



NREL Energy Storage Projects: FY2013 Annual Report

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**NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
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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, which 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 2013, 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 FY13 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.

Ahmad A. Pesaran
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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 FY13, DOE funded NREL to make technical contributions to all of these R&D activities. This report summarizes NREL's R&D projects in FY13 in support of the USABC; Battery Testing, Analysis, and Design; ABR; and BATT program elements. The FY13 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: A Tool for Evaluating the Economics of Electrified Vehicles and Related Infrastructure

In FY13, NREL made significant upgrades to the battery ownership model (BOM) to expand our consideration of driver habits, battery thermal response, and auxiliary loads. We applied these new capabilities to study the impacts of driver aggression; climate; cabin heating, ventilation, and air conditioning (HVAC); battery thermal management; and charging infrastructure on electric vehicle (EV) utility. These investigations have highlighted the need to improve standard drive cycles and have pointed towards vehicle configurations and charge infrastructure deployments that can optimize battery electric vehicle (BEV) utility.

PEV Battery Second Use

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 applications 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. The major uncertainty that remains is the longevity of repurposed batteries in post-automotive applications. To address this matter, 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) through a 50-50 cost share partnership with industry. NREL has also acquired additional aged batteries for on-site laboratory testing.

Battery Life Trade-Off Studies

In FY13, previously-developed NREL life models and framework were enhanced to capture: end-of-life effects, namely, accelerating fade driven by electrochemical-thermal-mechanical coupled processes; nickel-manganese-cobalt (NMC) chemistry cell lifetime, complementing previously-developed models for nickel-cobalt-aluminum (NCA) and iron-phosphate (FeP) chemistries; and pack-level degradation processes including temperature non-uniformity, cell performance, and aging variability. These life models directly support NREL analysis of cost-of-ownership for electric drive vehicle (EDV) consumers and fleets, battery second use techno-economic analysis, thermal management, and balance-of-plant design. The life models are also being applied as part of DOE's Advanced Research Projects Agency-Energy (ARPA-E) Advanced Management and Protection of Energy Storage Devices (AMPED) program, developing battery prognostic controls (with Eaton Corporation) and an active balancing system that seeks to eliminate non-uniform cell aging and life extension for multi-cell battery packs (with Utah State and Ford). Versions of the NREL life models have been licensed to external industry and academic partners.

Lower-Energy Energy Storage System (LEESS) Component Evaluation

Alternate hybrid electric vehicle (HEV) storage systems, such as lithium-ion capacitor (LIC) modules, 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. The vehicle test platform developed through this project is helping to validate the in-vehicle performance capability of alternative LEESS devices and identify unforeseen issues. In FY13, NREL successfully created a Ford Fusion Hybrid test platform for in-vehicle evaluation of such alternative LEESS devices, bench tested the initial LIC pack provided by JSR Micro, and performed final integration of the LIC pack into the test vehicle.

Updating USABC Battery Technology Targets for Battery Electric Vehicles

In FY13, NREL successfully analyzed BEV battery targets, and the findings were provided to DOE and USABC. USABC subsequently selected new targets for its BEV battery technology development programs using this input, which will be published in the near future. To conclude this work, NREL plans to publish on its target analysis process to guide future target-setting efforts.

Battery Thermal Analysis and Characterization Activities

NREL has thermally tested cells, modules, and/or packs from Actacell, Cobasys, LG Chem Power, Inc. (LGCPI), Johnson Controls, Quallion, K2 Energy Solutions, Inc. (K2), and SK Innovation. We've provided critical data to the battery manufacturers and original equipment manufacturers (OEMs) that can be used to improve the design of cells, modules, and packs, and their respective thermal management systems. The data included heat generation of cells under typical profiles for HEV, plug-in hybrid electric vehicle (PHEV), and EV applications. We found that the majority of the cells tested had a thermal efficiency greater than 93% when cycled

under a 2C constant current discharge. During thermal imaging of the cells, we identified areas of thermal concern and helped the battery manufacturers with the electrical design of their cells. Finally, we evaluated multiple packs during FY13 and determined that all aspects of the design need to be evaluated for the best thermal performance of the pack and the longest life.

Development of an On-Demand Internal Short Circuit

NREL's internal short circuit (ISC) is the only ISC in development that can be used selectively to connect different components (anode, cathode, aluminum current collector, and copper current collector) within a cell. When different components within a cell are connected, there should and will be a different outcome. For instance, directly connecting the anode and cathode within a cell is much less likely to lead to thermal runaway than connecting the aluminum and copper current collectors. The end goal is not to send the cell into thermal runaway when activating the ISC, but to accurately simulate an emergent short. The internal short device can be used to determine how changes to the battery affect the safety of the battery, either positively or negatively. Furthermore, the internal short can be used as a test methodology to evaluate how a battery would react to a latent defect.

Computer Aided Engineering of Batteries (NREL)

In FY13, the NREL Computer Aided Engineering of Batteries (CAEBAT) project subcontract teams continued their progress toward the objectives of their respective programs: monthly technical meetings and quarterly program review meetings were held to monitor technical progress, experimental data were collected by each team to validate the models, and first versions of cell software tools by each team were released for partner and NREL evaluation. NREL continued electrochemical-thermal modeling of cells through the multi-scale multi-dimensional (MSMD) framework and collaborated with Oak Ridge National Laboratory (ORNL) on development of the open architecture software (OAS) to link developed and existing models.

Development of Computer Aided Design Tools for Automotive Batteries (GM)

In FY13, the General Motors (GM) CAEBAT team made great progress in meeting project objectives and continuing technical advancement consistent with the project plan. The team developed non-linear model order reduction methods at the pack-level, extended cell-level models for aging and abuse of multiple active materials, and defined pack-level validation requirements for the production of battery packs to meet the future capability matrix for pack-level CAE. We also built a standard data exchange interface based on specifications from the OAS Workgroup and applied battery design tools to future vehicle programs, justifying the value of the CAEBAT project.

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

The CD-adapco CAEBAT project team accomplished several key objectives in FY13. The described flow, thermal, and electrochemistry simulation architecture is now established, and differing modeling domains, both lumped and three-dimensional, are available. Cell-level and module-level test work is now complete and validation of the lumped electrochemical models has been presented. A comparison of the modeling domains has been performed, and the differences between results are expected and explainable. Finally, the complex three-dimensional domains for module-level validation are constructed and a thermal result is presented. The technology developed through this project is now contained within the three-dimensional computer-aided engineering code STAR-CCM+, which is commercially available from CD-adapco.

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

Working hand-in-hand with our industrial partners Ford and Johnson Controls, the EC Power-led CAEBAT team has continued to make strides in the development of our Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model (ECT3D) software. In FY13, using feedback from our industrial partners and NREL, EC Power has added extra safety features/capabilities and greatly enhanced user interfaces. We have also begun detailed model validation, at both the cell- and pack-level, an activity which will continue through the end of the project.

Battery Multiscale Multidomain Framework & Modeling

In FY13, NREL developed the Discrete Particle Diffusion Model (DPDM) as an advanced option of the MSMD particle domain model. We demonstrated model applicability to a study on quantifying the impacts of distributed characteristics of electrode particulate attributes. In many practical battery systems, electrode particles are prepared in irregular shapes, and lithium transport in solid particulates and kinetics at surfaces of intricate geometry occur in complex relations. We will continue to enhance the model's capability and apply it to a general procedure of identifying a reduced order representation of an irregular particle electrode system.

Lithium-Ion Abuse Model Development

Using a rigorous model that captures the contribution of kinetic, thermal, and mechanical properties of cell components is critical to identifying the failure mode of individual cells during abuse testing and the direction of propagation of failure within a module. Simultaneously, it is pertinent to develop a set of parameters from independent experiments to characterize the rate constants and transport coefficients for abuse kinetics reactions, as well as the mechanical constants that are used in these models. Toward this end, in FY13, NREL began measuring heat generation rates of cell components, such as cathodes at different states of lithiation, electrolytes, and combinations thereof. These results are currently being compared with similar measurements made at the cell level, to identify the most appropriate experimental technique to measure these parameters.

Evaluate Impact of ALD Coating on Li/Mn-rich Cathodes

In FY13, NREL successfully coated large batches of cathode material powders (several tens of kg), coated sheet electrode samples in a modified reactor built the previous year, and demonstrated cell performance using pouch cells. The scalability of the atomic layer deposition (ALD) technique for coating battery materials is attractive. In fact, this technique has now become popular with several materials vendors, who are actively pursuing coating of cathodes to improve high-temperature performance. A roll-to-roll coating option has also been explored separately, for large-scale manufacturing.

Development of Industrial Viable Electrode Coatings

In FY13, the NREL/University of Colorado at Boulder (CU) team designed and completed construction of a new in-line ALD-based electrode coating reactor. Initial testing of the unit is currently underway. 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.

Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

In FY13, NREL has achieved growth of flexible metal-organic coatings on silicon (Si) electrodes using the molecular layer deposition (MLD) technique. Significantly-improved performance has been demonstrated for alucone-coated nano-Si electrodes, which exhibit sustainable cycling over hundreds of cycles with coulombic efficiency (CE) in excess of 99%. The thin and conformal coating, observed via advanced microscopy, accommodates complete volume expansion during lithiation, but also helps preserve structure integrity during delithiation. Given observed electrochemical and spectroscopic data, it is concluded that alucone MLD coating provides a mechanically-robust, resilient, and conductive network for Si composite electrodes, allowing for a long cycle life and remarkable stability.

List of Acronyms and Abbreviations

A123	A123 Systems
ABDT	ANSYS Battery Design Tool
ABR	Applied Battery Research
Al ₂ O ₃	aluminum oxide
ALD	atomic layer deposition
ANL	Argonne National Laboratory
AP-ALD	atmospheric pressure atomic layer deposition
AP-CVD	atmospheric pressure chemical vapor deposition
ARRA	American Recovery and Reinvestment Act
AVTA	Advanced Vehicle Testing Activity
BATT	Batteries for Advanced Transportation Technologies
BEC	bussed electrical center
BECM	battery energy control module
BEV	battery electric vehicle
BMS	battery management system
BOM	Battery Ownership Model
BPSM	battery pack sensor module
CAE	computer-aided engineering
CAEBAT	Computer Aided Engineering of Automotive Batteries
CAN	controller area network
CCSE	California Center for Sustainable Energy
CD	charge depletion
CE	coulombic efficiency
CFD	computational fluid dynamics
COP	coefficient of performance
CS	charge sustaining
CU	University of Colorado at Boulder
CV	conventional vehicle
DK	Dow Kokam
DoD	depth of discharge
DOE	U.S. Department of Energy
DPA	destructive physical analysis
DX	DesignXplorer (ANSYS)
ECM	equivalent circuit model
ECT3D	Electrochemical-Thermal Coupled 3-Dimensional Li- ion Battery Model
EDV	electric drive vehicle
EELS	electron energy loss spectroscopy
EG	ethylene glycol
EHS	Environment, Health, and Safety Office (NREL)
ESS	energy storage system
EV	electric vehicle
FeP	iron-phosphate

GM	General Motors
GUI	graphical user interface
HAADF	high-angle annular dark field
HEV	hybrid electric vehicle
HPC	high-performance computer
HPPC	hybrid pulse power characterization
HTVB	high-voltage traction battery
HVAC	heating, ventilation, and air conditioning
IBC	isothermal battery calorimeter
INL	Idaho National Laboratory
ISC	internal short circuit
JCI	Johnson Controls Inc.
K2	K2 Energy Solutions, Inc.
LEESS	lower-energy energy storage system
LGCPi	LG Chem Power, Inc.
Li	lithium
LIC	lithium-ion capacitor
Li-ion	lithium-ion
LTI	linear time invariant
MABx	Micro Auto Box
MLD	molecular layer deposition
Mn	manganese
MoO ₃	molybdenum trioxide
MSMD	multi-scale, multi- dimensional
NCA	nickel-cobalt-aluminum
NDA	non-disclosure agreement
NiMH	nickel metal hydride
NMC	nickel-manganese-cobalt
NTGK	Newman, Tiedemann, Gu, Kim
OAS	open architecture software
OEM	original equipment manufacturer
ORNL	Oak Ridge National Laboratory
P2D	Pseudo-2D Model (John Newman)
PAN	polyacrylonitrile
PEV	plug-in electric vehicle
PHEV	plug-in hybrid electric vehicle
PTC	positive thermal coefficient
PVDF	polyvinylidene difluoride
R&D	research and development
R2R	roll-to-roll
RFP	request for proposals
ROM	reduced order modeling
SEI	solid electrolyte interphase
SEM	scanning electron microscope

Si	silicon
SOC	state of charge
STEM	scanning transmission electron microscopy
TMA	trimethylaluminum
TOF-SIMS	time-of-flight secondary ion mass spectrometry
USABC	United States Advanced Battery Consortium
VMT	vehicle miles traveled
VSST	Vehicle Systems Simulation and Testing
VTO	Vehicle Technologies Office
WB	Workbench (ANSYS)
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

III.C.1.3 Battery Ownership Model: A Tool for Evaluating the Economics of Electrified Vehicles and Related Infrastructure

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Start Date: FY09

Projected End Date: FY14

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)

Objectives

- Identify cost-optimal EV use strategies and pathways capable of achieving national oil displacement goals in support of the DOE 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 BOM

Technical Barriers

- The economics of 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

Accomplishments

- Analyzed the economics of service providers offering fast charge infrastructure access; found that the total cost to the consumer is similar to that of battery swapping service plans
- Quantified variations in driver aggression and developed a drive cycle that can be employed to project median aggression vehicle efficiency across multiple powertrains
- Assessed the impact of climate, cabin HVAC, and battery thermal management on BEV utility; identified cabin heating loads as the primary source of utility reduction in cold climates, and saw that the added electrical load of battery cooling systems can offset their reductions in battery degradation
- Simulated multiple charging infrastructure deployments to investigate their impact on BEV utility; found that level 1 home chargers are nearly as good as level 2 home chargers; work chargers add little to overall utility on average; and when widely available, level 2 public chargers provide nearly as much added utility as DC fast chargers

Introduction

The eventual goal of the DOE EV Everywhere Grand Challenge is to have 5-passenger BEVs that are on par with conventional vehicles, based on performance and cost, by 2022. Battery cost reduction, widespread charging infrastructure, etc., is essential to meet this goal. Until that happens, the BEV market needs to become acceptable to various consumers through different business strategies. Wide-scale consumer acceptance of alternatives to CVs, such as HEVs, PHEVs, and BEVs, will depend at least in part on their cost effectiveness and their functionality, including driving range and ease of refueling. The present state of technology presents challenges in each of these areas when traditional ownership and usage models are employed. However, a number of advanced technical and business strategies have been proposed to enable the transition to these alternative powertrain technologies, including the electric utility utilization of the vehicle batteries as a distributed resource; battery leasing by a service provider who takes on the risk and upfront cost of battery ownership; public infrastructure development to recharge EVs while parked; fast-charge and/or battery swap stations that effectively extend BEV range; and alternative car ownership models that allow users to own a BEV but rent other vehicles for long-distance excursions. Each strategy has unique implications for vehicle design, operating characteristics, and battery life. Accordingly, it can be challenging to compare different system options on a consistent basis to assess their ability to support the consumer adoption of such advanced vehicles.

To address this issue in search of cost-optimal EV use strategies, NREL has developed a computer tool called the Battery Ownership Model.

Approach

The purpose of the BOM is to calculate the utility and total cost of vehicle ownership under various scenarios of vehicle and component cost, battery and fuel price forecasts, driving characteristics, charging infrastructure cost, financing, and other criteria, including advanced business and ownership models. The vehicle economics that are considered include vehicle purchase, financing, fuel, non-fuel operating and maintenance costs, battery replacement, salvage value, and any costs passed on by a third-party, such as a service provider, to account for the installation, use, and availability of infrastructure.

Through FY12, the BOM was developed to account for real-world daily driving distance distributions, the sensitivity of battery degradation to variances in usage and vehicle design, the cost of a BEV's limited range, and the inclusion of service providers for battery swapping and fast charging.

Studies were completed on the sensitivity of PHEV and BEV economics to drive patterns, charge strategies, electric range, and other operational considerations, under traditional ownership schemes and when battery swapping service providers were available.

In FY13, we applied this version of the BOM to the analysis of a service provider that offered fast charge services. This study closely mirrored the battery swapping study of FY12; the results are described briefly below. Subsequently, the BOM received a major overhaul that included adding the following features:

- Increased resolution of daily travel histories to the individual trip level, including identification of destination type
- Upgraded EV infrastructure model that considers location of the vehicle and time of day and enables consideration of level 1, level 2, and fast charging, as well as electric roadways
- Range estimation algorithms and driver decision criteria to model travel decision choices for BEVs
- Models for variable driver aggression to correlate energy consumption rates with trip speed and driver type
- Upgraded battery model to account for current, voltage, and thermal response to improve accuracy of driving and charging simulations
- Vehicle cabin thermal model, including cabin HVAC systems, and external climate data to better simulate the impact of cabin thermal response on battery temperature and auxiliary loads

These new capabilities were used to study the sensitivity of vehicle efficiency to driver aggression, develop a drive cycle that consistently represents vehicle efficiency observed in real-world driving across varying degrees of vehicle electrification, and study the impact of climate, vehicle auxiliary loads, battery thermal management, and charging strategies on BEV utility.

Results

Fast Charging Study

Using the FY12-developed BOM, we assessed the economics of a service provider offering access to fast chargers. This study paralleled the FY12 battery swapping study, beginning with identification of likely subscribers and their driving patterns, calculating their service usage statistics when under a service plan, quantifying infrastructure requirements and service fees for multiple deployment scenarios, and then comparing individual driver economics to traditional ownership scenarios of BEVs and CVs.

Our ultimate findings on driver economics are shown in Figure III.C.1.3-1. Interestingly, they are nearly identical to those of the battery swapping study, indicating that while a BEV operated under such a service plan in a single-vehicle household may likely be more cost effective than direct ownership of a BEV, it is unlikely to be more cost-effective than direct ownership of a CV. Although it was expected that the fast charge scenario would improve driver economics due to reduced infrastructure costs relative to the battery swapping case, we found that the longer duration of a range extension event under the fast charge scenario (~30 minutes vs. ~3 minutes) required the service provider to deploy a much larger number of fast charge stations than battery swap stations to provide the same level of range extension availability to its customers. This counteracted the decreased cost of range extension hardware at the per-site level and resulted in nearly identical total infrastructure costs.

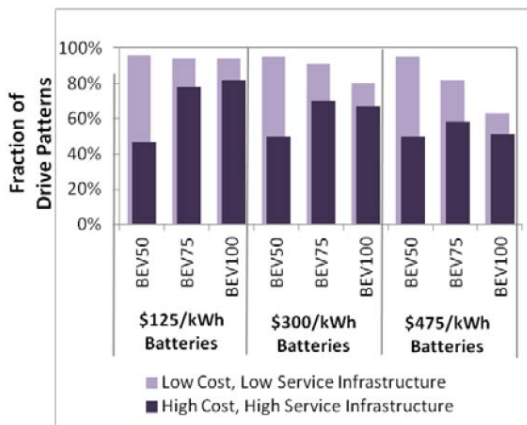


Figure III.C.1.3-1: Fraction of driver patterns where a fast charge service plan BEV is more cost effective than direct ownership of a BEV without fast charger access

Given the similarity in cost, but increased driver convenience of battery swapping, we hypothesize that a battery swapping service plan would be more successful than a fast charge service plan. However, it is unlikely that either option could compete well on a strictly economic basis with direct ownership of a CV.

Driver Aggression

Assessing the potential benefits of HEVs, PHEVs, and BEVs is complicated by the driving habits of the operator, as vehicle efficiency is sensitive to driver aggression. Quantifying the impact of driver aggression first requires an understanding of the variation of aggression within large, real-world drive datasets. For this, we collected and analyzed 2,154 unique 1- to 2-day-long vehicle records and assessed speed, acceleration, and kinetic intensity statistics.

Next, we applied high-fidelity vehicle simulation to each of these vehicle records and four standard drive cycles of four different light-duty vehicles: a CV, an

HEV, a PHEV, and a BEV. We found that normalized energy consumption rates can vary substantially around the mean in response to aggression, from -20% to +50%.

We also found that commonly used drive cycles (UDDS, HWFET, LA92, and US06) inconsistently represent various levels of aggression across all four powertrains. For example, in a CV, the fuel consumption predicted by US06 only slightly overestimates the median aggression fuel consumption. However, in a BEV, US06 very significantly overestimates the median aggression electricity assumption value. To rectify this issue, we developed the drive cycle shown in Figure III.C.1.3-2, which closely predicts median aggression fuel consumption regardless of powertrain type.

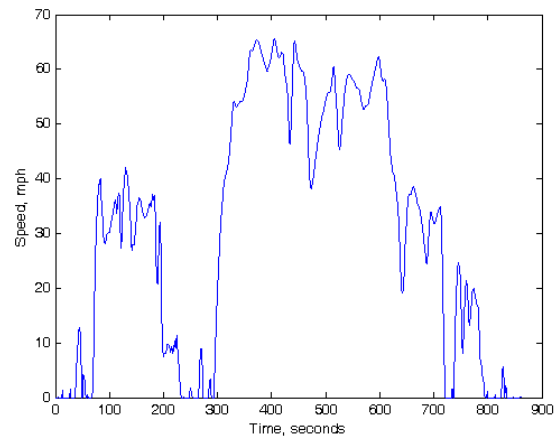


Figure III.C.1.3-2: Representative drive cycle produced from 2,154 vehicles using DRIVE

Climate, Cabin HVAC, and Battery Thermal Management

Following completion of the FY13 updated BOM, we studied the effects of climate, cabin HVAC, and battery thermal management on BEV utility. We modeled 10 years of vehicle operation under numerous scenarios, as described in Table III.C.1.3-1.

Table III.C.1.3-1: Design of Experiments for Thermal Analyses

Parameter	Values Simulated
Aggression	Low, Normal, High
Climates	Phoenix, AZ; Los Angeles, CA; Minneapolis, MN
Cabin HVAC	No HVAC; A/C+PTC heater; A/C+heat pump
Cabin Preconditioning	With and without
Battery Thermal Management	Passive; stand-by electrical heater; key-on refrigerant cooling; key-on and stand-by refrigerant cooling; stand-by refrigerant cooling

Our findings suggest that, in the absence of cabin HVAC loads, variations in climate have little effect on BEV utility in year one. However, warm climates can

significantly increase battery degradation rates, thereby impacting vehicle utility later in life. Once HVAC loads are considered, we find that the additional demand on the battery from air conditioning and heating systems can notably reduce both year one and year ten utility. Positive thermal coefficient (PTC) heater loads in cold climates have the largest impact; upgrading to a more efficient heat pump-based system appears worthwhile.

