advances in both energy density and rate capability for Li-ion batteries will be critical for their implementation in next generation EVs. Due to the high theoretical capacity of Si, 3579 mAh g<sup>-1</sup> for Li<sub>15</sub>Si<sub>4</sub>, and its natural abundance, Silicon has attracted much attention as a promising Li-ion anode material. However, progress towards a commercially-viable Si anode has been impeded by Si's rapid capacity fade caused by large volumetric expansion. Such a massive volumetric change can result in cracking and pulverization of Si particles, which leads to the interruption of electronic transport

pathways and electrochemical isolation of pulverized particles.

As part of DOE's BATT activity under the Focused Fundamental Research Program, the overall goal of this project is to stabilize silicon anodes with conformal ultrathin coatings. Both ALD and MLD have been developed to fabricate nanoscale coatings with desirable elastic properties and good conductivity, to accommodate volumetric expansion, protect the surface from reactive electrolytes, and ensure the electronic paths through the composite electrodes.

In the past, this project has developed ALD aluminum oxide ( $\text{Al}_2\text{O}_3$ ), cyclized polyacrylonitrile (PAN) and MLD aluminum glycerol (AIGL) coatings, which have greatly improved the electrochemical cycling performance of silicon anodes. Among the developed coatings, MLD shows the best performance for a thick electrode and the potential of scalable assembly for battery manufacturing. Using sequential and self-limiting reactions, the MLD method not only enables the formation of conformal and ultrathin coatings, but also integrates inorganic materials (herein  $\text{Al}_2\text{O}_3$ ) into the polymeric organic matrix. Thus, the resulting MLD aluminum alkoxide (alucone) materials have much lower elastic moduli than pure aluminum oxide coating via the ALD method. MLD coating creates a strong, flexible network within the electrode that binds the materials and ensures sufficient contact area throughout cycling.

This synthesis strategy has recently been applied to a new alucone coating composed of polymeric aluminum hydroquinone (AIHQ) to further enhance mechanical strength and stability. Both high rate and durable cycling have been achieved in AIHQ-coated Si anodes. Moreover, in-situ characterization has been applied to investigate the effect of coating on morphology and chemical evolution of electrodes during lithiation and delithiation. The results confirm that the coating is stable and conductive in the electrolyte, and resilient enough to host the extreme volumetric changes of silicon particles. This favorable combination of mechanical and electrochemical properties allows the alucone coating to greatly enhance the performance of nano-Si electrodes. This project will be concluded in FY15, with carryover funds from FY14.

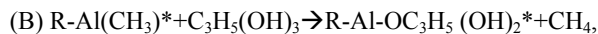
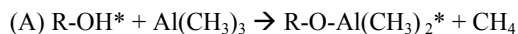
## Approach

The MLD method has been applied to synthesize hybrid inorganic-organic coatings, with both AIGL and AIHQ films grown directly on nano-Si composite electrodes using a pancake reactor.

The nano-Si-based composite electrodes were prepared by spreading nano-Si powder (50 nm, Alpha Aesar), acetylene black (AB), and polyvinylidene fluoride (PVDF) binder mixed in N-methyl pyrrolidinone solvent (60:20:20 weight ratio) on a piece of Cu foil. The electrochemical measurements were all normalized based

on the mass of nano-Si in each electrode (typically 0.5-0.8  $\text{mg}/\text{cm}^2$ ).

The typical growth rate is  $\sim 2.5 \text{ \AA}$  for the AIGL chemistry, per cycle, at a substrate temperature of  $140^\circ\text{C}$ . The reaction sequence for AIGL coating uses the sequential, self-limiting reaction of TMA ( $\text{Al}(\text{CH}_3)_3$ ) and glycerol ( $\text{C}_3\text{H}_5(\text{OH})_3$ ) according to:



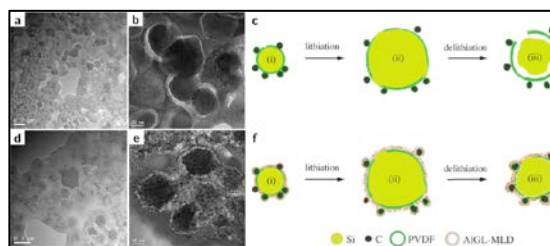
where asterisks indicate surface species. Due to the presence of more than two hydroxyl groups per glycerol molecule, sequential reactions between  $\text{Al}(\text{CH}_3)_3$  and  $\text{C}_3\text{H}_5(\text{OH})_3$  produce large degrees of cross-linking between polymer chains, which strengthen the alucone films and lead to higher fracture resistance.

This same strategy is applied in fabricating the AIHQ coating, based on the reaction between TMA ( $\text{Al}(\text{CH}_3)_3$ ) and HQ ( $\text{C}_6\text{H}_4(\text{OH})_2$ ). The typical growth rate is  $\sim 7 \text{ \AA}$  for the AIHQ chemistry at a substrate temperature of  $180^\circ\text{C}$ .