As we did not see significant decreases in vehicle utility in cold climates due to increased battery resistance, the addition of a stand-by electrical heater to keep the battery warm showed no ability to improve vehicle utility. While there was room for a battery cooling system to decrease degradation and improve year ten utility, we generally found that the increased load of key-on battery cooling systems had the opposite effect, resulting in slightly decreased utility.

Cumulatively, accurate accounting of trip distributions, driver aggression, climate, and cabin and battery thermal management yielded average utility factors that varied from 83% in the best case to 55% in the worst case (across a sampling of likely BEV driver trip histories). The latter value implies that estimates of BEV utility that do not account for these effects could be overestimating utility by nearly a factor of two, thereby stressing their importance in continued analyses.

Charging Infrastructure

We also investigated the impacts of home, work, public, and on-road power transfer on the utility of a 75-mile BEV. Our simulations included consideration of level 1 (120V, 15A AC) and level 2 (240V, 32A AC) at-home charging, level 1 and level 2 at-work charging, level 1, 2, and 3 (50 kW DC) public charging, and electrified roadway options. At-home charging considered cases with and without timing restrictions; all other charging scenarios assumed chargers available 24/7. The electric roadway power value was set such that battery state of charge (SOC) remained constant when on an electrified roadway due to limitations with our available dataset.

Comparisons of at-home charging revealed that level 1 charging, when unencumbered by time-based use limits, yields nearly as much utility as level 2. This implies that level 2 chargers are not a prerequisite for BEV ownership and can thereby reduce the total cost to consumers.

Somewhat surprisingly, we also found that the addition of at-work chargers had only a small impact on utility for drivers classified as “commuters,” who were most likely to benefit from the added infrastructure. We hypothesize that this is due to the fact that most long travel days that can benefit from additional charging infrastructure are either not workdays, or that the additional travel is longer than the increase in range provided by a work charger alone.

When we explored pairing level 1 home charging with ubiquitous public charging (but no charging at work), we found that the year ten achievable vehicle miles traveled (VMT) could be increased by 1,200 miles, resulting in an average utility factor of 93%. This corresponded to a decrease in average annual tours not taken from approximately 20 to less than five, as shown in Figure III.C.1.3-3. Interestingly, when public chargers are always available to the BEV driver, the additional benefit of access to 50-kW fast chargers over level 2 chargers is marginal.

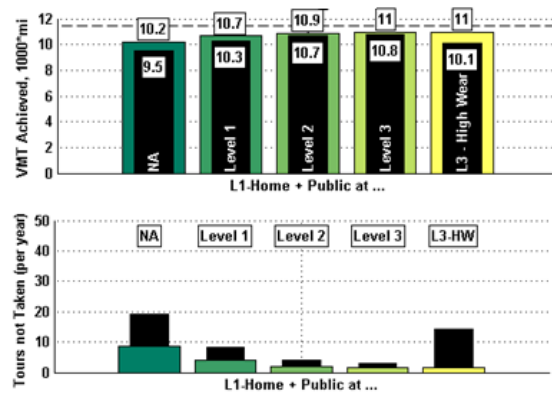


Figure III.C.1.3-3: Effect of ubiquitous public charging on achievable VMT and tours not taken

Conclusion and Future Directions

In FY13, we made significant upgrades to the BOM to expand our consideration of driver habits, battery thermal response, and auxiliary loads. We applied these new capabilities to study the impacts of driver aggression, climate, cabin HVAC, battery thermal management, and charging infrastructure on EV utility. These investigations have highlighted the need to improve standard drive cycles and have pointed toward vehicle configurations and charge infrastructure deployments that can optimize BEV utility.

In future work, we plan to upgrade our battery model to a multi-cell model, which will enable investigations of the impact of thermal gradients and electrical imbalance within a pack. We will also upgrade our handling of fast charge and battery swapping events, such that we can consider the impacts where such infrastructure is installed. We may consider the impact of car-sharing and rentals if resources and time permit.

FY 2013 Publications/Presentations

1. Neubauer, Jeremy, and Ahmad Pesaran, “A Techno-Economic Analysis of BEVs with Fast Charging Infrastructure,” EVS27, November 2013 (pending).

2. Neubauer, Jeremy, Eric Wood, and Ahmad Pesaran, "Analysis of Range Extension Techniques for Battery Electric Vehicles," DOE milestone report, July 2013.
3. Neubauer, Jeremy, and Eric Wood, "Accounting for the Variation of Driver Aggression in the Simulation of Conventional and Advanced Vehicles," SAE 2013 World Congress and Exhibit, April 2013.
4. Neubauer, Jeremy, and Ahmad Pesaran, "A Techno-Economic Analysis of BEV Service Providers Offering Battery Swapping Services," SAE 2013 World Congress and Exhibit, April 2013.
5. Neubauer, Jeremy, and Ahmad Pesaran, "Analysis on Kinetic Intensity, Climate, Vehicle Ancillary Loads, and Battery Thermal Management," DOE Milestone Report, March 2013.

III.C.1.4 PEV Battery Second Use

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Start Date: February 2009

Projected End Date: Projected September 2014

Objectives

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

Technical Barriers

- PEV end-of-service burdens (battery recycling, disposal) could impede PEV deployment; re-using PEV batteries in secondary applications and delaying recycling can shift these burdens away from the automotive industry
- Finding suitable second use applications for the large quantity of used PEV batteries that could become available from automotive markets is difficult
- 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
- Battery degradation in both automotive and post-automotive use is notoriously difficult to ascertain,

yet has a strong impact on the potential profitability of secondary use strategies

Technical Targets

- Identify and demonstrate sustainable second use applications for PEV Li-ion traction batteries
- 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

- Subcontract with CCSE and partners has resulted in an in-field test-bed for second use batteries and has begun testing used batteries in our identified second use applications to demonstrate viability and quantify long-term degradation
- Constructed framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications
- Applied the framework to a Li-ion PEV battery second use analysis that has highlighted the need for efficient repurposing strategies, identified a promising market for repurposed batteries, and began to quantify the potential of second use strategies to affect the cost of energy storage to both automotive and secondary markets
- Discussed partnership with BMW to support and assess deployment of a large pre-commercial-stage second use energy storage system

Introduction

Accelerated market penetration of PEVs as targeted by the DOE EV Everywhere Grand Challenge is presently limited by the high cost of Li-ion batteries. It has been estimated that more than a 50% reduction in battery costs is 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.

Approach

This effort investigates the application of used Li-ion PEV batteries to utility and other applications. The major technical barriers to success are second use application selection, long-term battery degradation, and cost and of certifying and repurposing automotive batteries.

To address these barriers, NREL has partnered with a team of hardware providers, utilities, and academic institutions led by the CCSE. This team is a testimony to the interest of industry in second use, as it has brought 50% cost share (amounting to more than \$600,000) to the effort with support from the California Energy Commission. Our team has worked collaboratively to perform techno-economic analyses, acquire aged batteries, and set up in-field and laboratory experiments to evaluate the performance and longevity of second use batteries as discussed below. Success of the project is measured by the completion of long-term testing and the determination of used battery value.

Results

Second Use Battery Availability

To guide subsequent investigation of relevant second use battery applications and value, it is worthwhile to project the availability and state of health of used automotive batteries. From a detailed BOM analysis, we found that it is generally not economically advantageous for PEV owners to replace their batteries prior to the end of life of the vehicle. Assuming an average vehicle life of 15 years and total battery lifetime of 20 years leaves a conservative 5-year second use lifetime estimate. Using these values, along with a spectrum of PEV deployment scenarios, yields the projection of functional second use batteries in Figure

III.C.1.4-1. Note that the mean scenario predicts more than 20 GWh of second use energy storage could be available by 2030.

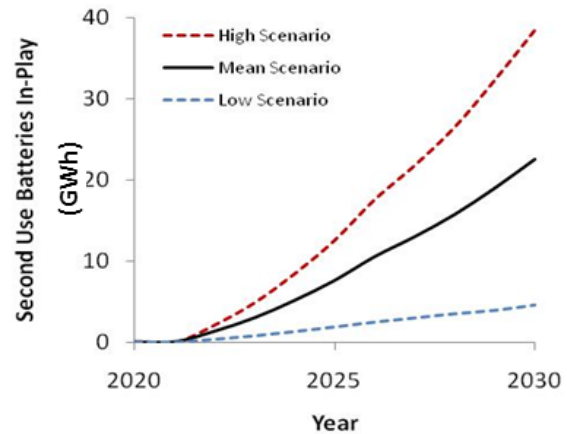


Figure III.C.1.4-1: Projected amount of functional second use battery energy storage available; high, mean, and low scenarios correspond to different PEV deployment rates

Stationary Applications Analysis

The preceding projection of used battery availability suggests that an extremely large market must be found to absorb such a large quantity of energy storage capacity. This, along with expected performance capabilities, price levels, and industry trends, motivates investigating stationary storage applications. An assessment of grid-based secondary use applications accounting for the value of service, expected limitations of repurposed automotive batteries, and costs of the balance of system necessary to provide said service, suggests that area regulation, electric service power quality and reliability, and transmission and distribution upgrade deferral offer considerable value, as seen in Figure III.C.1.4-2.



Figure III.C.1.4-2: Preliminary analysis results show multiple applications that could profitably employ second use batteries

However, market potential may be an issue for these applications. Area regulation—a service intended to balance the supply of and demand for energy on a

relatively fast time scale—is an inherently small market. While the regulation market is expected to change in response to the increased penetration of renewables on the grid, as well as changing consumer load profiles, it is not expected by itself to fully support the supply of used PEV batteries. Power quality and reliability is a high-value end user market that is well established today (e.g., uninterruptible power supplies) and is growing. While the market is larger than that of area regulation (in terms of GWh) and there are synergies with other behind-the-meter applications, by itself, this application cannot absorb the full quantity of second use batteries expected. Similarly, the projected need for transmission upgrade deferral—using energy storage to reduce peak loads on transmission assets with projected overloads, enabling the upgrade or replacement of such assets to be deferred—is small in comparison to anticipated battery supplies.

While our analysis predicts that these markets are insufficiently deep to support the expected quantity of used PEV batteries available in the long run, they are nonetheless important to study as they may be the first applications targeted by the earliest available second use batteries. Further, they will potentially play a role in the long run as secondary applications aggregated with some primary application to increase the value that individual storage systems will capture.

Our current expectation is that second use batteries should be deployed in a distributed fashion with peak-shaving as their primary service, reaping their value from reducing peak power loads on grid assets. Peak-shaving can take place in many forms, be it behind the meter as demand charge reduction, by a utility to reduce generation capacity requirements, etc. Value is generated primarily by reducing or eliminating the need for other, more expensive hardware investments. While this created value is often significantly less than that achievable with the three high-value applications discussed previously, this market is much larger and more likely capable of absorbing the quantities of second use batteries expected.

Repurposed Battery Costs

To assess if second-use batteries can be deployed as peak-shaving assets cost-effectively, it is important to estimate the cost at which a battery can be repurposed and sold. Using a bottom-up approach that considers all labor, capital equipment, facility needs, required rate of return by the operating entity, and many other factors, we calculate the cost of repurposing used PEV batteries as a function of the size of the module being processed and the frequency of occurrence of irreparable cells (cell fault rate). Some example results of this process are shown in Figure III.C.1.4-3.

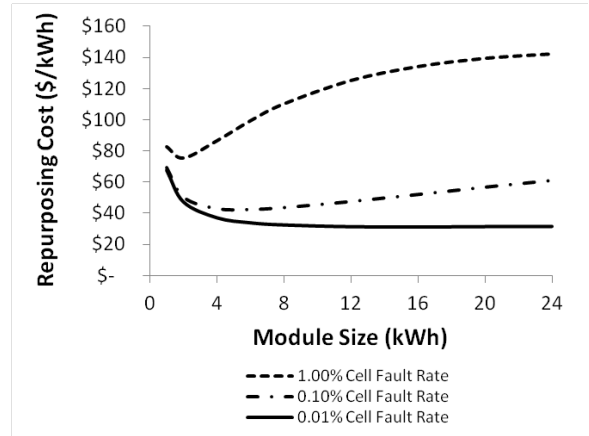


Figure III.C.1.4-3: Projected second-use battery repurposing cost for a repurposed battery selling price of \$132/kWh

Our results imply that the technician labor and costs of capital are the most significant cost elements of repurposing activities. These sensitivities have two considerable implications: first, the effect of technician labor rules out the possibility of labor-intensive repurposing operations (such as addressing individual instances of faulty cells). This requires that facilities repurpose modules or packs and creates large variations in repurposing costs due to the interplay of module size and cell fault rate. Efficiencies of scale encourage repurposing larger modules, but larger modules also mean more waste when a faulty cell is identified.

The sensitivity to cost of capital (e.g., return on investment requirements, cost of debt) makes repurposing costs a strong function of the price at which a repurposing facility can sell the repurposed batteries. To address this, we evaluate both high- and low-price approaches.

In the high-price approach, we assume that repurposed PEV batteries are priced competitively with newly manufactured Li-ion batteries. Accounting for the anticipated future decline in new battery prices, degraded battery health at automotive retirement, and a repurposed product discount factor, we can then forecast anticipated repurposed battery sale prices (Figure III.C.1.4-4). The possible variations in the aforementioned inputs—particularly for future battery prices—lead to significant uncertainty in the results, but in all cases the expected cost of repurposed batteries to grid or other applications is low.

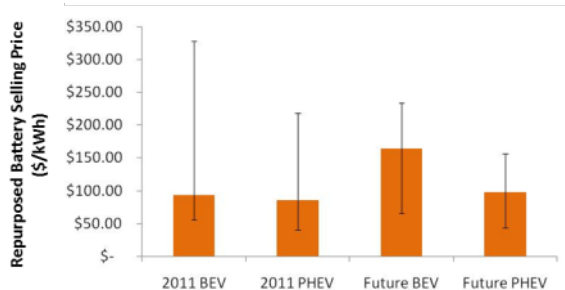


Figure III.C.1.4-4: Projected repurposed battery selling price, competitive pricing scenario

Note that the high-cost approach results in a small but not insignificant salvage value for the automotive battery owner in most cases. However, with repurposed battery prices mostly above \$100/kWh, it may be difficult to cost-effectively provide peak-shaving services at a large enough scale to consume the number of available used PEV batteries. If a market that values repurposed PEV batteries greater than our calculated selling price, then the use of a competition-based price model is in error.

Alternatively, in the low cost approach, we assume that an overabundance of used PEV batteries is present and seek to calculate the lowest economically feasible repurposed battery selling price. To do so, we set the used battery buying price equal to the assumed cost of removing the batteries from the vehicle, such that the net cost (value) of second use to the automotive owner is zero. This removes economic disincentives for the automotive owner, minimizes the price paid for batteries by the repurposing facility, and thereby minimizes the repurposing cost and selling price of repurposed batteries.

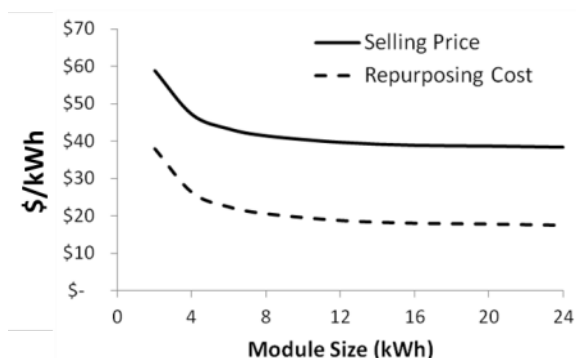


Figure III.C.1.4-5: Repurposing cost and repurposed battery selling price for the low cost scenario

We find that the minimum repurposed battery selling price in this scenario is approximately \$40/kWh. This is highly encouraging, as it is probable that peak-shaving applications could be performed cost effectively at a large scale when batteries are available at this price point.

Validating Second Use Viability

Based on these findings, it is our anticipation that large supplies of second-use batteries will suppress repurposed battery selling prices until a suitably large market is found that adequately values this resource. We believe this market will be peak-shaving services on the grid. Secondary services, such as area regulation, power quality, power reliability, and asset deferral will likely be paired with this service to increase value (and may serve as primary applications in early second-use battery deployments).

To enable this market for second-use batteries, it is necessary to demonstrate the capability of such batteries to adequately provide these services. In particular, quantifying system response in real-world scenarios and validating the longevity of these batteries in these applications are critical.

To this end, we have acquired numerous aged automotive battery packs spanning multiple Li-ion chemistries, including iron phosphate, nickel manganese cobalt, and manganese oxide cathodes, and graphite, hard carbon, and lithium titanate anodes. Acceptance testing to quantify basic battery performance and state of health has been completed, as has short-term application tests for peak shaving, area regulation, and power reliability services. Furthermore, a long-term field test site on the University of California – San Diego microgrid has also been completed. Control strategies to provide real-time peak shaving services for select sites on campus have been completed, and real-time testing has been initiated. As testing continues, we will begin to assess the degradation characteristics of second-use batteries, and learn more about optimizing deployment strategies for this resource.

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 that has been 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 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.

Conclusions and Future Directions

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 applications of this framework to Li-ion PEV batteries has highlighted the need for efficient repurposing strategies, and identified a promising market for repurposed batteries.

The major uncertainty that remains is the longevity of repurposed batteries in post-automotive applications. To address this matter, NREL has acquired aged batteries, developed a long-term field test site and strategy, and initiated long-term testing via a subcontract with CCSE through a 50-50 cost share partnership with industry. NREL has also acquired additional aged batteries for on-site laboratory testing. These efforts will be the focus of continued project work in FY 2014. Additionally, we will be working 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.

FY 2013 Publications/Presentations

1. Ferry, Mike, William Torre, Jeremy Neubauer, and Peter Dempster, "Second-Life Applications for PEV Battery Systems: Early Testing to Early – Commercialization," EESAT, October 2013.
2. Neubauer, Jeremy, et al., "Analyzing the Effects of Climate and Thermal Configuration on Community Energy Storage Systems," EESAT, October 2013.
3. Neubauer, Jeremy, and Mike Simpson, "Optimal Sizing of Energy Storage and Photovoltaic Power Systems for Demand Charge Mitigation," EESAT, October 2013.
4. Neubauer, Jeremy, and Ahmad Pesaran, "Uncertainties and Challenges for Battery 2nd Use Strategies," The Battery Show, September 2013.
5. Neubauer, Jeremy, and Ahmad Pesaran, "Analysis of Community Energy Storage as a BEV Battery Second Use Application," 2013 DOE Milestone Report.
6. Neubauer, Jeremy and Ahmad Pesaran, "Analysis and Testing of Plug-In Electric Vehicle Batteries in Second Life Applications," The 30th International Battery Seminar and Exhibit, March, 2013.

III.C.2.1 Battery Life Trade-Off Studies

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Start Date: FY08

End Date: FY15

- Quantified electrochemical-thermal-mechanical fade mechanisms that accelerate capacity loss and lead to sudden end-of-life
- Integrated cell-level life model with multi-cell pack electrical-thermal model, creating pack-level life prediction models that reduce the need for expensive pack aging experiments
- Validated NMC cell- and pack-level aging models under cooperative research and development agreement (CRADA) with General Motors

Objectives

- Develop physics-based battery life prediction models that quantify longevity over a range of real-world temperature and duty cycle conditions
- Extend cell models to pack-level, capturing impacts of temperature non-uniformity, cell performance, and aging variability on system lifetime
- Perform trade-off studies to quantify potential battery lifetime extension and cost reduction achievable via advanced systems, controls, and operating strategies for EDV 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 years of battery life for EDVs in disparate geographic environments and duty cycles
- Battery lifetime predictive models validated against real-world data with less than 10% error
- Thermal and control systems that reduce cell energy content and still meet 10-15 year lifetime

Accomplishments

- Developed new life model for Li-ion graphite/NMC chemistry, complementing previous models for graphite/NCA and graphite/FeP chemistries

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 more than ten degradation factors that must be considered to predict lifetime. Worst-case cell aging conditions within a multi-cell battery pack drive 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. 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 FY13, NREL's existing life model framework, developed for NCA and FeP chemistries, was extended to the NMC chemistry. End-of-life effects were further studied for the FeP chemistry. Cell-level aging models were coupled to pack multi-cell electrical-thermal models to capture limiting mechanisms inherent in complete battery systems, including balance of plant effects.

Cell-level life models were based on the life modeling and regression framework previously developed at NREL. The physics-based models capture

changes in resistance and capacity with lifetime due to factors such as:

- Side reactions forming electrode impedance films and consuming Li
- Impedance film fracture and regrowth
- Lithium plating at low temperatures
- Binder decomposition at high temperatures
- Electrolyte decomposition at high temperatures and voltages
- Solid electrolyte interphase (SEI) fracture and reformation
- Particle and electrode fracture/fatigue/isolation due to electrochemical-thermal-mechanical cycling
- Separator pore closure due to viscoelastic creep caused by cycling
- Gas pressure build-up
- Break-in process releasing excess Li and enhancing initial reaction/transport at beginning of life

Surrogate models for the above degradation mechanisms are implemented in NREL's software framework to be statistically regressed to cell aging data. The rate of each process is coupled to calendar and charge/discharge duty cycle in an appropriate manner to properly extrapolate lifetime from accelerated aging experiments. 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.

Results

Accelerating Fade and Sudden End-of-life

Accurate prediction of end-of-life is the most critical factor for analyses of EDV battery lifetime. Mature Li-ion chemistries typically fade in a graceful manner from the beginning through the middle of their lifetime. Nearing end-of-life, however, performance can sometimes rapidly degrade depending on the aging duty cycle. From a database of more than 50 aging tests for a 2.3 Ah FeP cell, Figure III.C.2.1-1 highlights 13 such conditions where capacity fade accelerates.

A hypothesized model was developed that attributes the acceleration of fade to a change in mechanism. Early in life, capacity is controlled by available-Li, but late in life, capacity is controlled by remaining electrode-active sites. Rate laws for loss of electrode-active sites were developed depending on:

- C-rate (intercalation gradient strains)
- Depth of discharge (bulk intercalation strains)

- Low temperature (exacerbates Li intercalation-gradients)
- High temperature (exacerbates binder degradation in the composite electrode)
- Temperature swings with cycling (causing stress due to differential thermal expansion of components)

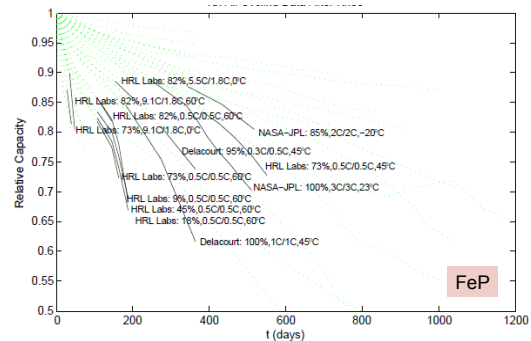


Figure III.C.2.1-1: Aging test conditions with apparent sudden acceleration in fade nearing end-of-life; labels indicate data source, percent DoD, discharge/charge C-rate, and temperature

Figure III.C.2.1-2 shows good agreement of the life model compared to experimental data. At room temperature 1C cycling, the model predicts:

- 83% of capacity fade is caused by cycle depth of discharge (bulk intercalation strains)
- 13% of capacity fade is caused by particle fracture due to C-rate (intercalation gradient strain)
- 4% of capacity fade is caused by temperature swings encountered by the cell

These conclusions, to be further investigated in future studies, provide guidance as to the relative importance of different mechanically-coupled fade mechanisms in Li-ion cells.

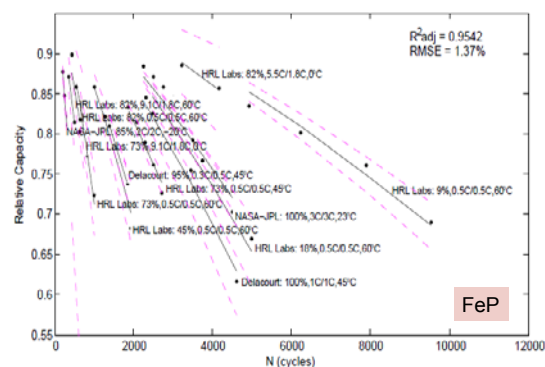


Figure III.C.2.1-2: Experimental data (symbols) with life predictions (solid black lines) and 95% confidence (dashed purple lines)

Pack-level NMC Life Prediction

In addition to cell-level aging effects, lifetime of EDV batteries is also impacted by pack-level effects. For accurate life prediction, it is important to capture factors that contribute to non-uniform aging of cells in a multi-cell pack. These include the effect of temperature gradients within the pack and cell non-uniform aging processes.

In FY13, NREL combined previously-developed cell and pack models to create a pack-level life prediction tool. The tool was validated using proprietary data shared by GM under a CRADA. First, a cell-level life model was regressed to aging data for an NMC chemistry Li-ion cell. Next, a cell electrical circuit model was regressed to hybrid pulse power characterization (HPPC) data for the same cell and linked to the life model to describe cell performance changes with aging. A pack thermal model was regressed to pack thermal characterization experiments, capturing cell heat generation with drive cycle and heat dissipation through passive and active cooling paths.

Shown in Figure III.C.2.1-3, the cell life and electrical models were linked with the pack-level thermal/electrical model to create a predictive tool for pack-level lifetime. The model-based process greatly reduces the need to run pack-level aging experiments, saving substantial cost from the battery engineering development process. The proprietary NMC pack life models are being implemented in NREL's BOM to enhance the fidelity of future techno-economic analysis of EDV batteries.

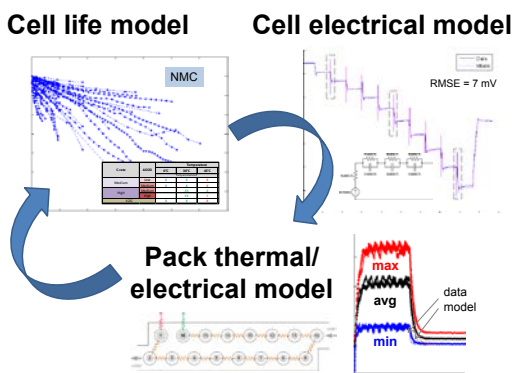


Figure III.C.2.1-3: Integrated models for battery pack-level life prediction

Conclusions and Future Directions

In FY13, previously-developed life models and framework were enhanced to capture:

- End-of-life effects, namely accelerating fade driven by electrochemical-thermal-mechanical coupled processes
- NMC chemistry cell lifetime, complementing previously-developed models for NCA and FeP chemistries
- Pack-level degradation processes, including temperature non-uniformity and cell performance and aging variability

These life models directly support NREL analysis on cost-of-ownership for EDV consumers and fleets, battery second use techno-economic analysis, thermal management, and balance of plant design. The life models are also being applied in ARPA-E AMPED projects developing battery prognostic controls (with Eaton Corporation) and an active balancing system that seeks to eliminate non-uniform cell aging and life extension for multi-cell battery packs (with Utah State and Ford). Versions of the NREL life models have been licensed to external industry and academic partners.

Pending opportunities, future work may enhance the models' descriptions of cell electrochemical-thermal-mechanical degradation processes and integrate the life models with commercial battery computer-aided engineering software.

FY 2013 Publications/Presentations

1. K. Smith, J. Neubauer, E. Wood, M. Jun, A. Pesaran, Models for Battery Reliability and Lifetime: Applications in Design and Health Management, Battery Congress 2013, Ann Arbor, MI; April 15-16, 2013. NREL Report No. PR-5400-58550.
2. K. Smith, J. Neubauer, E. Wood, M. Jun, A. Pesaran, SAE World Congress, Detroit, MI; April, 2013

III.C.2.2 Lower-Energy Energy Storage System (LEESS) Component Evaluation

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Collaborators:
Ford Motor Company
JSR Micro
USABC

Start Date: April 2007
Projected End Date: December 2013

functionality using the LEESS devices (with the production battery disconnected)

Background

Automakers have been mass-producing HEVs for well over a decade, and the technology has proven to be very effective at reducing per-vehicle fuel use. However, the incremental 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 vs. benefit relationship. Such an improvement would, in turn, lead to larger HEV market penetration and greater aggregate fuel savings.

Objectives

- Establish reusable vehicle test platform for evaluating LEESS devices for power-assist or “full” HEVs
 - HEVs with lower cost or better performing energy storage systems could improve cost vs. benefit ratio, market penetration, and aggregate fuel savings
- Perform bench testing on one prospective LEESS device and integrate it into the test vehicle

Accomplishments

- Completed bench testing on LIC LEESS devices supplied by JSR Micro
 - Results indicate sufficient device energy to satisfy standard drive cycle demands and improved efficiency relative to the production battery system
- Completed conversion of the Ford Fusion Hybrid research vehicle into the reusable test platform for in-vehicle LEESS device evaluation
 - Test vehicle retains the ability to switch back and forth between the conversion and the production vehicle configuration
- Completed integration of the JSR Micro LIC modules into the vehicle test platform, and confirmed successful operation and hybrid system

Introduction

In recognition of these potential benefits, the 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 LEESS targets and issue a request for proposals to support their development. In order to validate the fuel savings and performance of an HEV using such a LEESS device, this jointly-funded activity—between the DOE Vehicle Technologies Office (VTO) Energy Storage and Vehicle Systems Simulation and Testing (VSST) programs—has designed a test platform in which alternate energy storage devices can be installed and evaluated in an operating vehicle.

Approach

In FY12, NREL entered into a CRADA with Ford Motor Company to support conversion of a Ford Fusion Hybrid into a test platform for evaluating LEESS devices. NREL subsequently acquired a 2012 Fusion Hybrid and began designing the conversion. NREL also established a non-disclosure agreement (NDA) and a bailment agreement with JSR Micro, Inc. to provide

(at its expense) LIC modules as the first LEESS device to be evaluated in the vehicle, along with proprietary information about the modules to support their integration and testing. The LICs are asymmetric electrochemical energy storage devices possessing one electrode with battery-type characteristics (lithiated graphite) and one with ultracapacitor-type characteristics (carbon). Additional project steps in FY13 included completing the vehicle conversion, conducting bench testing on the LIC replacement pack in comparison to the production nickel metal hydride (NiMH) battery pack from the 2012 Fusion Hybrid, and integrating the LIC modules into the Fusion Hybrid test platform.

Results

Designing the conversion required first understanding the construction of the production high-voltage traction battery (HVTB) and its integration with the rest of the vehicle. 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 charging/discharging of the battery and also communicates with the other vehicle control modules over the high-speed controller area network (CAN) bus. Figure III.C.2.4-1 shows a schematic of the HVTB, including these components, and a photo of the HVTB in the vehicle, which mounts between the rear seat and the trunk area.

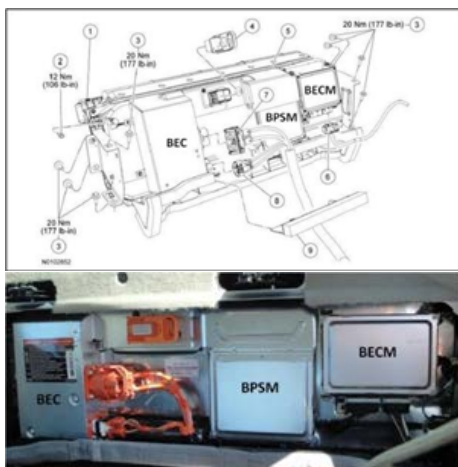


Figure III.C.2.4-1: Schematic and photo of Fusion Hybrid's HVTB (Photo credit: John Ireland, NREL)

With the conversion strategy established in FY12, NREL elected to keep 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 III.C.2.4-2 shows a schematic of this configuration, where 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 during the testing.

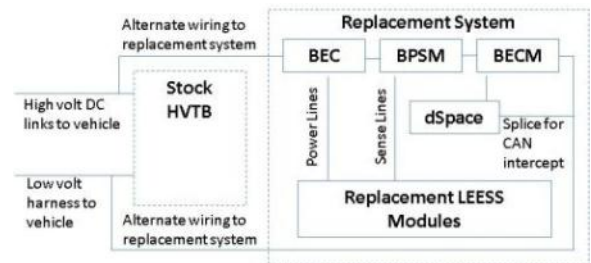


Figure III.C.2.4-2: Schematic of connections between replacement components and the vehicle

Figure III.C.2.4-3 provides the schematic for an additional electronics component established between the voltage sense leads for the alternate LEESS under test and the production BPSM sense leads. This voltage divider circuit divides the full voltage of the alternate LEESS into the 26 evenly-divided increments that the BPSM is expecting to measure (corresponding to the 26 NiMH modules that make up the production battery pack). This helps keep the BECM operating as if the production batteries were still connected and leaves actual module-level voltage measurement and safety controls for the LEESS under test to be handled by the MABx.

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 III.C.2.4-4). 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.

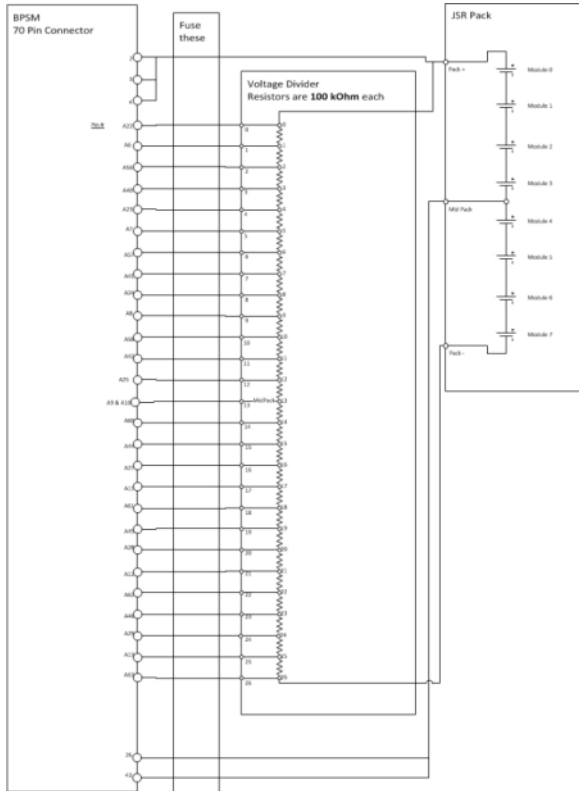


Figure III.C.2.4-3: Schematic of voltage divider circuit between the replacement BPSM and the LEESS modules



Figure III.C.2.4-4: JSR LIC modules in an environmental chamber during bench testing, with the production 2012 Fusion Hybrid NiMH modules in the background (Photo credit: John Ireland, NREL)

Figure III.C.2.4-5 shows the performance results from HPPC testing on the LIC pack. The results show greater open circuit voltage variation, but also two to three times lower resistance as compared to the production NiMH pack, based on calculations from pack testing performed for DOE's Advanced Vehicle Testing Activity (AVTA). In order to evaluate the LIC pack operation during bench testing against a representative in-vehicle load profile, NREL referenced production Fusion Hybrid chassis dynamometer test results available from Argonne National Laboratory

(ANL). The LIC modules were able to satisfy the exact load profile provided by the production NiMH pack during chassis dynamometer testing over the aggressive US06 drive cycle. Figure III.C.2.4-6 shows the resulting profile for the internal energy state of the stock NiMH battery (from chassis testing) compared to that of the LIC modules (from bench testing). The results indicate a rise in the internal energy state for both devices, but a roughly 50-Wh larger rise for the LIC pack due to its lower internal resistance. The follow-on in-vehicle testing of the LIC pack will help reveal to what extent the lower energy losses help offset any limitations caused by its lower total energy content as compared to the NiMH pack.

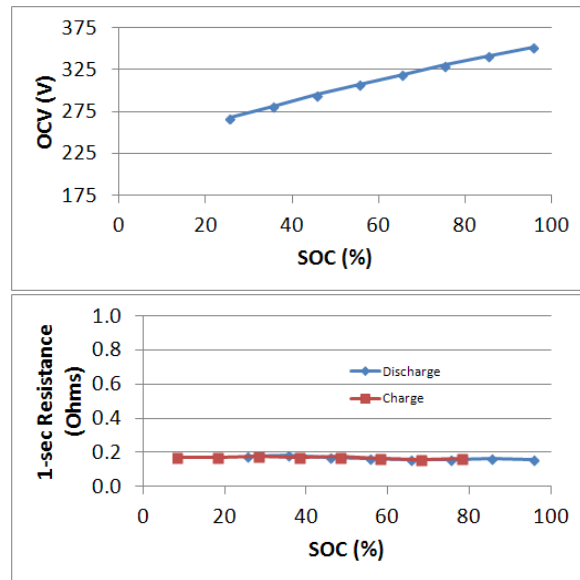


Figure III.C.2.4-5: LIC pack performance calculations from bench testing

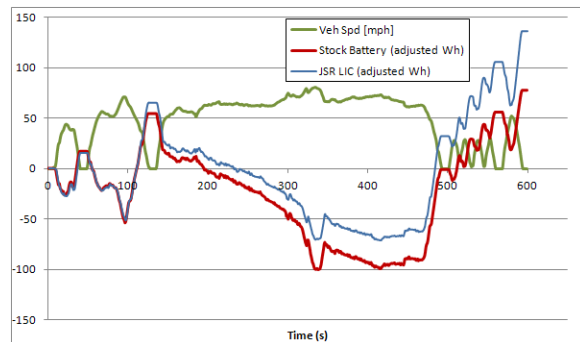


Figure III.C.2.4-6: ESS energy profile comparison over the aggressive US06 drive profile

The final FY13 result highlighted in this summary report is the integration of the LIC modules into the Fusion Hybrid test platform to enable the in-vehicle comparison testing (which will wrap up in the early part of FY14). Figure III.C.2.4-7 shows a picture of the fully-integrated conversion system, including LIC modules, mounted in the trunk of the Fusion Hybrid.

The LIC modules along with the replacement BEC are shown in the large box with the clear lid; off to the side, the picture shows the MABx mounted on top of an electronics box containing the voltage divider circuit and related components.



Figure III.C.2.4-7: Fully-integrated conversion system mounted in trunk of Fusion Hybrid test platform (Photo credit: Jon Cosgrove, NREL)

Along with the physical components shown in Figure III.C.2.4-7, the custom state estimator code (to estimate the LEESS state of charge and charge/discharge capability at any moment in time) has been validated against the bench test data and incorporated into the MABx, with temperature dependence functionality included. The ability to operate the vehicle while intercepting and re-broadcasting modified signals over the vehicle CAN bus has also been confirmed. Finally, following validation testing of the safety controls implemented in the vehicle, the project team completed NREL's safety readiness verification and received a Safe Work Permit to operate and test the vehicle platform in the conversion configuration from NREL's Environment, Health and Safety Office (EHS).

Conclusions and Future Directions

Alternate HEV storage systems such as the LIC 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. The vehicle test platform developed through this project is helping to validate the in-vehicle performance capability of alternative LEESS devices and identify unforeseen issues.

This report describes 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, and final integration of the LIC pack into the test vehicle. Ongoing work into FY14 will include completion of in-vehicle comparison testing between the LIC pack and the production NiMH batteries and subsequent testing with LEESS devices from other manufacturers. An NDA and bailment agreement has been initiated with Maxwell Technologies to provide ultracapacitor modules as the next system to evaluate for the project. Other possible future work topics include evaluating the potential offered by LEESS devices with more extensive vehicle modification, such as by increasing the motor size to leverage a higher-power capability ESS.

Future work will include completing repeatable back-to-back in-vehicle testing over a variety of driving profiles using the JSR Micro LIC devices compared with the production battery system. Work will also involve removing the JSR Micro LIC devices and repeating the testing with two different LEESS devices.

FY13 Publications/Presentations

1. Gonder, J., Ireland, J., Cosgrove, J., and Pesaran, A. "Evaluation of a Lower-Energy Energy Storage System for Full-Hybrid Electric Vehicles." SAE 2013 Hybrid and Electric Vehicle Technologies Symposium, February 2013.
2. Cosgrove, J., Gonder, J. and Pesaran, A., "Performance Evaluation of Lower-Energy Energy Storage Alternatives for Full-Hybrid Vehicles." Abstract accepted for presentation at the Supercapacitors USA International Conference and Tradeshow, November 2013.

III.C.2.3 Updating USABC Battery Technology Targets for Battery Electric Vehicles

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Start Date: FY12

Projected End Date: FY13

Objective

- Provide analysis to support the EV Everywhere Grand Challenge and the USABC identification of battery available energy, mass, volume, cost, discharge power, and charge power requirements that will enable broad commercial success of BEVs

Technical Barriers

- Current USABC BEV battery targets were developed more than 20 years ago; documentation on their development is scarce, and the necessary vehicle performance for market success has changed since their creation

Accomplishments

- Developed a simulation-based approach to calculate BEV battery technology requirements necessary to deliver the vehicle-level performance required for commercial success of BEVs
- Implemented the process across a range of inputs and provided results to USABC and DOE for finalizing inputs and assumptions

Introduction

BEVs offer significant potential to reduce the nation's consumption of gasoline and production of greenhouse gases as identified in the DOE EV Everywhere Grand Challenge. However, one large impediment to the commercial success and proliferation of these vehicles is limited battery technology. BEVs on the market today come with a significant cost premium relative to their conventionally-powered counterparts, even after significant federal and state purchase incentives. In addition, the range of the vehicle is typically restricted by limited battery energy to less than 100 miles. Furthermore, when a BEV is based upon a platform designed for a conventional powertrain, the size of the battery necessary to achieve this limited range often subtracts from available passenger or cargo volume.

Improvements in battery technology have the capacity to resolve all of these issues. Accordingly, in support of the president's EV Everywhere Grand Challenge, the DOE VTO, working with USABC and others, are directing significant resources toward the development of batteries for BEVs. Historically, these developments have been focused toward a set of USABC BEV battery targets developed more than 20 years ago. Documentation providing insight into the development of these targets is exceptionally scarce; thus, the justification for these values is unclear. For this reason, and on the basis that the necessary vehicle performance for market success has changed since the creation of the original targets, there is motivation to develop an updated set of BEV battery technology targets.

In 2012, the USABC and DOE began the process of creating a new set of battery technology targets for BEVs. It was desired that the requirements be designed to deliver a BEV capable of broad market success in support of the EV Everywhere Grand Challenge. To this end, the resources provided by the DOE VTO to NREL were leveraged to supply detailed technical analysis, guided by the insight of USABC vehicle OEM members on consumer requirements and future technology trends.

Approach

The objective of this analysis is to support USABC and DOE identification of battery available energy, mass, volume, cost, discharge power, and charge power requirements that will enable broad commercial success of BEVs once achieved. Working closely with USABC and DOE, NREL has developed a simulation-based approach to achieving this objective.

It begins by first specifying the relevant vehicle-level performance requirements necessary for commercial success; most relevant to this analysis are acceleration and range. Next, we select a vehicle platform with broad market appeal and define its mass and aerodynamic properties using forecasted values for our timeframe of interest. At this point, we calculate the required energy and power to meet our range and acceleration targets, then analyze the charge and discharge power requirements of varying durations across multiple drive cycles using vehicle simulation software. Finally, we calculate available battery mass and volume, followed by allowable battery cost to provide cost-parity with a comparable conventionally-powered vehicle. We leverage OEM input via the USABC throughout to ensure that all assumptions are relevant to the anticipated level of future vehicle technology and market expectations.

Results

At the request of the DOE and USABC, we applied this approach to multiple vehicle platforms (compact car, midsize sedan, and small SUV) and vehicle ranges (150 and 300 miles). For each vehicle platform, we defined the total vehicle mass using a vehicle mass factor parameter (the ratio of total BEV mass to total conventional vehicle mass) and varied this as well. Some high-level results are shown in Figure III.C.2.3-1.