## Results

### Alucone Coating Ensures Good Cohesion in Composite Electrode

Figure 1 presents the transmission electron microscopy (TEM) images of bare and coated electrodes after first delithiation. The severance between nano-Si particles and the electrode network was observed after delithiation (during volumetric contraction), as shown in Figure 1a, b. As depicted in Figure 1c, the massive volume change during lithiation/delithiation of Si particles contributes to the isolation of Si particles, and eventually results in rapid capacity degradation. On the contrary, the alucone-coated electrode shows an intimate adherence between Si particles and the surrounding network during cycling, as indicated in Figure 1d, e, f. The alucone coating grown by MLD was covalently bound on the surface of the electrode, which dramatically enhances cohesion of the electrode components. It is this covalent coating that ensures the continuous and conductive matrix, even while large volume changes occur during cycling.

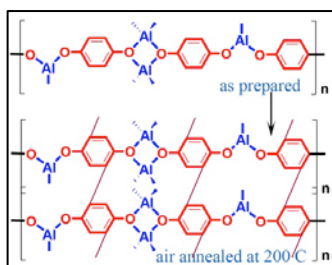


**Figure 1. TEM images of bare electrode (a and b) and coated electrode (d and e); schematics of bare and coated electrodes during lithiation/delithiation (c and f)**



## New Alucone Coating Material Synthesized via MLD Method

A new alucone coating has recently been developed on Si anodes using MLD sequential reactions of TMA and HQ. HQ ( $C_6H_4(OH)_2$ ) is an aromatic diol that has a rigid structure with a central benzene ring, which can potentially increase electronic conductivity due to the conjugated  $\pi$ -electrons in the aromatic rings. As illustrated in Figure 2, the aromatic rings have enclosed the AlOx and appear polymerized after annealing above 200°C in Argon. The cross-linked alucone coating has shown greatly improved critical tensile strain from 1.0% to 1.8%. The improved mechanical properties of this conductive coating can ensure structural integrity of the composite electrodes, which is critical to high capacity Si anodes with massive volume changes.



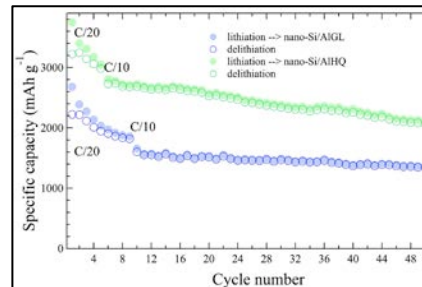
**Figure 2. Chemistry structure of TMA-HQ MLD coating: as-prepared coating (top), and cross-linked coating after annealing at 200°C in Argon**

Different from the ALD  $Al_2O_3$  layer, an organic group was integrated in the MLD alucone coating from the reaction between TMA and glycerol/HQ. It results in a largely-reduced elastic modulus from  $\sim 195$  GPa in ALD  $Al_2O_3$  coating to  $\sim 39$  GPa in the AIGL coating, and  $\sim 29$  GPa in the AIHQ coating. The flexible alucone coating greatly accommodates the massive volume changes in cycling Si anodes, which ensures the highly reversible capacity in the alucone-coated Si anodes. Among the coatings developed during this project, the MLD AIHQ coating shows the best mechanical properties in terms of elasticity and robustness.

### Improvement of Electrochemical Performance Achieved in AIHQ-Coated Si Anode

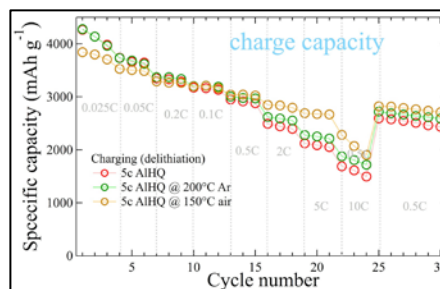
AIHQ-coated Si anodes showed greatly improved performance, as indicated in Figure 3. The Si anode, coated with this new AIHQ coating, has even higher reversible capacity than the AIGL-coated Si anode. Both coatings have improved first cycle coulombic efficiency from 65% in bare Si anode to 85% for the coated anode. Interestingly, both MLD-coated anodes show different first voltage profiles than that of the bare Si anode. The reaction at  $\sim 0.7$  V, primarily attributed to SEI formation in the bare Si anode, has been largely mitigated in the coated anodes. This behavior implies that the coatings modify the interfacial chemistry, as well as SEI formation. Since the hybrid coatings are chemically grown on the surface of the electrode, the conformal coatings act as an

artificial SEI to prevent direct contact between the silicon and electrolyte.



**Figure 3. Significantly improved cycling performance achieved in MLD AIGL- and AIHQ-coated Si anodes**

Further enhanced rate performance was achieved after post-annealing resulting from the cross-linked polymerization of the aromatic rings in the AIHQ coating. These results are displayed in Figure 4. After annealing, the AIHQ-coated Si anode exhibits a higher rate capability than the as-prepared AIHQ coating. This behavior suggests that enhanced conductivity results from cross-linking in the AIHQ coating.