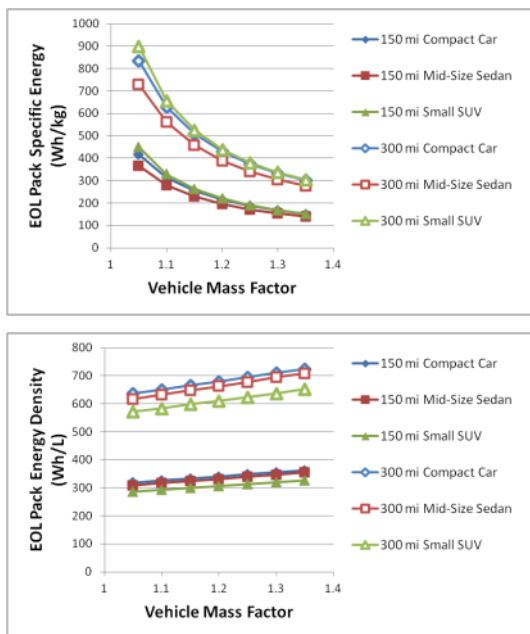


Figure III.C.2.3-1: Required end-of-life pack-specific energy/energy density as a function of vehicle range, platform, and mass factor

We have also simulated these configurations to multiple drive cycles to calculate discharge and charge power requirements. Results for a mid-size sedan with 1.2 vehicle mass factor are shown in Figure III.C.2.3-2.

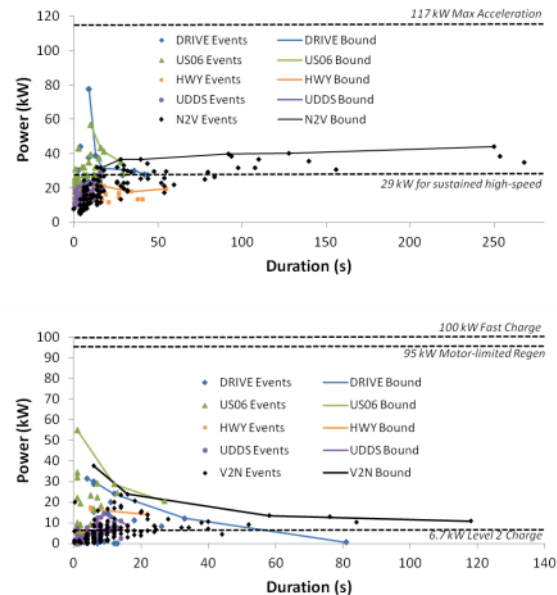


Figure III.C.2.3-2: Discharge (top) and charge (bottom) power requirements for a mid-size sedan with a vehicle mass factor of 1.2

In addition, cost requirements were calculated and implications for beginning-of-life cell-level targets were extrapolated. All of this data was presented to USABC to support their target-setting process.

Conclusions and Future Directions

This project successfully analyzed BEV battery targets and the findings were provided to DOE and USABC. USABC subsequently selected new targets for its BEV battery technology development programs using this input, which will be published shortly. To conclude this work, NREL plans to publish on its target analysis process to guide future target-setting efforts.

III.D.5 Battery Thermal Analysis and Characterization Activities

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Collaborators:

D. Long, J. Ireland, S. Santhanagopalan, NREL

GM, Ford, Chrysler, USABC

Start Date: October 1, 2009

Projected End Date: September 2014

- Obtained thermal and electrical performance data of cells under HEV, PHEV, and EV power profiles
- 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 the thermal performance of battery systems in order to aid battery developers with improved thermal designs.

Approach

Using NREL's unique 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 Actacell, Cobasys, JCI, LGCPI, Quallion, and SK Innovations Workgroups.

Results

NREL's Calorimeter Development leads to R&D 100 Award

Advanced energy storage devices, such as lithium-based batteries, are very sensitive to operating temperature. High temperatures degrade batteries faster and pose safety hazards, while low temperatures decrease power and capacity. The Isothermal Battery Calorimeters (IBCs), developed by NREL, are the only calorimeters in the world capable of performing the precise thermal measurements needed to make safer, longer-lasting, and more cost-effective batteries for the next generation of EDVs.

Recently recognized with an R&D 100 Award, the IBCs are the most accurate devices of their kind—able to determine heat levels and battery energy efficiency with 98% accuracy. The IBCs make it possible to precisely measure the heat generated by EDV batteries, analyze the effects of temperature on battery systems,

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 Targets

- Battery operating temperature from -30°C to 52°C
- 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 Actacell, Cobasys, Johnson Controls Incorporated (JCI), Quallion, LGCPI, and SK Innovation
- Obtained infrared thermal images of cells provided by USABC battery developers and identified any areas of thermal concern
- Used NREL's unique calorimeters to measure heat generation from cells and modules under various charge/discharge profiles

and pinpoint ways to manage temperatures for the best performance and maximum life.

Capable of testing a wide size range of samples, the calorimeters can determine the heat generated by battery cells, modules, sub-packs, and even some full-size packs. The IBCs also evaluate system heat generation, from the individual cells within a module, interconnects between cells, and entire battery systems.

The cell/module version of the IBC has the capacity to test more than 95% of EDV energy storage cells and small modules. The IBCs can also be used to test a variety of cell formats (i.e., pouch, cylindrical, and prismatic), while most other calorimeters on the market are limited to a single format.

The incredible precision of the IBCs can be attributed to patent-pending features that deliver total thermal isolation and highly sensitive temperature readings across a wide range of conditions. NREL has licensed the IBC technology to NETZSCH Instruments North America, LLC, a leading provider of thermal analysis instruments, for commercial production and distribution. The commercially-available IBC-284 being developed by NETZSCH and NREL is shown in Figure III.D.5-1.



Figure III.D.5-1: NETZSCH IBC-284

Calorimeter Testing

Figure III.D.5-2 shows the efficiency of cells tested in FY12/FY13 at NREL. 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 represent both power and energy cells, and have been developed for the HEV, PHEV, EV, or LEASS programs with USABC. The figure shows that most of the lithium-ion cells, A-J, 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, considering a 50 kW pulse from the battery in an electrified advanced vehicle, a 1% difference in

efficiency results in an additional 500 W of heat for the pulse duration.; thus, a 4% difference results in 2000 W of additional heat. The efficiency differences between cells requires tailoring the thermal management system to cell thermal characteristics to avoid affecting cycle life.

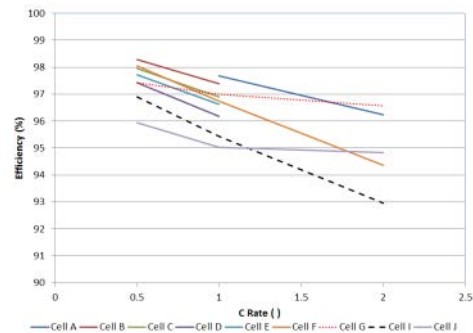


Figure III.D.5-2: Efficiency of cells tested at 30°C in NREL's calorimeter during FY12/FY13

Figure III.D.5-3 compares the efficiency of Gen 2 and Gen 3 cells from the same manufacturer. The cells were discharged under a constant current from 100% to 0% SOC. The efficiency of the Gen 3 cell is slightly below the efficiency its predecessor, the Gen 2 cell, indicating from this snapshot of data that the cell design has not improved from one generation to the next. However, cells are not typically used over their full capacity range due to life cycle limitations. In this particular case, the cells will be used in a vehicle application from approximately 70% to 30% SOC. Figure III.D.5-4 compares the efficiency of the Gen 2 and Gen 3 cells over this usage range. As can be seen from the figure, the efficiencies of the two cells are fairly well matched. Battery manufacturers use NREL calorimeter data to ensure that cells have desired efficiency over the usage range while making trade-offs on other aspects of cell design, such as low temperature operation, safety, cost, and ease of manufacturing.

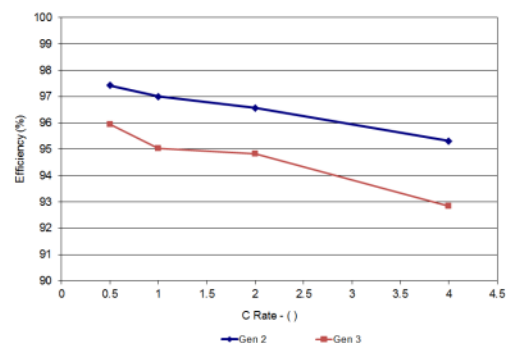


Figure III.D.5-3: Efficiency of two generations of cells tested at 30°C from 100% to 0% SOC

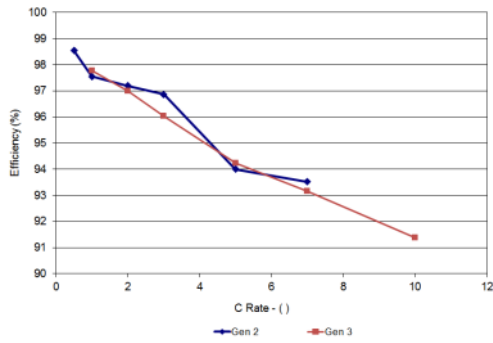


Figure III.D.5-4: Efficiency of two generations of cells tested at 30°C from 70% to 30% SOC

Figure III.D.5-5 shows the entropic heat signature of the cell with regard to temperature. The battery in this figure was cycled from 0% to 100% SOC at a very low charge current, which is used to limit the ohmic heating within the cell. As shown in the figure, the battery undergoes endothermic and exothermic heat generation over the cycling range. The figure also shows how temperature affects the entropic signature of the battery during operation—the battery is endothermic at the beginning of the charge for all temperatures above 15°C. Furthermore, the data indicates that the ohmic losses in the cell dominate at temperatures below 0°C. A closer look at the graph indicates inflection points that correspond to phase changes occurring within the cathode or anode during cycling. Knowing where these phase transitions occur allows the manufacturers and OEMs to cycle their battery outside of these areas to increase the cycle life of the battery. Measuring the phase transition requires an extremely accurate calorimeter with a very stable baseline that only NREL’s calorimeters can provide for these large-format cells.

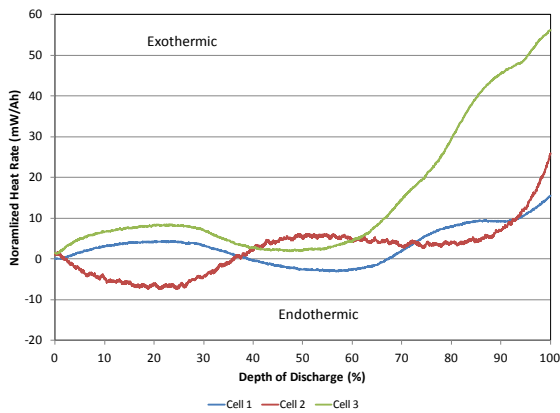


Figure III.D.5-5: Entropic heat signature of cell from 0% to 100% SOC

Infrared Imaging

NREL performs infrared (IR) imaging of battery manufacturers’ cells to determine areas of thermal concern. NREL combines the IR imaging equipment with a battery cycler to place the cells under various drive cycles, such as the US06 charge-depletion cycle for a PHEV, to understand the temperature differences within the cell. We then make recommendations to the battery manufacturers and USABC on how to improve the thermal design of the cell to increase its cycle life and safety.

Figures III.D.5-6 and III.D.5-7 show the thermal images of two PHEV cells from different manufacturers at the end of a constant current discharge—the Ah capacities of the cells are within 5% of one another. Each figure contains a thermal image of the cell at the end of the constant current discharge, as well as a plot indicating the horizontal contour lines across the face of the cell—L01, L02, L03, and L04. Figure III.D.5-6 shows a hot spot in the upper right corner of the thermal image of the cell as well as a wide spread in temperature across the face of the cell from top to bottom and left to right. Figure III.D.5-7, on the other hand, shows a very uniform temperature distribution across the face of the cell at the end of discharge. When the cell temperature is uniform and consistent, all areas within the cell age at the same rate, leading to better cycle life. NREL is working with battery developers to understand how these temperature non-uniformities affect the efficiency and cost of the cell over its life.

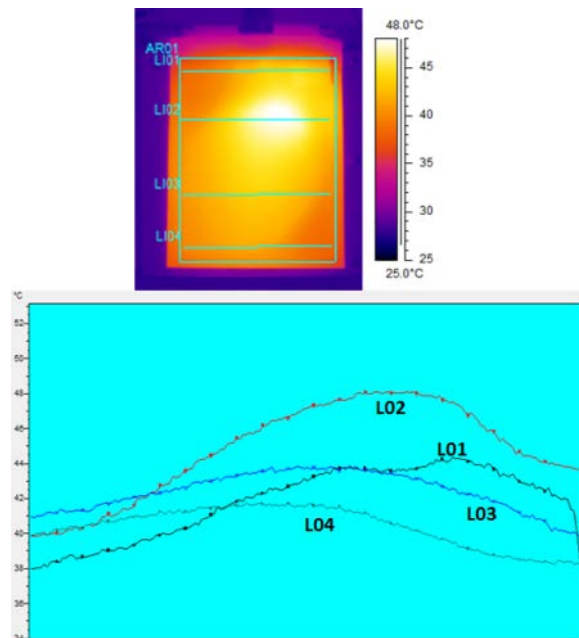


Figure III.D.5-6: Thermal image of a cell from manufacturer A under constant current discharge from 100% to 0% SOC

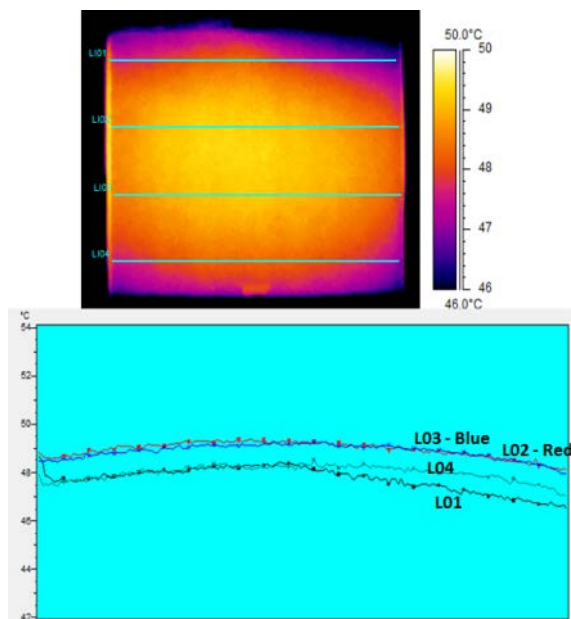


Figure III.D.5-7: Thermal image of a cell from manufacturer B under constant current discharge from 100% to 0% SOC

Pack Thermal Studies

In FY13, NREL evaluated air-, liquid-, and vapor compression-cooled packs for USABC battery developers. We measured 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. The higher temperature cells within a pack are also typically more efficient and, therefore, work harder than the cells at lower temperatures—higher temperature cells typically provide more power. If different cells within the pack provide different amounts of energy over time, then the cells age differently and may cause imbalances within the pack, resulting in possible warranty issues.

Figure III.D.5-8 shows the average cell temperature in a pack with the cooling system on and off. The pack underwent a US06 charge-depletion cycle followed by a US06 charge-sustaining cycle. The difference in temperature at the end of the charge-depletion cycle between the cooling and no-cooling case is about 1°C. The negligible change in temperature is due to the high thermal impedances between the cooling system and where the heat in the cell is generated. The coefficient of performance (COP) of the cooling system is on the order of 0.10. We are working with the battery manufacturers and OEMs to improve the temperature uniformity of the cells within a pack and the effectiveness of the thermal management system.

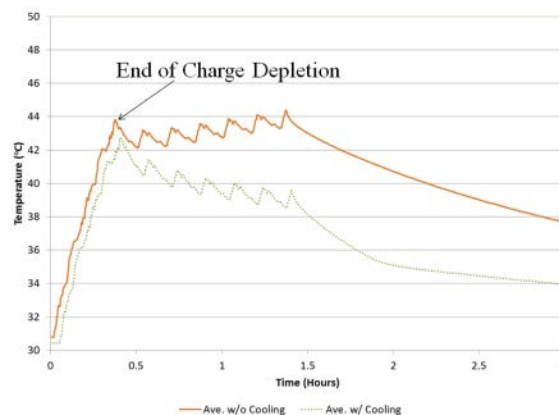


Figure III.D.5-8: Average cell temperature in a pack with and without cooling; the pack underwent a US06 CD cycle followed by a US06 CS cycle

Conclusions and Future Directions

NREL has thermally tested cells, modules, and/or packs from Actacell, Cobasys, LGCP, Johnson Controls, Quallion, K2, and SK Innovation. We've provided critical data to the battery manufacturers and OEMs that can be used to improve the design of cells, modules, and packs, and their respective thermal management systems. The data included heat generation of cells under typical profiles for HEV, PHEV, and EV applications. We found that the majority of the cells tested had a thermal efficiency greater than 93% when cycled under a 2C constant current discharge. During thermal imaging of the cells, we identified areas of thermal concern and helped the battery manufacturers with the electrical design of their cells. Finally, we evaluated multiple packs during FY13 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 FY14, NREL will continue to thermally characterize cells, modules, and packs for USABC, DOE, and USDRIVE.

FY 2013 Publications/Presentations

1. Thermal data was shared with the Energy Storage Tech Team and each of the individual battery manufacturers' workgroups
2. March 2013 DOE Milestone Report, "Thermal Analysis and Characterization of Advanced Lithium-Ion Batteries"
3. September 2013 DOE Milestone Report, "Thermal Analysis and Characterization of Advanced Lithium-Ion Batteries and Packs"

III.D.6 Development of an On-Demand Internal Short Circuit

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Collaborators:

Dirk Long, John Ireland, NASA, Dow Kokam, E-One Moli, Leyden

Start Date: October 2009

Projected End Date: September 2014

- The NREL ISC emulator was improved and successfully tested in cylindrical 18650 cells and a large format pouch cell

Introduction

Battery safety is the key to widespread acceptance and market penetration of electrified vehicles into the marketplace. NREL has developed a device to test one of the most challenging failure mechanisms of Li-ion batteries—a battery internal short circuit.

When battery internal shorts occur, they tend to surface without warning and usually after the cell has been in use for several months. While some failures simply result in the cells getting very hot, in extreme cases, cells go into thermal runaway, igniting the device in which they are installed. The most publicized failures involved burning laptop batteries, and resulted in millions of recalls, as well as consumer injuries and lawsuits.

Many members of the technical community believe that this type of failure is caused by a latent flaw that results in a short circuit between electrodes during use. As electric car manufacturers turn to Li-ion batteries for energy storage, solving these safety issues becomes significantly more urgent.

Due to the dormant nature of this flaw, battery manufacturers have found it difficult to precisely identify and study. NREL's device introduces a latent flaw into a battery that may be activated to produce an internal short circuit. NREL uses the internal short circuit device to better understand the failure modes of Li-ion cells and to validate NREL's abuse models.

The device can be placed anywhere within the battery, and can be used with both spirally-wound and flat-plate cells containing any of the common Li-ion electrochemical systems. Producing a true internal short, the device is small compared to other shorting tools being developed by the industry, and does not rely on mechanically deforming the battery to activate the short, as do most other test methodologies. With the internal short in place, the battery can be used and cycled within normal operating conditions without activating the internal short device. This allows the battery to be aged prior to activation.

The internal short produced by NREL's device is consistent and is being developed as an analysis tool for battery manufacturers and other national laboratories as well as OEMs. This has broad-reaching applications as automakers bring electrified vehicles to market in larger numbers.

Objectives

The objective of this effort is to establish an improved internal short circuit (ISC) cell-level test method that:

1. Replicates a catastrophic field failure due to latent flaws that are introduced during manufacturing
2. Demonstrates the capability to trigger all four types of cell internal shorts
3. Produces consistent and reproducible results
4. Allows the cell to behave normally until the short is activated—the cell can be aged before activation
5. Establishes test conditions for the cell—SOC, temperature, power, etc.
6. Provides relevant data to validate ISC models

Technical Targets

It is critical for any new vehicle technology (including advanced energy storage systems) to operate safely under both routine and abuse conditions, which can include conditions of high temperature, overcharge, or crush. Lithium-ion cells need to be tolerant to internal short circuits.

Accomplishments

- USABC/NREL continues to make progress towards the development of an on-demand internal short circuit for lithium-ion batteries
- Our internal short circuit emulator does not affect the performance of the battery under test and can be activated without puncturing or deforming the battery

Approach

NREL conceptualized and initiated laboratory testing of an internal short that has an insulating wax layer that is wicked away by the battery separator once the melting point of the wax is reached. A graphical representation of the ISC concept is shown in Figure III.D.6-1 below.



Figure III.D.6-1: ISC schematic—not to scale

A unique feature of NREL’s internal short device is that it has the ability to simulate all four types of shorts within a battery: 1) cathode active material to anode active material, as shown in Figure III.D.6-2; 2) cathode active material to anode current collector; 3) cathode current collector to anode active material; and 4) cathode current collector to anode current collector, also shown in Figure III.D.6-2. Furthermore, the resistance of the short can be tuned to simulate a hard (more energetic) or soft (less energetic) short. Once the short is activated, the positive and negative components of the battery are internally connected within the cell and an internal short circuit begins.

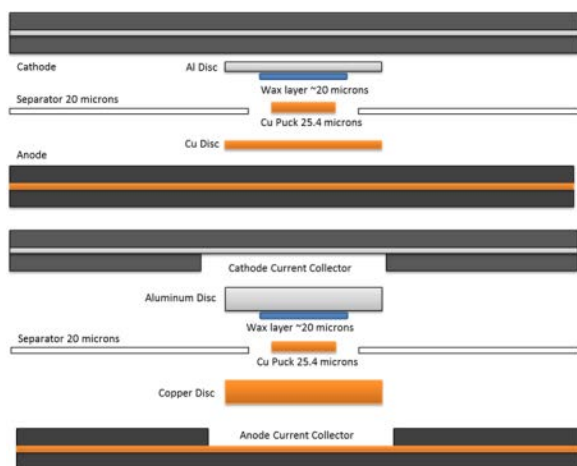


Figure III.D.6-2: Cathode-to-anode ISC (top) and collector-to-collector ISC (bottom)—not to scale

Results

In FY12, NREL developed a spin coating apparatus to evenly distribute a thin layer of wax across the aluminum disc of the ISC. We performed design experiments on wax type, wax mixture, spin temperature, spin coating speed, amount of wax, and duration of spin coating. After several months of testing and modifying the various input parameters, we were able to attain a uniform coating of wax, approximately 15 μm thick, where the copper puck contacts the wax surface. The thin coating was then tested to determine how much pressure could be applied to the wax without premature activation. The pressure tests showed that the ISC could withstand pressures exceeding 780 psi without premature activation, and, using this data, we developed a go/no-go gauge for the ISCs to be placed in cells. Finally, we reduced the burrs on the metal components of the ISC through manufacturing improvements—we did not want to accidentally introduce a flaw into the battery that would generate an unwanted internal short.

During FY13, we took the improved ISC and incorporated all four types of shorts in an 8 Ah Dow Kokam cell (prismatic stacked pouch). Figure III.D.6-3 shows the device implanted in the DK 8 Ah pouch cell.

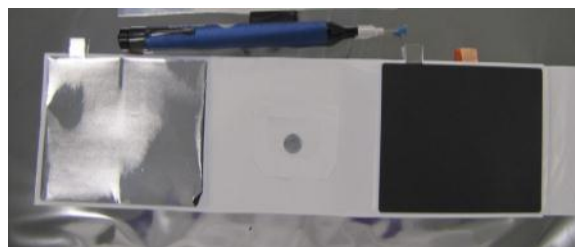


Figure III.D.6-3: ISC placed in DK 8 Ah cell; note the actual diameter of the short (Cu puck) is 0.125"

Figure III.D.6-4 shows the voltage response to all four types of activated ISCs within the DK cell at 10% SOC. NREL’s previous modeling indicated that different types of shorts should exhibit different voltage and temperature responses within the cell. In particular, the cathode and anode materials for most lithium cells have high impedances as compared to the aluminum or copper electrode/collector material. Thus, if the active material is part of the ISC circuit, then the voltage should decay slowly or act as a “soft” short. If there is an aluminum collector to copper collector internal short, then the voltage should drop precipitously, or act as a “hard” short. Figure III.D.6-4 confirms NREL modeling data, showing that the collector to collector (Al-Cu) short is the most severe.

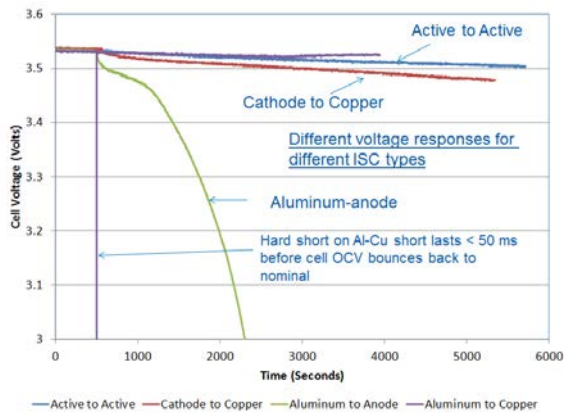


Figure III.D.6-4: Voltage response to various ISC activations in DK 8 Ah pouch cell at 10% SOC

The collector to collector short, however, only lasted about 50 ms. In order to understand why the voltage recovered after activation, NREL performed a destructive physical analysis (DPA) of the cell. The DK 8 Ah cell has multiple cathode and anode plates stacked in parallel. The ISC is in contact with only one set of these anode/cathode plates. When the ISC is activated, the remaining anode and cathode plates supply current through the aluminum (cathode) and copper (anode) tabs on the plates in contact with the ISC. The individual tabs are not meant for these high currents, though. In particular, the aluminum tab has a higher electrical resistance than the copper tab and acts as a fuse. Figure III.D.6-5 shows a macro image of an aluminum tab that melted upon ISC activation. Once the tab experienced a higher than normal current, the aluminum melted and prevented the current from flowing from the adjacent cathode plates to the ISC, effectively isolating the short circuit.

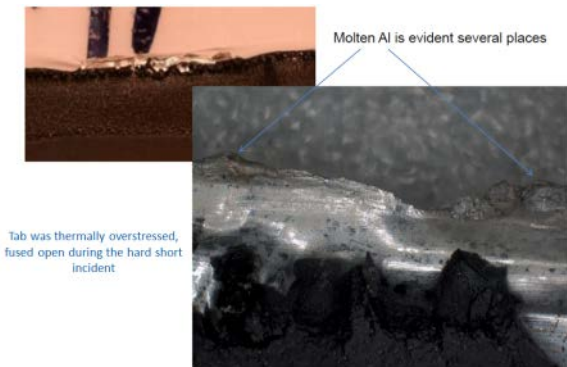


Figure III.D.6-5: Melted aluminum tab in DK 8 Ah cell upon activation of collector-to-collector ISC

NREL also performed a number of tests with the 8 Ah DK cells at 100% SOC with variable success. When an ISC is activated, gas generation quickly results. The underlying problem is that the pouch material acts as a balloon when pressurized and prevents the electrical components within the ISC from

continuing to make contact. In order to maintain contact with the ISC, we experimented with placing the pouch cell between two rigid aluminum plates, as typically occurs within a battery pack. Initial tests of this type of setup (and others) were positive, and NREL is presently assessing how these new tests work with a larger sample set.

In FY12, NREL showed good progress when combining the ISC with an E-One Moli 18650 cell. In FY13, NREL used these cells to assess if the ISC affected the performance of the cell during cycling and how safety features incorporated into the cell were affected by the type of short. NREL placed a collector-to-collector (Type 4) short and aluminum-to-anode (Type 2) short into the E-One Moli 18650 cell with the standard shutdown separator made of polypropylene (PP) and polyethylene (PE) (PP/PE/PP). The tests on both types of shorts were performed at 100% SOC. Twenty cells were fabricated for the test—10 cells with a Type 4 ISC and 10 cells with a Type 2 ISC. All 20 cells successfully went through formation and were put through 20 full discharge cycles consisting of a C/2 discharge cycle, a C/10 discharge cycle, and eighteen C/1 discharge cycles. We achieved nominal cycle stability for all 20 cells.

Table III.D.6-1 shows the Type 4 ISC activation results—7 out of 10 of the ISCs activated when the cell's temperature was brought to the melting point of the wax at 57°C. Of the seven ISCs that activated, one of the cells went into thermal runaway. Figure III.D.6-6 shows a plot of the cell temperature after activation of the Type 4 ISC. Cell #2 was the only cell to go into thermal runaway and achieved a maximum temperature of about 710°C. In the remaining six cells, the shutdown separator activated and prevented the cells from going into thermal runaway. The maximum temperature that each of these cells attained was around 120°C, which is the melting point of the polyethylene component of the shutdown separator.

Table III.D.6-1: Results from Type 4 ISC implantation in 10 E-One Moli 18650 cells

Cell	Successful Activation?	Thermal Runaway?
1	Yes	No
2	Yes	Yes
3	Yes	No
4	No	-
5	No	-
6	Yes	No
7	No	-
8	Yes	No
9	Yes	No
10	Yes	No

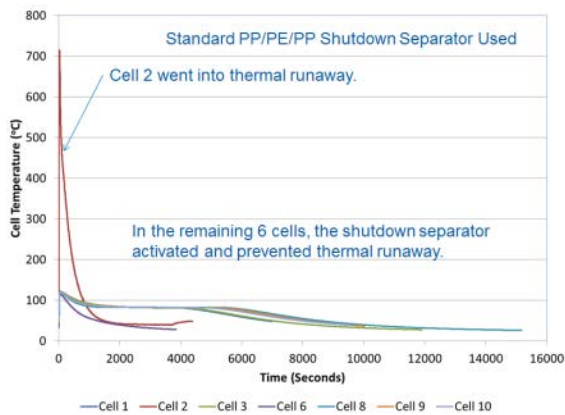


Figure III.D.6-6: Temperature response to Type 4 ISC (aluminum-to-copper) implantation in E-One Moli 18650 cells

From previous test results at lower SOCs, NREL determined that the Type 4 ISC was the most severe, but this appears to be a benefit when a shutdown separator is incorporated into the cell. The Type 4 ISC results in the quickest temperature rise within the cell and causes more of the separator to shut down more quickly. In contrast, a Type 2 ISC is more resistive than a Type 4 ISC due to the electrical resistance of the anode. The higher resistance initially delays the temperature rise within the cell and allows for more of the cell's energy to be dissipated through the ISC—the higher energy eventually overwhelms the separator and allows the cell to go into thermal runaway.

Conclusions and Future Directions

In summary, our goal was to develop an ISC that:

1. Is small, with a low profile, which can be implanted into a Li-ion cell, preferably during assembly
2. Is triggered by heating the cell above the melting temperature of the phase change material (wax)
3. Can handle currents in excess of 200 amps; this has already been proven in laboratory testing

4. Has impedance that is consistent and can be selected to simulate a hard or soft short
5. Can short between any of the battery components within a cell

NREL's ISC is the only ISC in development that can be used selectively to connect different components (anode, cathode, aluminum current collector, and copper current collector) within a cell. When different components within a cell are connected, there should be a different outcome. For instance, directly connecting the anode and cathode within a cell is much less likely to lead to thermal runaway than connecting the aluminum and copper current collectors. The end goal is not to send the cell into thermal runaway when activating the ISC, but to accurately simulate an emergent short.

The internal short device can be used to determine how changes to the battery affect the safety of the battery, either positively or negatively. Furthermore, the internal short can be used as a test methodology to evaluate how a battery would react to a latent defect.

NREL hopes to have the opportunity to continue researching how the type of internal short affects the performance of safety devices incorporated into lithium-ion cells. In the future, NREL hopes to use the ISC to verify the abuse models being developed by battery manufacturers and other national laboratories.

FY 2013 Publications/Presentations

1. 2013 NASA Aerospace Battery Workshop, Alabama
2. 2013 DOE Milestone Report titled, "Evaluate NREL Improved Version of Internal Short-Circuit Instigator in Large Cells"
3. Presented concept to Underwriter's Laboratory and USABC ISC working groups
4. Battery Safety Conference 2013, San Diego, CA

III.E.1 Computer Aided Engineering of Batteries (NREL)

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S. Pannala, J. Turner, ORNL

Subcontract Teams:

GM, ANSYS, and ESim
EC Power, Ford, JCI, and PSU
CD-adapco, Battery Design, JCI, and A123

Start Date: April 2010

Projected End Date: September 2015

- Large investment and long lead time in cell and pack research, design, prototyping, and test cycle—and repeating the design-build-test-break cycle many times over several iterations—increases production costs
- Lack of advanced computer-aided engineering tools to quickly design and simulate battery packs for electric drive vehicles impedes the optimization of cost-effective solutions

Technical Targets

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

Objectives

The overall objective of the CAEBAT project is to develop electrochemical-thermal software tools for design and simulation of 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 US industry with cost-shared funding 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
- Collaborate with ORNL in their development of an OAS platform to link material and battery models developed under DOE Energy Storage R&D
- Disseminate project results to the public and promote collaboration on modeling and software tools within the automotive battery community

Technical Barriers

- Cost, life (calendar and cycle), high performance at all temperatures, and safety are barriers for widespread adoption of lithium-ion batteries in EDVs

Accomplishments

- In mid FY11, after a competitive procurement process, NREL entered into subcontract agreements with three industry-led teams to develop CAEBAT tools with 50-50 cost sharing
- Three subcontract teams started the technical work in July 2011:
 - **CD-adapco** (teamed with Battery Design LLC, Johnson Controls-Saft and A123 Systems); NREL technical monitor: Kandler Smith
 - **EC Power** (teamed with Pennsylvania State University, Johnson Controls Inc., and Ford Motor Company); NREL technical monitor: Shriram Santhanagopalan
 - **General Motors** (teamed with ANSYS and ESim); NREL technical monitor: Gi-Heon Kim
- In FY13, NREL continued to monitor the technical performance of the three subcontract teams through monthly conference calls, quarterly review meetings, and annual reports with DOE/HQ; quarterly review meetings took place at subcontractor sites, NREL, and DOE/HQ
- The three subcontractors have already delivered the first version of their software tools to end users, and are on track to deliver software tools to the industry by the end of their period of performance

(specific progress for each subcontract is provided in Section III.E of this report)

- The following are major accomplishments from each team in FY13:
 - **CD-adapco** delivered the overall modeling framework, both electrochemical and thermal, for spirally-wound cells in the computer-aided engineering tool STAR-CCM+; JCI validated the model
 - **EC Power** developed and delivered improved versions of ECT3D software to Ford, JCI, and NREL for evaluation, and performed localized current distribution measurement in large-format cells for model validation
 - **GM and ANSYS** delivered the first battery pack-level software tool to team members for evaluation; the team also completed validation of the tool with electrochemical-thermal testing of a 24-cell module
- NREL collaborated closely with ORNL on evaluation of elements of the OAS, such as battery input and battery state
- NREL continued its electrochemical-thermal modeling of cells through the MSMD platform for CAEBAT; particularly, NREL accomplished the following:
 - Developed the Discrete Particle Diffusion Model (DPDM) as an advanced option for the MSMD particle domain model
 - Solved solid-phase lithium diffusion dynamics and transfer kinetics in a discrete diffusion particle system with the DPDM

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 was 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, life, and cost. The work would address the existing practices under which battery and pack developers operated—tediously experimenting with many different cell chemistries and geometries in an attempt to produce greater cell capacity, power, battery life, thermal performance and safety, and lower cost. Introducing battery simulations and design automation at an early stage in the battery design life cycle, would make it possible to significantly reduce product cycle time and cost, thus significantly reducing the cost of the battery. Despite extensive modeling efforts at national laboratories, universities, private companies, and other institutions to capture the electrochemical performance, life, thermal profile, and cost of batteries, including NREL's development of an electrochemical-thermal model of lithium-ion cells with three-dimensional geometries, these tools were not integrated with a 3-D computer-aided engineering (CAE) approach, which automotive engineers routinely use for other components. In many industries, including automotive and combustion engine development, CAE tools have been proven pathways to:

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

DOE initiated the CAEBAT project to extend these improvement pathways to battery CAE tools to the benefit of the entire industry. The CAEBAT project is broken down into four elements, as shown in Figure III.E.1-1:

- Material- and component-level models (developed under the BATT and ABR program elements of DOE Energy Storage R&D)
- Cell-level models
- Pack-level models
- Open architecture software to interface and link all models, particularly those from national labs

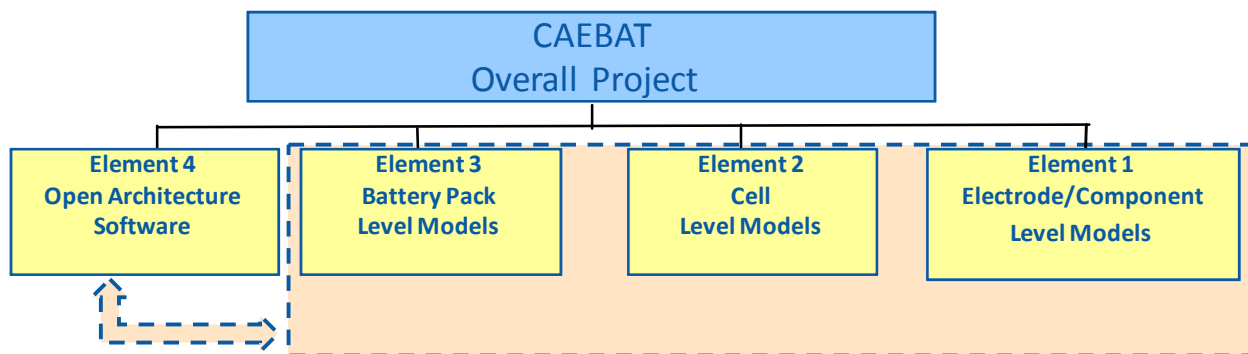


Figure III.E.1-1: The four elements of CAEBAT activity

Since the goal of CAEBAT is to develop suites of software tools for automobile manufacturers, battery developers, pack integrators, and other end users, involvement by industry (car makers, battery developers, and pack integrators) in the CAEBAT activity, particularly for Elements 2 and 3 (development of cell and pack models), is essential. DOE's major strategy to address this was to solicit active participation of industry partners in the development of cell and pack software tools from the beginning of the project.

To oversee the successful execution of the CAEBAT program, DOE designated NREL as the overall project coordinator, with the project tasks divided as follows:

- *Cell-Level Modeling and Pack-Level Modeling*: performed by industry, national laboratories, and academia; coordinated by NREL
- *Open Architecture Software*: performed by national laboratories; coordinated by ORNL

In order to engage serious involvement of the industry, NREL, with guidance from DOE, issued a Request for Proposals (RFP) in FY10 for the development of cell and pack battery design tools over a period of three years with 50-50% cost sharing. Teams led by CD-adapco, GM, and EC Power were awarded subcontracts, and the technical work began in July 2011. Additionally, NREL continued development and improvement of 3D electrochemical-thermal models, and collaborated with ORNL on development of open architecture software.

Results

Subcontracts with Industry

Significant progress has been reported by each subcontractor, according to each team's statement of work, and initial versions of their software tools have been released. More details on GM's progress may be found in Section III.E.3 of this report. CD-adapco's progress is described in Section III.E.4. Finally, Section III.E.5 provides details on the progress made by

EC Power. A summary of major accomplishments for each subcontractor is provided below.

GM

- Delivered several cell-level software tools
 - NREL's MSMD framework implemented in FLUENT with three electrochemistry sub-models
 - Cell-level validation completed for equivalent circuit model (ECM) and Newman, Tiedemann, Gu, Kim (NTGK) model; validation of pseudo-2D (P2D) model in progress
 - Developed user-defined electrochemistry capability allowing users to apply their own models while utilizing FLUENT's battery framework
- Delivered first pack-level software tool to GM, NREL, and ESim
 - Auto electrical connection by detecting cell configurations in the pack
 - Built in internal electric circuit model to speed up potential field convergence in the pack
- Completed cycle life test at room temperature with 30% capacity fade
 - Cycle life test at elevated temperature in progress
 - Physics-based cycle life model has been developed
- Completed pack-level validation for 24-cell module (Figure III.E.1-2)
 - Full field simulation validated, and satisfactory comparison with test data obtained
 - System-level model completed and validated compared to full field simulation, and test data and comparisons are satisfactory

- Linear time invariant (LTI) system-level reduced-order model (ROM) approach validated and compared to full field simulation results

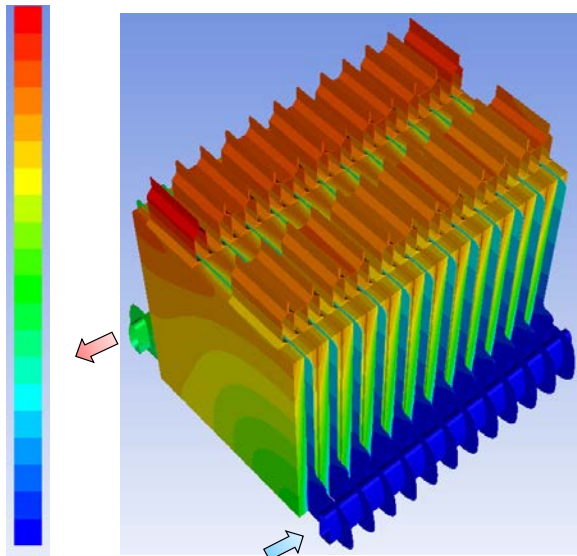


Figure III.E.1-2: Simulated temperature distribution for 24-cell module

CD-adapco

- The project has now delivered the overall modeling framework, both electrochemical and thermal, in the computer-aided engineering tool STAR-CCM+, produced by CD-adapco
- An enhanced electrochemistry model has now been created; this model has been significantly extended to include the effect of concentration dependence of the solid-phase diffusion coefficient 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 spiral cells; these have been created after the provision of cell-specific data from Johnson Controls, Inc; a process to extract unknown electrochemical properties from specific test work has been developed
- The electrochemistry model and resultant datasets have been implemented in STAR-CCM+; this implementation allows the use of parallel computations within the electrochemistry model
- A dataset of contemporary electrolytes modeled by Idaho National Laboratory (INL) has been added to the simulation environment; the dataset contains molarity, conductivity, diffusion coefficient, transport number, activity coefficient, density, and viscosity for twelve electrolytes, as shown in Figure III.E.1-3

- An approach to simulate aging within lithium-ion cells has been formulated, which considers SEI layer growth and associated capacity reduction driven by lithium loss

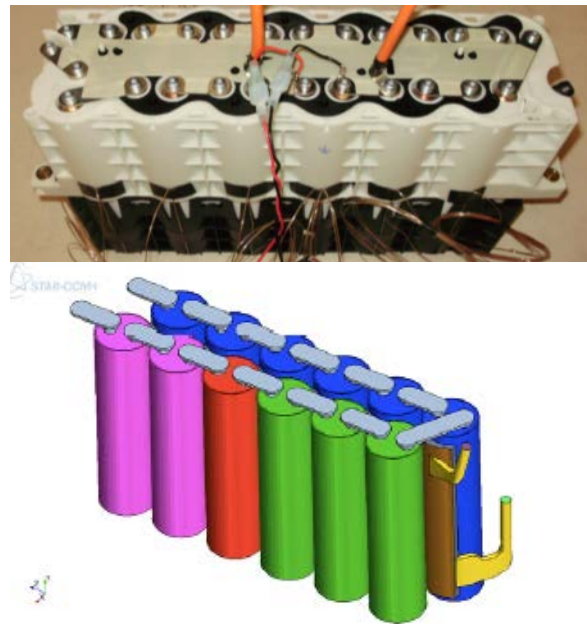


Figure III.E.1-3: Validation of electrochemical-thermal STAR-CCM+ model with 12-cell lithium-ion module

EC Power

- Released two new and improved versions of ECT3D software to Ford, JCI, and NREL
- Performed localized current distribution measurement in large-format cell for model validation (Figure III.E.1-4)
- Demonstrated compatibility with ORNL's Open Architecture Software
- Conducted software validation with JCI pack
- Delivered final safety report
- Began life testing and data acquisition

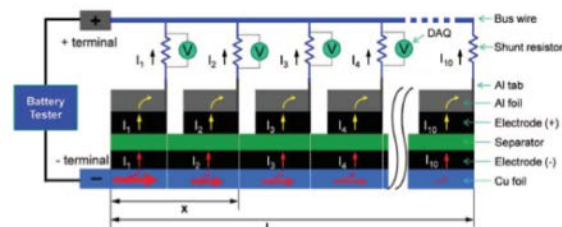


Figure III.E.1-4: Current distribution measurement in large-format cell

Collaboration with ORNL on Open Architecture Software

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

Development of Multi-Physics Battery Models at NREL

NREL continued its electrochemical-thermal cell modeling through the MSMD platform for CAEBAT. The GM team is working with NREL to incorporate the MSMD lithium-ion battery modeling framework in their CAEBAT tools. We expect this approach to lead to more efficient computational time, reducing the time required to run different battery design scenarios.