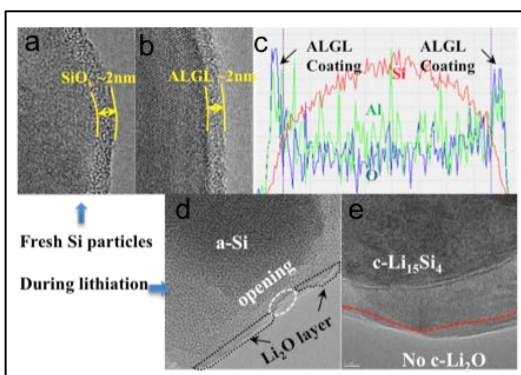
**Figure 4. Rate capability of MLD AIHQ-coated electrodes under different annealing conditions**

### In-situ Characterization Utilized to Better Understand Effects of Alucone Coatings on Morphology and Structure of Si Particles

Surface modification via the MLD method has been proven to significantly improve the electrochemical performance of silicon anodes. Here, specially designed in-situ TEM equipped with electron diffraction was used to investigate the impact of coating on the morphology and chemical evolution of Si particles upon cyclic lithiation/delithiation. The results show that the native oxide layer (silicon oxide) on the surface of the silicon converts to crystalline  $Li_2O$  islands during initial lithiation. The formation of crystalline  $Li_2O$  islands essentially increases the impedance on the particle, resulting in ineffective lithiation/delithiation, and therefore low Coulombic efficiency. In contrast, the alucone MLD-coated particles show extremely fast, thorough, and highly-reversible lithiation behaviors, which are clarified to be associated with mechanical flexibility and fast  $Li^+/e^-$  conductivity of the alucone coating. Surprisingly, the alucone MLD coating process chemically changes the silicon surface, removing the native oxide layer, and,



therefore, mitigates the side reactions and detrimental effects of the native oxide. This study provides a vivid picture of how MLD coating works to enhance Coulombic efficiency and preserve capacity and clarifies the role of the native oxide on silicon nanoparticles during cyclic lithiation and delithiation. More broadly, this work also demonstrates that the effect of subtle chemical modification of the surface during the coating process might be of equal importance as the coating layer itself (see Figure 5).



**Figure 5.** Morphology of as-received (a) and alucone-coated Si nanoparticle (b), featuring a native amorphous oxide layer of ~2 nm in as-received uncoated particle and ~2 nm alucone MLD coating in coated particle; morphology of lithiated uncoated Si nanoparticle (d) and lithiated coated Si nanoparticle (e), showing appearance of  $\text{Li}_2\text{O}$  islands only in uncoated Si nanoparticle and continuous lithiated-ALGL coating; (c) EDS with elemental line across coated Si nanoparticle

## Conclusions and Future Directions

The MLD method has been used to grow a mechanically robust, flexible coating for high capacity Si nanocomposite anodes. Different from ALD, using MLD can form hybrid polymeric inorganic-organic coatings by integrating various organic groups into an inorganic structure, such as aluminum oxide. The thin, conformal, and flexible MLD coating is able to penetrate the electrode's porous structure and covalently bind to available surfaces.

The employment of alucone coatings on conventional nano-Si composite electrodes provides significant improvement in cycling stability, rate, and coulombic

efficiency. The stable coating acts as a passivating agent to protect the active material from unwanted secondary reactions. Due to its unique mechanical properties, the alucone coating proves to be robust and resilient enough to accommodate the extreme volumetric changes of the Si nanocomposite electrodes, helping maintain an intimately-linked conductive network and allowing for faster ionic and electronic conduction.

In-situ characterization was applied to understand the impact of coating on the morphology and surface chemistry of Si particles. Instead of forming crystalline  $\text{Li}_2\text{O}$  islands in the uncoated Si particles, the native oxide was removed during the MLD coating process. The continuous and conductive coating has been observed under in-situ characterization. Without forming  $\text{Li}_2\text{O}$ , the mechanically flexible and electron/ $\text{Li}^+$  conductive alucone coating effectively facilitates rapid and thorough reversible electrochemical reactions.

Although this BATT project was expected to be completed by the end of FY14, we carried over some funds to FY15 to complete the project with further material synthesis, MLD coatings, testing, and final report preparation. We also plan to work with battery and electrode developers to transfer what we have learned to them for improving their Si anode cycleability.

## FY 2014 Publications/Presentations

1. D. M Piper, J. J. Travis, M. Young, S.-B. Son, S. C Kim, K. H. Oh, S. M. George, C. Ban and S.-H Lee, *Adv. Mater.* doi: 10.1002/adma.201304714
2. Z. Li, C. Ban, N. A. Chernova, Z. Wu, S. Upretia, A. Dillon, M. S. Whittingham, *J Power Sources*, DOI: 10.1016/j.jpowsour.2014.05.142
3. THERMEC' 2013, Las Vegas, Dec, 2013 "Atomic Layer Deposition for Stabilization of Si Anodes for Lithium-ion Batteries" (Invited talk)
4. 247 ACS, 2014, Dallas, TX, "Understand the effect of conformal coatings on electrochemical performance and interfacial chemistry of Si anodes" (Invited talk)
5. 40th Annual symposium AVS, East Lansing, Michigan: Surface modification of silicon anodes for advanced Li-ion batteries. (Invited talk)