Conclusions and Future Directions

- The CAEBAT subcontract teams continued their progress toward the objectives of their respective programs; monthly technical meetings and quarterly program review meetings were held to monitor technical progress; experimental data are being collected by each team to validate the models, and first versions of cell software tools by each team have been released for partner and NREL evaluation
- Each subcontractor released first, or even third, versions of their CAEBAT software tools to selected industry end users for evaluation
- NREL continued electrochemical-thermal modeling of cells through the MSMD and collaborated with ORNL on development of the OAS to link developed and existing models
- In FY14, we will continue to monitor the technical progress of each team through monthly and quarterly meetings to ensure success; we anticipate that software tools will be released to the public for purchase and evaluation; we will also continue to collaborate with ORNL on OAS development and example problem performance

FY 2013 Publications/Presentations

1. A. A. Pesaran, Taeyoung Han, Steve Hartridge, Christian Shaffer, "Annual Progress Report on CAEBAT Subcontracts," NREL Milestone Report, September 2013
2. A.A. Pesaran, G.-H. Kim, K. Smith, and S. Santhanagopalan, "Progress of Computer-Aided Engineering of Electric Drive Batteries," presented at Vehicle Technologies Office Annual Merit Review (AMR), May 14-17 2013, Washington, DC. NREL Report No. PR-5400-58202
3. A.A. Pesaran, Matt Keyser, Gi-Heon Kim, Shriram Santhanagopalan, and Kandler Smith. "Tools for Designing Thermal Management of Batteries in Electric Drive Vehicles." Presented at the Large Lithium Ion Battery Technology & Application Symposia Advanced Automotive Battery Conference; Pasadena, CA. February 4-8, 2013. NREL Report No. PR-5400-57747
4. A.A. Pesaran, G-H. Kim, S. Santhanagopalan, and K. Smith, "Update on Computer-Aided Engineering of Batteries for Designing Better Li-Ion Batteries," presented at the USABC Technical Advisory Committee Meeting, USCAR, Southfield, MI, August 2013

III.E.3 Development of Computer Aided Design Tools for Automotive Batteries (GM)

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Subcontractors:
ANSYS Inc. and ESIM LLC

Start Date: June 2011
Projected End Date: Dec 2014

- 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 ROM is required to simulate integrated pack-level physics; however, ROM approaches for battery packs are not well understood
- Collaboration to date has been difficult to achieve since software developer commercial code, automaker electrification strategies, and battery developer cell designs and chemistry are all well-guarded intellectual property

Objectives

- 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

Technical Targets

Project goals for the GM team are summarized schematically in Figure III.E.3-1. To be useful to automotive engineers, battery cell and pack design tools should have the following analytical capabilities:

1. Predict optimum cell energy capacity in terms of electrical performance, cooling requirements, life, safety, and cost
2. Predict battery pack life for various vehicle operating conditions
3. Predict optimum SOC range for maximum life and safety
4. Evaluate battery pack thermal management by predicting max intra/inter cell temperature difference under various drive cycles
5. Ability to provide system simulations with ROM that allows for trade-off studies between the cooling cost and the battery pack warranty cost in the early stage of vehicle development
6. Ability for real-time system simulations that can lead to battery management system (BMS) development and enhancement

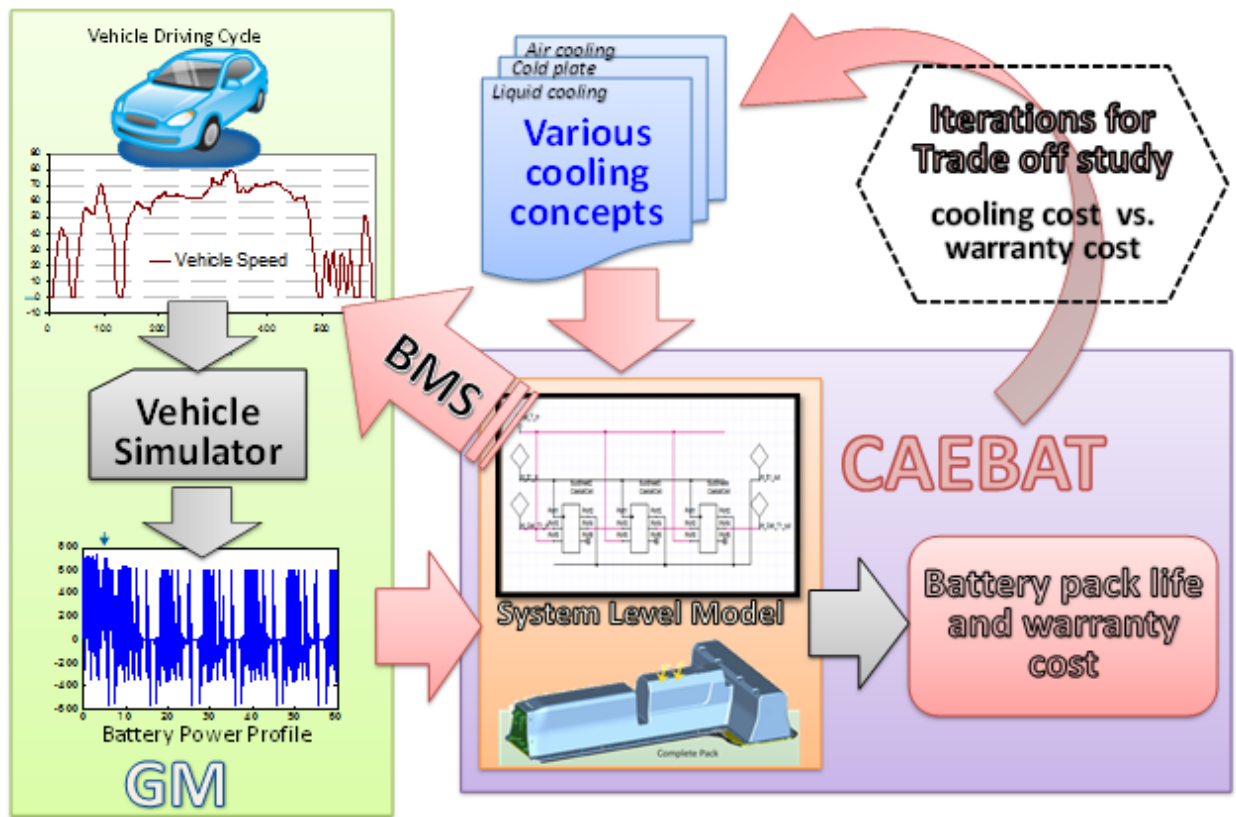


Figure III.E.3-1: Project goals for CAEBAT battery design tool development

Accomplishments

- Several software deliverables for cell-level tools:
 - NREL's MSMD framework implemented in FLUENT with three electrochemistry sub-models
 - Cell-level validation completed for ECM and NTGK models and validation of P2D model is in progress
 - Developed user-defined electrochemistry capability that allows users to apply their own models while utilizing FLUENT's battery framework
 - Detailed release note/tutorial has been provided; official public release of these tools in December 2013 (version 15)
- First pack-level software tool delivered to GM, NREL, and ESim
 - Auto electrical connection by detecting cell configurations in the pack
 - Built in internal electric circuit model to speed up potential field convergence in the pack
 - Code is completely parallelized
- Cycle life test at room temperature completed with 30% capacity fade
 - Cycle life test at elevated temperature is in progress
 - Physics-based cycle life model has been developed
- Pack-level validation completed for 24-cell module
 - Full field simulation validated, and satisfactory comparison with test data has been obtained
 - System-level model completed and validated compared to full field simulation and test data and comparisons are satisfactory
 - LTI system-level ROM approach validated in comparison with full field simulation results
 - Demonstration for various driving cycles is in progress

Introduction

The US DOE established the CAEBAT activity to develop multi-physics design tools, and NREL, with guidance from DOE, funded three subcontractors, including the GM team, to develop software tools for the program. 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 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 Professor White of the University of South Carolina and his ESim staff. In partnership with DOE/NREL, the project team will interact 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 tools. The GM team will also create interfaces to enable these new tools to interact and interface with current and future battery models developed by others. NREL has provided technical consultation and monitored the project's overall progress, and ORNL has provided the standard for the 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.

Approach

The objective of CAEBAT is to develop an open, flexible, efficient software tool for multi-scale, multi-physics battery simulation based on the ANSYS Workbench framework. ANSYS is leveraging and enhancing its 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.

ANSYS Battery Design Tool (ABDT) is a graphical user interface layer that automates and customizes battery simulation workflow using ANSYS software products. The essential role of the ABDT is to automate and integrate ANSYS tools to make the various components emulate battery applications for cell and pack capabilities. ABDT ties ANSYS building blocks together to provide a unified, intuitive simulation workflow, as shown in Figure III.E.3-2.

GM engineers and ESim tried out the sub-models and cell- and pack-level design tools, evaluated the ABDT, and provided further enhancements. The GM team also built battery module and pack prototypes and performed experimental tests to validate the tools. At the pack level, the tools will be significantly advanced by the development of innovative reduced-order models, derived and calibrated from the cell-level models, and carefully validated through experiments.

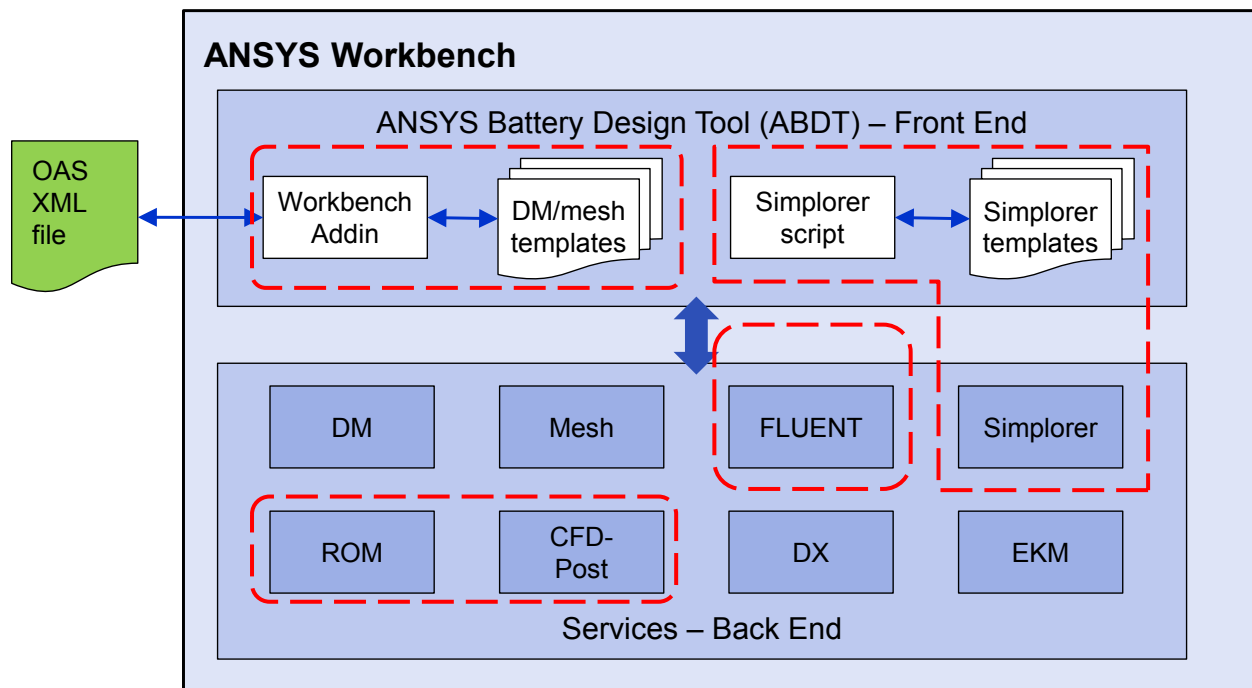


Figure III.E.3-2: ABDT software architecture for combined cell-level, pack-level, and OAS-interface capability

Results

In FY13, ANSYS delivered several versions of their cell- and pack-level battery simulation tools. First, the ECM model was enhanced to allow users to choose different functions in the charge and discharge process. Second, the electrochemistry model options were expanded, allowing customization of models or development of new ones. Users can specify system voltage, current, power, or C-rate, and the battery module is fully coupled with all other ANSYS Fluent models and physics.

Cell-level Model Validation

Validation of cell-level models with ECM and NTGK for LGCPI pouch cells (P1.4 chemistry) was also completed. Comparison with cell temperature test data is satisfactory, as shown in Figure III.E.3-3. Room temperature cycle life tests were completed and test data has been delivered to ESim for modeling.

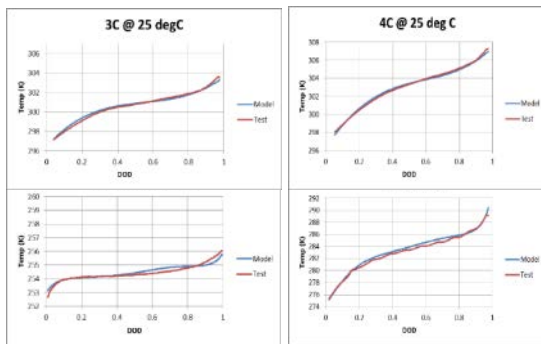


Figure III.E.3-3: Comparison of cell-level models with test data at various C-rates and operating temperatures

Wound cells with continuous tabs can be handled with capability developed previously for stacked cell configurations, but wound cells with discrete tab configuration require further developments. The GM team has developed two approaches to handle wound cell configurations with discrete tabs. The first is based on the MSMD model, which has been extended and demonstrated on wound cylindrical cell battery designs, as shown in Figure III.E.3-4. In this geometry, electric current cannot conduct radially through layers while thermal temperature can. The second approach introduces coordinate transformation and variable extrusion developed by ESim (Figure III.E.3-5). This approach significantly reduces mesh requirements and simulation time.

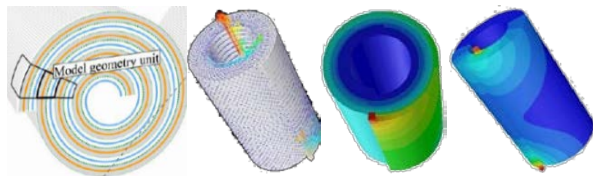


Figure III.E.3-4: Cylindrical cell simulation results based on MSMD approach

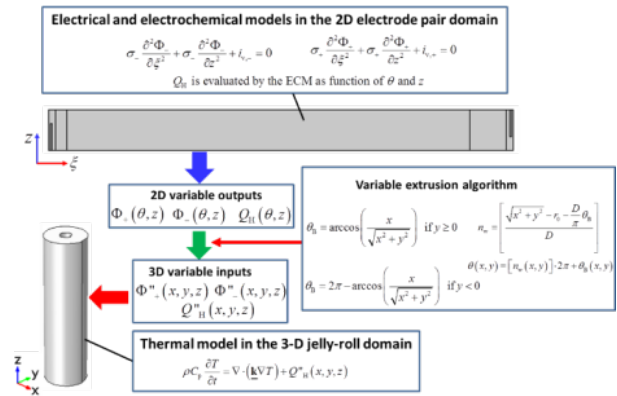


Figure III.E.3-5: Flowchart for solution procedure using coordinate transformation

ANSYS Battery Design Tool

ANSYS has developed and delivered the first version of the ABDT, which is the Workbench (WB) graphical user interface layer that automates and customizes battery simulations using ANSYS software products (Figure III.E.3-6). Within WB, the ABDT adds a new toolbox section named Battery Design Tools. In addition, in the Custom Systems section, two entries appear as the top-level templates for battery workflow. These entries, named Battery Cell Multiphysics and Battery Pack Multiphysics, follow the cell and pack organization of the CAEBAT project. Each template can also be further customized as needed. For example, a user can manually add links for data flow, or include ANSYS DesignXplorer (DX) for parametric exploration, and then store the settings back to the toolbox under Custom Systems for future use. The user can also display results based on standard visualization capabilities augmented with built-in menus for electrochemistry results.

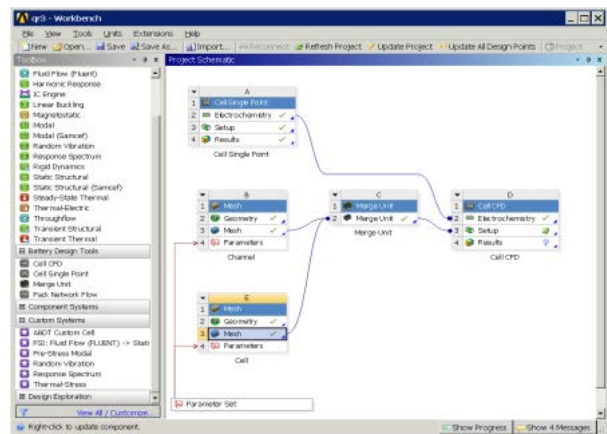


Figure III.E.3-6: ABDT cell-level design in Workbench

Customized ABDT components typically present one or more tabbed dialogs and data entry fields with default values already entered. In addition, fly-out context menus available by right-clicking components

in the project schematic can be used to access WB-standard utility functions. Both of these features can be seen in Figures III.E.3-7 and III.E.3-8.

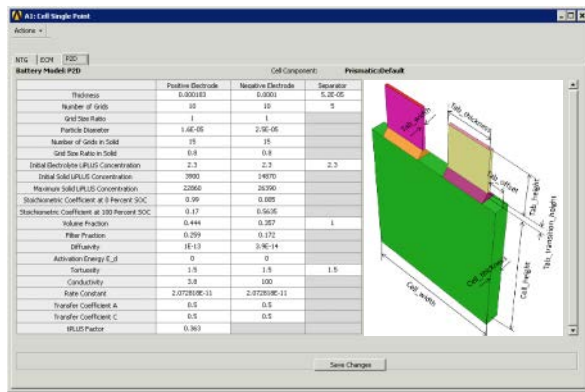


Figure III.E.3-7: Tabbed panel for P2D sub model

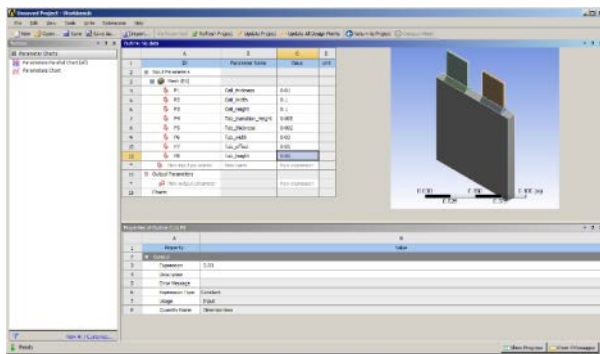


Figure III.E.3-8: Cell geometry based on parameterized templates

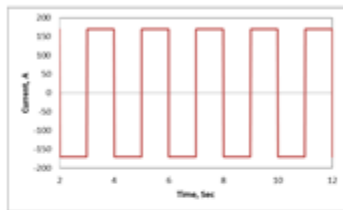
Full-field CFD Model Simulation

GM has built a 24-cell module with a liquid-fin cooling system (Figure III.E.3-9) and thermocouples located throughout to compare full-field computational fluid dynamics (CFD) simulations (Figure III.E.3-10). A full CFD model for the module was constructed by GM engineers and has been used to compare simulation results with test data. The module simulations have been verified, and most temperature comparisons are very successful, with predictions within 1°C accuracy (Figure III.E.3-11). For final validation of the pack-level tools, we will leverage existing battery pack CAE models and test data sets.



Figure III.E.3-9: Module validation test setup for full-field simulation against test data for high-frequency pulse charge-discharge

1-sec Charge/Discharge pulse
(170A) @ SOC 50%

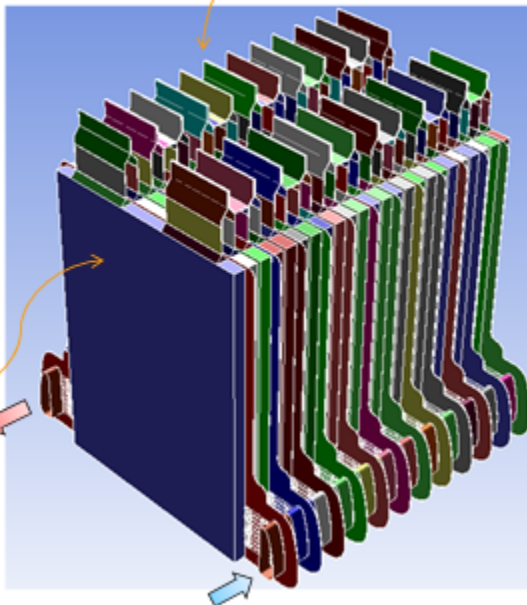


Battery Model:
Equivalent Circuit Model

Foam-facing
cell walls: Adiabatic

Model size:
~23M cells

Tabs & bars:
Natural Convection



Ambient
Temperature:
 T_{amb}

Liquid coolant:

- constant flow rate, \dot{m}
- constant inlet temperature: T_{in}

Figure III.E.3-10: 24-cell module CFD full-field simulation

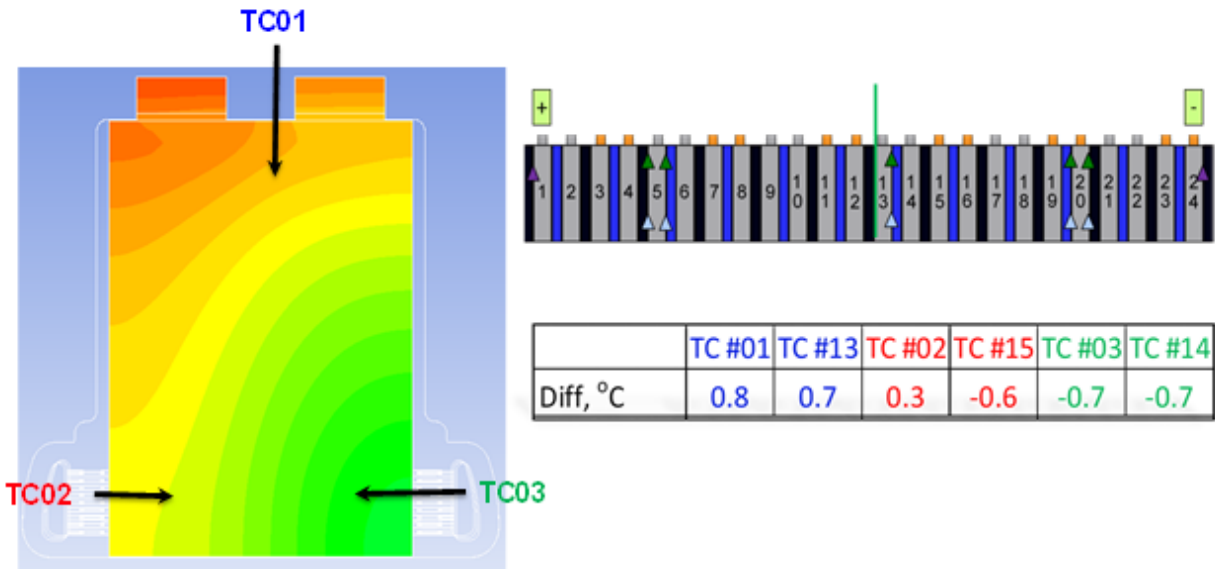


Figure III.E.3-11: Temperature comparison between full-field simulation and test data

System Simulation

ANSYS has developed a layered software approach to balance automation and flexibility, which is analogous to the cell-level approach, with mesh templates and ABDT. An automated, intuitive interface can build and solve a system-level battery pack model using ANSYS Simplorer, with the option to represent selected items in the pack using CFD models and/or ROMs derived from CFD. This tool captures the effects of manifold geometry, coolant properties, and flow distribution through the micro-channels, and produces a look-up table for mass flow rate distribution among cells for Simplorer system simulations.

In FY13, the GM team continued making progress on full battery pack simulation and development of linear and nonlinear ROMs. Research and development has also continued on algorithms for an LTI ROM. In order to validate the LTI ROM with respect to test data, GM engineers built it from a set of pre-generated Fluent step-responses. The LTI ROM was then validated against realistic US06 drive cycles, as shown in Figures III.E.3-12 to III.E.3-15.

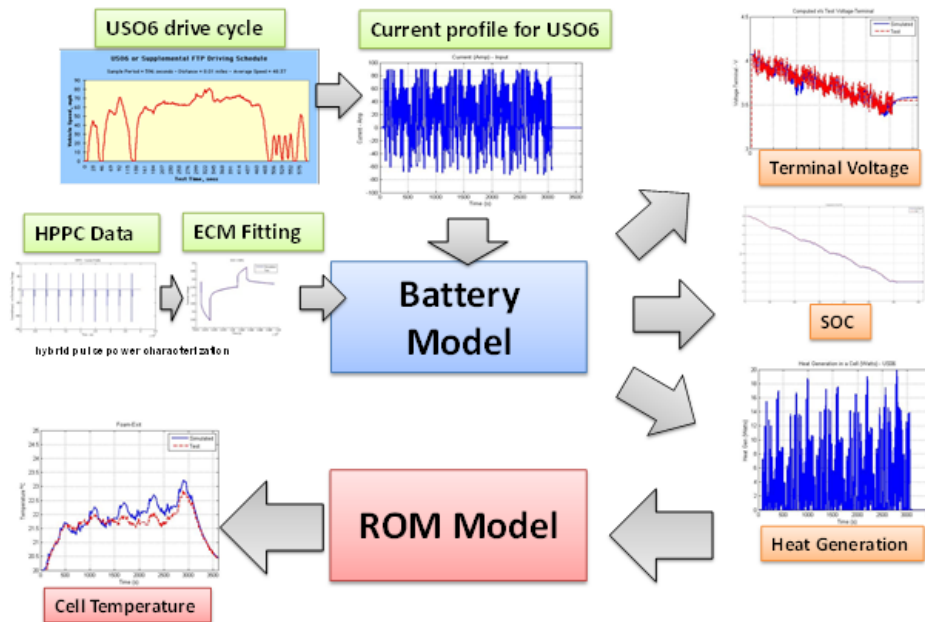


Figure III.E.3-12: LTI ROM system modeling approach for battery thermal modeling



Figure III.E.3-13: Module validation test setup for LTI ROM validation against test data for US06 drive cycle

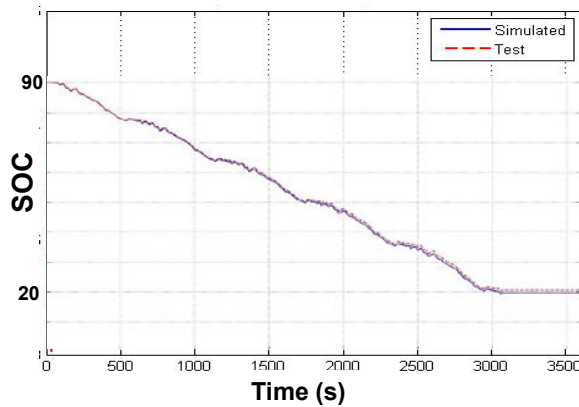


Figure III.E.3-14: Comparison of SOC between model and test data during US06 drive cycle

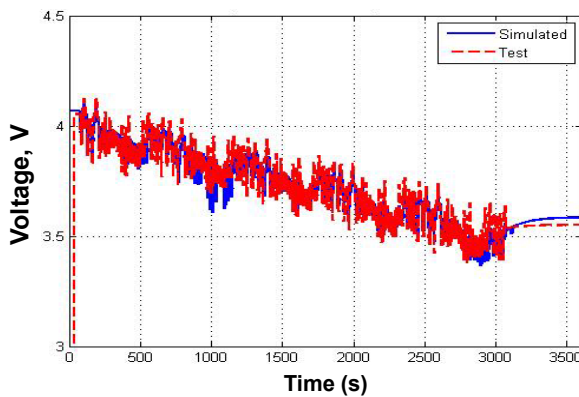


Figure III.E.3-15: Comparison of voltage during US06 drive cycle

A highly-accurate CFD/thermal model was employed to generate the training data for ROM creation. Validation of the linear ROM system simulations for the 24-cell module was completed and the predicted temperatures were within 1°C in comparison with test data at various cell locations, as shown in Figure III.E.3-16. The GM team has also developed a procedure to obtain empirical parameters

from HPPC test data that performs and accurately predicts load voltage, and thus, heat generation in cells under various drive cycles. Heat generation in tabs and interconnects is also included in LTI ROM simulations.

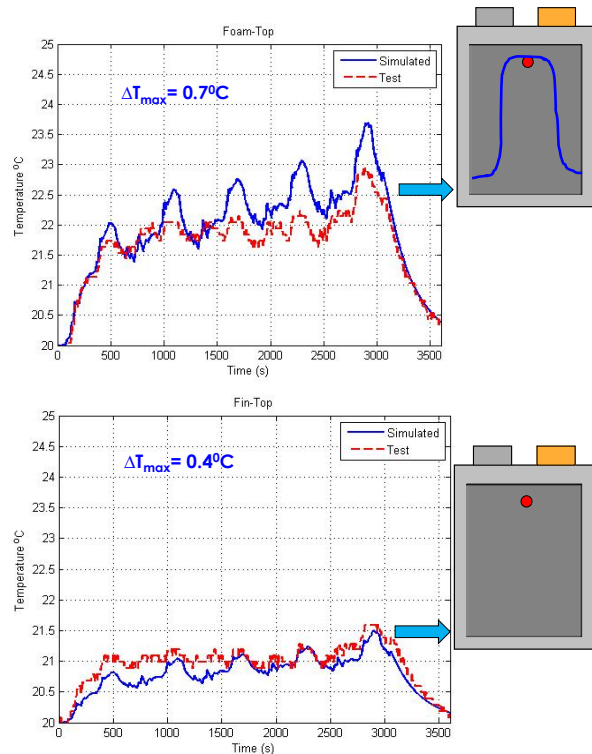


Figure III.E.3-16: US06 drive cycle cell temperature comparison

Simulation of the five back-to-back US06 drive cycles, representing a total of 30 minutes of drive cycle time, took less than a few seconds of computational time with the LTI ROM. Training data generation, using the CFD model of a 2-cell/1-fin unit, took roughly seven hours for two million cells on a high-performance computer (HPC) using 64 CPUs. The agreement for cell total heat generation is satisfactory compared with measured total heat rejection by the coolant mass flow rate and the coolant temperature difference between the inlet and the outlet. We demonstrated that the LTI ROM accurately characterizes thermal behavior of the cells in the 24-cell module.

Conclusions and Future Directions

Overall, the project is on-track to meet all objectives, and year 2 technical progress is consistent with the project plan.

1. Develop non-linear model order reduction methods for the pack level
2. Extend cell-level models for aging and abuse, with multiple active materials

3. Define pack-level validation requirements for production battery packs to meet the future capability matrix for pack-level CAE
4. Build a standard data exchange interface based on specifications from the OAS workgroup
5. Apply battery design tools to future vehicle programs and justify the value of the CAEBAT project
6. An updated and validated version of the software will be available in FLUENT/SIMPLORER from ANSYS in July 2014

Acknowledgment

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

FY 2013 Publications/Presentations

1. Xiao Hu, Scott Stanton, Long Cai, Ralph E. White, "Model order reduction for solid-phase diffusion in physics-based lithium ion cell models," *Journal of Power Sources* 218 (2012) 212-220.
2. Meng Guo, Ralph E. White, Gi-Heon Kim "A distributed thermal model for a Li-ion electrode plate pair," *Journal of Power Sources* 221 (2013) 334-344.
3. Meng Guo, Gi-Heon Kim, Ralph E White, "A three-dimensional multi-physics model for a Li-ion battery", *Journal of Power Source*, 240 (2013) 80-94.
4. Saeed Asgari, Xiao Hu, Michael Tsuk, Shailendra Kaushik, "Application of POD plus LTI ROM to Battery Thermal Modeling: SISO Case, to be presented in 2014 SAE World Congress.
5. Ramesh Rebba, Justin McDade, Shailendra Kaushik, Jasmine Wang, Taeyoung Han, "Verification and Validation of Semi-Empirical Thermal Models for Lithium Ion Batteries ," to be presented in 2014 SAE World Congress.

III.E.4 Development of Computer Aided Design Tools for Automotive Batteries (CD-adapco)

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Subcontractor:
Battery Design, LLC

Start Date: August 2011
Projected End Date: July 2014

Objectives

- As one of the subcontract teams, support DOE/NREL CAEBAT activity
- Provide simulation tools that expand the inclusion of advanced lithium-ion battery systems into ground transportation
- 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 governing fundamental equations within lithium-ion battery cells to enable advanced electrochemical models to be used in module and pack simulations

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 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 several categories, so flexible templates are necessary. Users then provide appropriate data to populate the templates, creating a complete electrochemical and thermal cell model. The creation of such

electrochemical and thermal templates and the 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 challenging. 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 including two electrodes, one positive and one negative, that are wound together to create a spiral jellyroll; this method should resolve 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 subcontractors, including both cylindrical and prismatic forms of spiral cells, as well as power- and energy-focused chemistry
- Use the validated methods within a larger framework to create simulations of battery modules that include such cells; these methods will be validated against electrical and thermal results from appropriate battery modules

Accomplishments

- The project has now delivered the overall modeling framework, both electrochemical and thermal, as described above, into the computer-aided engineering tool STAR-CCM+, produced by CD-adapco
- An enhanced electrochemistry model has now been created from the original model based on the work of Newman, et al.; this model has been significantly extended to include the effect of concentration dependence of the solid phase diffusion coefficient 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

- The above listed electrochemistry model and datasets has also been implemented in STAR-CCM+; the implementation allows the use of parallel computations within the electrochemistry model; this development addresses one of the major drawbacks often repeated regarding Newman-type models, which is the runtime of the calculation
- 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

Introduction

The US DOE established the CAEBAT activity to develop multi-physics design tools, and NREL, with guidance from DOE, funded three subcontractors, including CD-adapco, to develop software tools for the program. 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 development created additional coding and methods which focus on the electrochemistry analysis of the spirally-wound electrodes. This coding has been developed in collaboration with Battery Design, LLC., a subcontractor 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 the tabbing of the electrode in the overall performance.

This model has now been applied to the lithium-ion cells listed below, excluding the pouch cell, where an empirical model was used.

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

The inclusion of a pouch cell to this project is to provide a control through which to validate the results for analysis methods on components around the cell itself. The A123 test work includes considerable measurements from the conducting components around the cells to ensure their thermal and electrical effects are also represented correctly.

Approach

Detailed design information was obtained from the cell supplier to describe the dimensions of the electrode, the details of the can, and 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 INL (also part of this project). Tightly controlled cell-level test work was specified to enable the remaining modeling parameters to be extracted. This has now been done for all four 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

Once the electrochemistry models were fully defined and confirmed using controlled cell test work, 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 was compared with experimentally-obtained voltage curves. Validation results are shown below in Figure III.E.4-1.

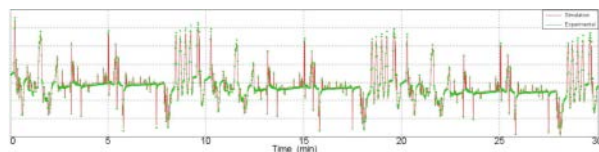


Figure III.E.4-1: Voltage response for JCI VL6P cell over 30min drive cycle compared to test work (voltage scale removed)

The mean error for the VL6P simulation model (Figure III.E.4-2) over the 30-minute drive cycle is 9mv. Similar error levels are seen in the other models (as in Figure III.E.4-3).

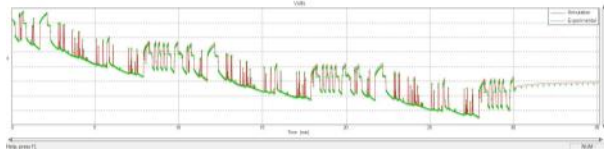


Figure III.E.4-2: Voltage response for JCI VL41M cell over 30min drive cycle compared to test work (voltage scale removed)

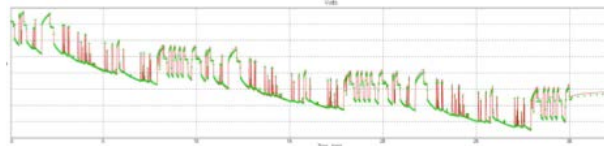


Figure III.E.4-3: Voltage response for PL27M cell over 30min drive cycle compared to test work (voltage scale removed)

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 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. Figure III.E.4-4 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 modeling domains, hence engineers can use the same cell data within either modeling framework, lumped or detailed 3D.

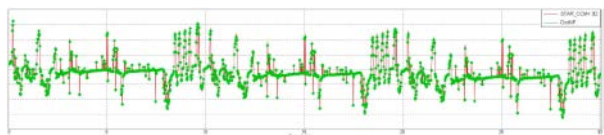


Figure III.E.4-4 Comparison of lumped electrochemistry model vs. 3D electrochemistry model over 30min drive cycle (voltage scale removed)

Thermal

Thermal validation was completed using the 3D model within STAR-CCM+, and module test work for the VL6P, PL6P, and PL27M is now complete. Figure

III.E.4-5 shows the VL6P-12 module that is used for the module tests. This arrangement is liquid cooled.

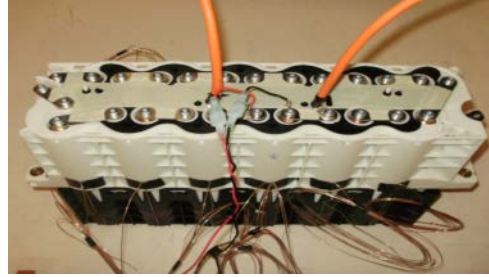


Figure III.E.4-5: Liquid-cooled VL6P-12 module used for module testing

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 the coolant system.



Figure III.E.4-6: STAR-CCM+ model of cell components

A number of thermocouples were located on the cell of interest, and Figure III.E.4-7 shows one result compared to the appropriate test result. These thermocouples were located on the outer surface of the cell can. The scales have been removed, as this is sensitive data.

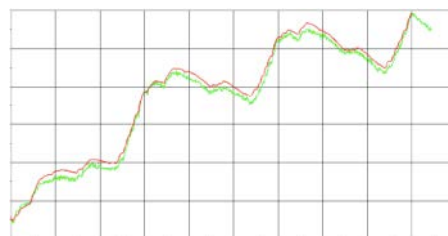


Figure III.E.4-7: Thermal result for cell within VL6P module (red line is simulation, green is experiment)

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.

Electrolyte

Complimentary to the core simulation technology, a suite of contemporary electrolytes has been added to the database to enable users to rapidly select appropriate properties. These are used within the overall electrochemical models that represent the cells. As a sample of the data, Figure III.E.4-8 shows the conductivity of EC31_PC10_DMC59_LiPF₆ compared to published data by Valoen, et al.

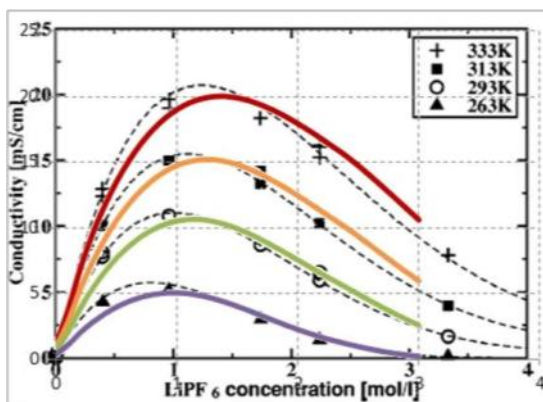


Figure III.E.4-8: Conductivity of LiPF₆ in PC/EC/DMC as a function of LiPF₆ concentration for 333, 313, 293, and 263 K

The electrolyte properties were used in a physics-based model to correlate discharge energy as a function of rate and temperature to electrolyte properties.

Conclusions and Future Directions

The project is 2/3 complete. The described flow, thermal, and electrochemistry simulation architecture is now established, and differing modeling domains—lumped and three-dimensional—are available. Cell- and module-level test work is now complete, and validation of the lumped electrochemical model has been presented. A comparison of the modeling domains has been performed, and the differences between results are expected and explainable. Finally, the complex three-dimensional domains for the module-level validation are constructed and a thermal result is presented. The technology developed in this project is now contained within the three-dimensional computer-aided engineering code STAR-CCM+, which is commercially available from CD-adapco. An updated and validated version of the software will be available from CD-adapco in July 2014.

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 US Department of Energy, specifically Dave Howell and Brian Cunningham. The authors would like to acknowledge the subcontractors, namely JCI Inc. and A123 Systems, for their support in sharing some of the results from this work.

III.E.5 Development of Computer Aided Design Tools for Automotive Batteries (EC Power)

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Subcontractors:

Ford Motor Company

Johnson Controls, Inc.

Pennsylvania State University

Start Date: May 2011

Projected End Date: May 2014

Objectives

- Develop an 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 set them apart from the 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 new versions of large-format software tool, ECT3D, to partners during FY13; updates include additional safety features and capabilities, enhanced user interfaces, and upgrades based on Ford, JCI, and NREL user feedback
- Property characterization for materials database ~80% complete
- Cell in-situ current distribution measurements at varying C-rates and temperatures complete; data used for initial validation, additional validation to be performed in final year of project
- Initial life models complete
- Demonstrated compatibility of ECT3D with OAS developed by ORNL

Introduction

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

The design, build, and test process for batteries and packs is extremely time consuming and expensive. Additionally, many technical characteristics of batteries and packs that are critical to battery performance and safety are impossible to measure experimentally. EC Power's code, ECT3D, directly addresses the issues related to the design and engineering of automotive batteries in a virtual environment.

The use of advanced software such as ECT3D allows the design engineer 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 is developing large format Li-ion battery simulation software to analyze battery cells and packs for electrified vehicles. Team member Pennsylvania State University is primarily responsible for performing materials characterization experiments and diagnostic experiments for multi-dimensional validation. The materials characterization experiments will supply data for the extensive materials database being incorporated into ECT3D. Significant progress has been made, and is ongoing in this area.

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

Figures III.E.5-1 and III.E.5-2 illustrate a pack simulation investigating the effects of thermal management on cell balancing for a 2.8 kWh battery pack, consisting of a serially connected string of 12 "cell groups"; each cell group contains two cells in parallel. The pack is initially at -10°C and undergoes a 1C discharge, along with heating by warm air pre-heated at 50°C . Figure III.E.5-2 highlights a current imbalance, as a result of cell 1 remaining substantially

colder than its parallel-connected partner, cell 2, during pack heating. Such current imbalance will have substantial impact on pack life, safety, and performance.

This pack simulation of a 1-hour discharge took only 15 minutes on an 8-CPU workstation. Only a thermally-coupled battery pack model is capable of capturing this type of thermally-driven cell imbalance.

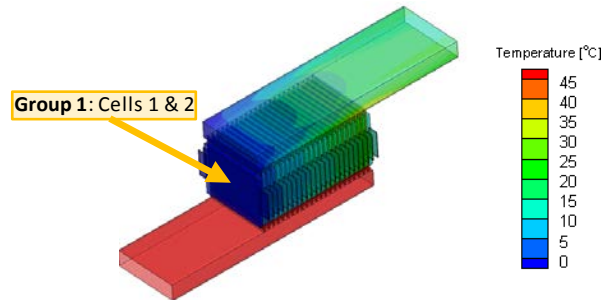


Figure III.E.5-1: Thermal contours at $t=500$ sec under cold-start discharge scenario

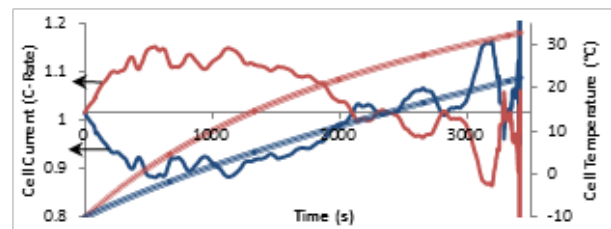


Figure III.E.5-2: Current and temperature of cells 1 and 2 (group 1); cell 1: blue, cell 2: red

Figure III.E.5-3 illustrates some of the ongoing work on intra-cell current measurement and model validation. Specifically, the figure shows the measured normalized current distribution ($I_{\text{local}}/I_{\text{average}}$) over the length of an electrode sheet (x/L), shown over cell depth of discharge (DoD), for a 1C discharge current at 21°C . The results highlighted in figure III.E.5-3 are for a cell with one positive tab and one negative tab with the tabs co-located at $x/L = 0$. Data for additional temperatures, C-rates, etc., has been gathered, and model validation is ongoing.

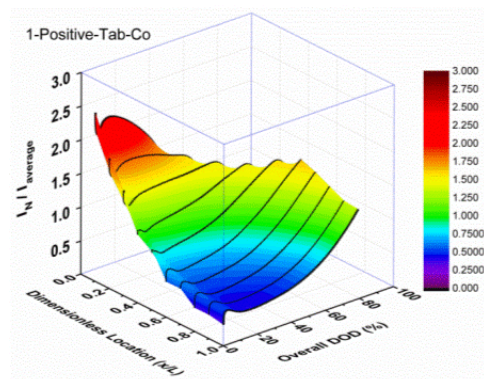


Figure III.E.5-3: Normalized current distribution over electrode sheet at 1C discharge current at 21°C

Conclusions and Future Directions

Working hand-in-hand with our industrial partners Ford and Johnson Controls, the EC Power-led team has continued to make strides in the development of our ECT3D software. In the past year, using feedback from our industrial partners and NREL, EC Power has added extra safety features and capabilities and greatly enhanced user interfaces. We have also begun detailed model validation, at both the cell- and pack-level, an activity which will continue through the end of the project.

Future work will include the following:

- Complete materials characterization and acquisition of database properties
- Final testing and validation for spatio-temporal data testing and acquisition
- Life/degradation modeling
- Additional work with Ford/JCI
 - Complete software validation
 - Continued application of software to technical challenges

FY 2013 Publications/Presentations

1. 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
2. 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
3. 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
4. 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
5. 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
6. Ji, Y., Zhang, Y., and Wang, C.Y. (2013). "Li-Ion operation at low temperatures," Journal of the Electrochemical Society, 160(4), A636-A649
7. Zhang, G., Shaffer, C. E., Wang, C. Y., & Rahn, C. D. (2013). "In-situ measurement of current distribution in a li-ion cell," Journal of the Electrochemical Society, 160(4), A610-A615
8. Ji, Y., Wang, C.Y. (2013). "Heating strategies for Li-ion batteries operated from subzero temperatures," Electrochimica Acta, 107, 664-674
9. Zhang, G., Shaffer, C.E., Wang, C.Y., and Rahn, C.D. (2013), "Effects of Non-uniform Current Distribution on Energy Density of Li-ion Cells," Journal of the Electrochemical Society 160(11), A2299-A2305

III.E.6 Battery Multiscale Multidomain Framework & Modeling

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Start Date: April 2010

Projected End Date: September 2015

Objectives

- Continue to develop models, methods, and codes in context of the MSMD, and perform multiphysics battery simulations to enhance knowledge and help accelerate adoption of electric drive vehicles
- Develop advanced option for MSMD particle domain model to address precisely-controlled particulate attribute's impact

Technical Barriers

Significant efforts continue on improving energy-power capability and reliability of batteries by controlling particulate morphology and size, modifying particle surface, or redesigning thermodynamics. However, due to the complex nonlinear interactions across wide range-scale physics, it is not straightforward to quantify such improvements for benefits in device-level response.

In the conventional macro homogeneous porous electrode model approach, first suggested by Doyle, et al., the active material was often assumed to be made up of spherical particles, with diffusion being the mechanism of transport of the lithium. Thanks to the self-balancing nature of LIBs, these macro-homogeneous model approaches have been successfully adopted to represent lithium-ion battery behaviors. However, this approach often suffers difficulties in properly representing complex kinetic/dynamic behavior.

In many practical battery systems, electrode particles are prepared in irregular shapes. However, capturing the diffusion dynamics by directly resolving three-dimensional irregular geometry of particles is too costly to apply in device-level multiscale modeling.

Technical Targets

- Provide a methodology quantifying improvements for controlling particulate morphology and size, enhancing particle surface characteristics, and modifying thermodynamics as benefits in battery device-level responses
- Provide an advanced particle domain model to effectively represent diffusion dynamics and transfer kinetics in complex transport and kinetics systems

Accomplishments

- Develop DPDM as an advanced option for MSMD particle domain model
- This model solves solid phase lithium diffusion dynamics and transfer kinetics in a discrete diffusion particle system
- The particles are considered electronically continuous, but ionically discrete
- An arbitrary number of quantized discrete particles can be given as a user input
- Kinetic, transport, and thermodynamic model parameters of each discrete particle can be independently determined

Introduction

NREL has developed the MSMD model framework, which is an expandable development platform providing pre-defined but expandable protocols and generic and modularized flexible architecture, resolving interactions among multiple physics occurring in varied length and time scales with various fidelity and complexity. NREL researchers continue to develop models (governing equations and geometries), methods (numerical/analytical solution strategies), and codes (implementation into computer programming) in the context of the MSMD, and perform computer simulations to answer scientific and engineering questions to help accelerate market adoption of electric drive vehicles. In FY12, we focused on development of cell domain models and solution methods applicable to all major cell formats, such as stacked pouch and wound cylindrical/prismatic cells. The objective of the FY13 task was to develop an enhanced particle domain model, the Discrete Diffusion Particle Model.

Approach

The well-accepted porous electrode model suggested by Doyle, et al., typically treats a composite electrode as a homogeneous porous medium, without regard for the details of its particulate geometry, thus greatly simplifying its numerical complexity. The active material is often assumed to be made up of spherical particles, with diffusion being the mechanism of transport of the lithium. Thanks to the self-balancing nature of LIBs, macro-homogeneous model approaches have been successfully adopted to represent LIB behaviors with only a few characteristic diffusion lengths. However, for better representation of complex kinetic/dynamic interactions critical in certain systems, an advanced particle model is desired to address kinetic, transport, and geometric particulate attributes, including morphology, size distribution, surface modification, and mixture composition of active materials. NREL has developed the DPDM for advanced particle kinetics as a particle-domain option of the MSMD. Solving solid phase lithium diffusion dynamics and transfer kinetics in a discrete diffusion particle system, the particles are considered electronically continuous, but ionically discrete. An arbitrary number of quantized discrete particles can be given as a user input, and kinetic, transport, thermodynamic, and geometry parameters of each discrete particle can be independently determined. The model's governing equations are shown below [1-6].

Butler-Volmer equation for charge transfer kinetics:

$$i_{\xi_s, k}^{\pm}(\bar{\xi}_s) = i_{o, k}^{\pm}(\bar{\xi}_s) \left\{ \exp \left[\frac{\alpha_a F}{RT} \eta(\bar{\xi}_s) \right] - \exp \left[-\frac{\alpha_c F}{RT} \eta(\bar{\xi}_s) \right] \right\} \quad [1]$$

$$\eta(\bar{\xi}_s) = \phi_s - \phi_e - i_{\xi_s, k}^{\pm}(\bar{\xi}_s) R_{film} - U(\bar{\xi}_s) \quad [2]$$

$$i_{o, k}^{\pm}(\bar{\xi}_s) = k_i (c_e)^{\alpha_a} (c_{s, max} - c_{s, k}(\bar{\xi}_s))^{\alpha_c} (c_{s, k}(\bar{\xi}_s))^{\alpha_c} \quad [3]$$

Fick's law of diffusion for solid diffusion in k-th particle:

$$\frac{\partial c_{s, k}}{\partial t} = \nabla_{\xi} \cdot (D_s \nabla_{\xi} c_{s, k}) \quad [4]$$

$$\nabla_{\xi} c_{s, k} \Big|_{A_{\xi}} \cdot \mathbf{n}_{\xi} = \frac{-i_{\xi_s, k}^{\pm}}{D_s F} \quad [5]$$

Kirchhoff's current law for charge conservation:

$$\bar{i}_{\xi}^{\pm} = \sum_k \frac{\int_{A_{\xi}} i_{\xi_s, k}^{\pm}(\bar{\xi}_s) dA_{\xi}}{A_{\xi}} a_{s, k}^{\pm} f_{v, k} \Big/ \sum_k a_{s, k}^{\pm} f_{v, k} \quad [6]$$

Results

Significant efforts are being invested to improve the performance and life of batteries by controlling electrode particulate characteristics. Once certain electrode materials are produced by suppliers, various battery cells can be made in combination with other components for different cell design targets. After that, the cells become building blocks integrated into larger battery pack systems operated with different control and management strategies for varied types of electrified vehicles. Therefore, it is important to understand how the changes in physical and chemical characteristics of materials impact system-level performance and life through the complex nonlinear interactions across multiple layers of design and physics. In the present study, solid diffusion length, x_s , is selected to investigate for distributed particulate characteristics: $0.5 \leq x_s \leq 5.0$ [μm]; number of discrete diffusion particle: $N=100$; uniform weight (volume) fraction for each bin: $f_{v, k}=0.01$; electrode chemistry: $\text{Li}_x(\text{NCA})\text{O}_2$; particle geometry: 1D sphere. Other model parameters commonly used for all discrete particles are summarized in Table III.E.6-1.

Table III.E.6-1: Particle-domain Model Parameters

Domain	Parameter	Value/Model
Particle		$\text{Li}_x(\text{NCA})\text{O}_2$
	Maximum Li capacity, $c_{s, max}$ [mol m ⁻³]	4.90×10^4
	Characteristic diffusion length, R , [m]	
	Stoichiometry at 0% SOC, $x_{0\%}, y_{10\%}$	0.9802
	Stoichiometry at 100% SOC, $x_{100\%}, y_{100\%}$	0.3171
	Reference exchange current density at 100% SOC, i_o^{ref} [A m ⁻²]	4.0
	- activation energy, E_{act}^{\pm} [J/mol]	3.0×10^4
	Charge-transfer coefficients, α_a, α_c	0.5, 0.5
	Film resistance, R_{film} [Ω m ²]	0.015
	Solid diffusion coefficient, D_s [m ² s ⁻¹]	3×10^{-15}
	- activation energy, E_{act}^D [J/mol]	2.0×10^4
	Positive electrode, U_s [V]	$U_s(x) = 1.638 x^{10} - 2.222 x^9 + 15.056 x^8 - 23.488 x^7 + 81.246 x^6$ $- 344.566 x^5 + 621.3475 x^4 - 554.774 x^3 + 264.427 x^2 - 66.3691 x$ $+ 11.8058 - 0.61386 \exp(5.8201 x^{12.4})$

Figure III.E.6-1 presents evolutions of particle bulk stoichiometry deviation (left) and particle bulk stoichiometry deviation (center) from system average stoichiometry and charge transfer current density (right). During discharge, smaller particles discharge

faster than larger ones. As a result, bulk stoichiometry in small particles grows higher than the system average, while large particle stoichiometry falls behind. An increase in the rate of surface stoichiometry of large particles (which is catching up the small particle's

surface stoichiometry) slows down in the middle of discharge where the equilibrium potential slope flattens. Particle surface stoichiometry tends to converge toward the end of discharge. As a result, small particles suffer from a larger depth of discharge and large particles experience a larger concentration gradient. Transfer

current densities are initially identical in all different size particles. However, the magnitudes start to diverge afterward; larger particles have larger surface current density and the magnitudes keep increasing during discharge.

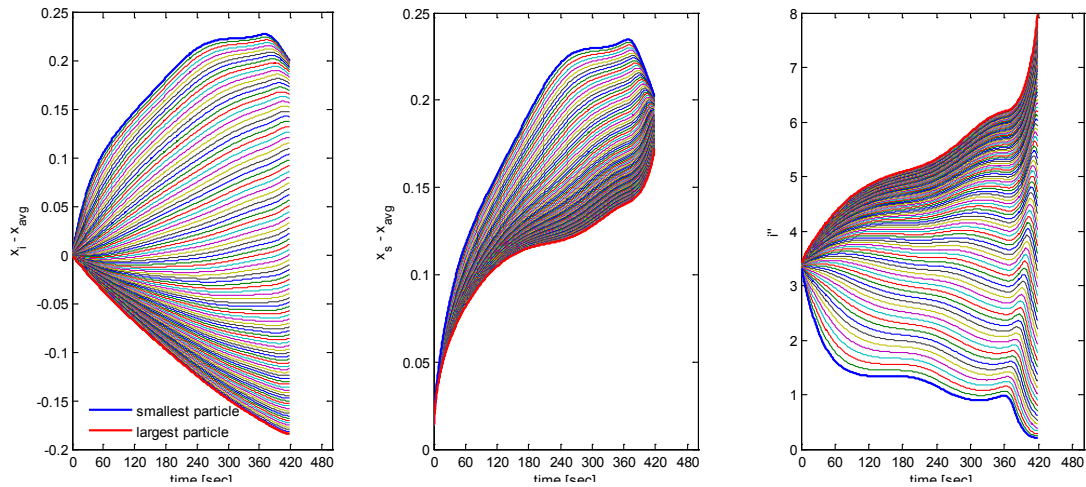


Figure III.E.6-1: Particle transfer current density and stoichiometry evolution during 6C constant current discharge (N=100)

Figure III.E.6-2, plots of particle bulk stoichiometry evolution during US06 driving cycles, shows how the environmental and design factors affect the use of active materials in batteries. Batteries made of identically-prepared NCA cathode particles (distributed in size between 0.5 μm and 5 μm) were cycled to power 20 minutes of US06-profile driving of a hybrid-electric vehicle (left), and a plug-in hybrid electric vehicle with 10-mile electric range (right). In the HEV application, particles are cycled near the predetermined SOC range. Small particles are cycled with a wider SOC window than large particles since they respond more sensitively to high frequency load variation. Both amplitude and frequency of stoichiometry (lithium concentration) is larger in small particles than in large particles. In the PHEV10

application, particle average stoichiometry increases in the initial charge-depleting stage and stays around predetermined SOC during the rest of the charge-sustaining mode. Differences in SOC among the particles tend to increase initially and reduce again during charge-sustaining mode. The change of SOC is nearly monotonous in large particles, while the SOC in small particles fluctuates. This implies that large particles respond mostly to energy demand and small particles to both power and energy demand from the system. Identical particle sets are used in significantly different patterns for different EV applications. This result emphasizes the importance of capturing such inhomogeneity to properly predict a battery's long-term aging behaviors.

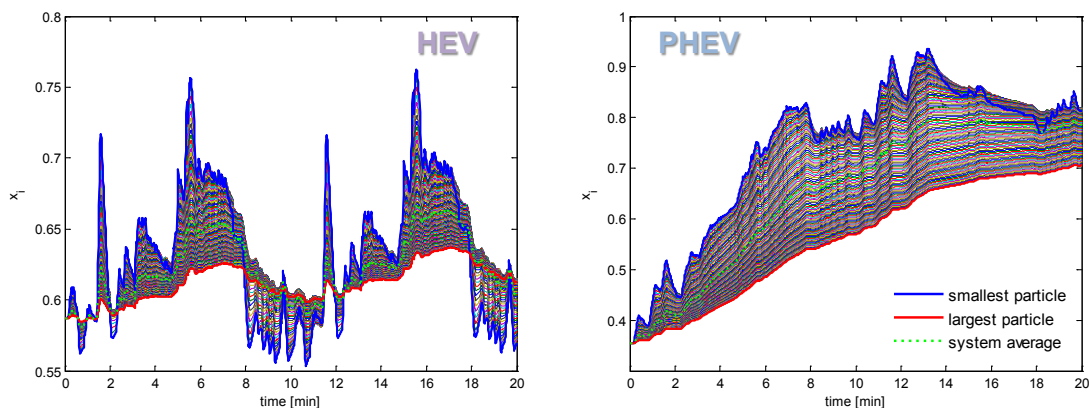


Figure III.E.6-2: Particle stoichiometry evolution during mid-size sedan HEV (left) and PHEV (right) US06 driving (N=100)

Conclusions and Future Directions

NREL developed the DPDM as an advanced option of the MSMD particle domain model. We demonstrated model applicability to a study on quantifying the impacts of distributed characteristics of electrode particulate attributes. In many practical battery systems, electrode particles are prepared in irregular shapes, and lithium transport in solid particulates and kinetics at surfaces of intricate geometry occur in complex relations. We will continue to enhance the model capability and apply it to a general procedure of identifying a reduced order representation of an irregular particle electrode system.

FY 2013 Publications/Presentations

1. 2013DOE Annual Peer Review Meeting Presentation
2. K.-J. Lee, K. Smith, A. Pesaran, G.-H. Kim, "Three dimensional thermal-, electrical-, and electrochemical-coupled model for cylindrical wound large format lithium-ion batteries", J. of Power Sources, 241 (2013) 20-32

III.E.7 Lithium-Ion Abuse Model Development

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Start Date: October 2008
Projected End Date: September 2013

Objectives

Build theoretical tools to:

- Assess the safety of large format lithium-ion batteries
- Extend the temperature range for safe operation at higher rates of charge/discharge—especially at low temperatures—for batteries used in vehicles

Technical Barriers

- Concern over the safety of lithium-ion batteries in EDVs is one of the major barriers to widespread adoption
- The number of design parameters for lithium batteries is large, and the interaction among them is complicated, so it is not feasible to experimentally identify the weakest link by conducting tests on a case-by-case basis
- Safety evaluation results for battery packs built with the same material by different manufacturers are very different; the cost associated with building and testing the safety of large format cells, modules, and packs is quite high; whenever such data is collected, it is treated as proprietary, thus preventing the use of lessons learned by other battery developers
- Scaling up a battery greatly changes the response of a system developing a defect and its consequent behaviors during fault evolution
- Timely detection of fault signals in large capacity battery systems is extremely difficult

Technical Targets

- Incorporate deformation of cell components and casing into pressure buildup models developed in FY12

- Develop electrochemical models that can reliably predict the origin of failure and the location of venting of a lithium-ion cell under pressure

Accomplishments

- Built model for venting of individual lithium-ion cells; this model was tested with parameters from cells of different form factors
- The model was used to analyze the safety implications for the cell choices made by TARDEC

Introduction

In FY13, NREL's modeling activity to improve lithium-ion battery safety focused on correlating the failure mechanism within an individual cell (e.g., due to an internal short or decomposition of the electrolyte resulting in the formation of gaseous species) to the results observed during external testing. Testing a fully-charged cell yields very different results from those of a discharged cell. For instance, when a cell is subjected to a crush test at low states of charge (i.e., 30% or lower), the point of failure of the cell almost always coincides with the point where the external force is applied. In a fully-charged cell, however, the point of failure is significantly farther from the location of crush. These differences imply that there is a difference between two cells of identical make, even when subjected to the same test procedure, depending on their energy content.

In order to capture the relationship between the energy content of a cell and its failure mechanism, a rigorous thermal-electrochemical model that includes the origin and distribution of pressure within the cell casing was developed. This model is an extension of results shown in FY12—the pressure due to gas generation during overcharge of a cell was previously shown as a case study for this model. In the current effort, the mechanical strength of the casing and cell components was used to determine the location of cell venting, which eventually follows the accumulation of pressure from abuse reactions and phase changes. These results are significant in making the transition from developing an abuse mechanism for individual cells to analyzing the propagation of failure from one cell to the others within the module.

Approach

The interaction between the electrochemical-thermal response and mechanical behavior of cell components was captured using a rigorous jump momentum balance across the interface to calculate pressure at any given point within the cell. The following expression is a modified form of the abuse reaction models previously reported by us in FY12:

$$f^i = -\mathbf{n} \cdot \left(P^i \mathbf{I} + \eta \left[\nabla \mathbf{u}^i + (\nabla \mathbf{u}^i)^T \right] \right)$$

Here, the force (f^i) experienced at any point on the interface between two components (e.g., the electrode and the separator or the separator and the gaseous species produced by the reactions) is related to the pressure at that point P^i and the extent of deformation tolerated by the corresponding components. The deformation is tracked using the velocity of the interface, \mathbf{u} .

The pressure is comprised of three terms:

$$P^i = P_1^i + P_2^i + P_3^i$$

P_1^i represents pressure buildup due to gas generation reactions; P_2^i , pressure due to expansion from evaporation of volatile components, and P_3^i , restrictions imposed by mechanical deformation of the individual cell components. The pressure generation models use the first one or two terms, depending on the nature of the problem studied. The interaction between the reactions, heat generation, and mechanical deformation is introduced by the use of the P_3^i term, which is computed from stress-strain measurements of individual components, as shown in Figure III.E.7-1.

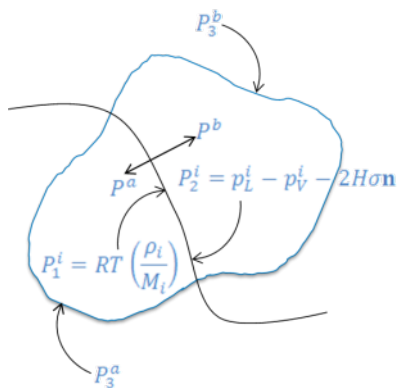


Figure III.E.7-1: Illustration of interaction between thermal, electrochemical, and mechanical components of pressure generation within a lithium-ion cell

Results

Figure III.E.7-2 shows the contribution of individual factors to overall pressure within the cell, as a function of time, when the cell is subjected to mechanical deformation. As shown, the pressure due to external deformation increases instantaneously and remains fairly constant through the entire duration of the test. The reaction and vaporization pressures are strong functions of the energy content and temperature of the cell. As the abuse test progresses in time, the relative magnitude of the different components changes—the deformation term which dominates the pressure value at the beginning of the test is eventually overcome by the reaction term—at which point, the pressure exceeds the threshold for failure. Thus, in this instance, when a fully-charged cell is subjected to an external load or hot-box test, the point of failure is determined by the location within the cell at which the total pressure value—which, as described above, is dominated by the reaction term—exceeds the failure threshold.

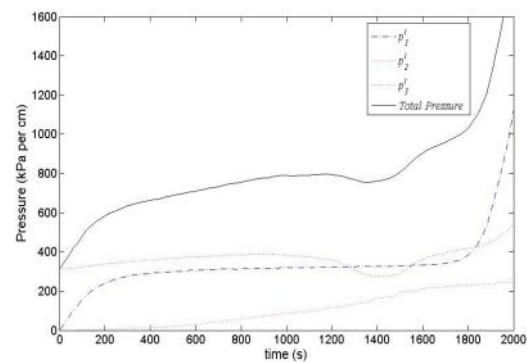


Figure III.E.7-2: Contribution of gas-generating reactions, vaporization of volatile components, and mechanical constraint imposed by the casing to overall pressure buildup within a lithium-ion cell; purely mechanical terms dominate the beginning of the test, while kinetic and thermal terms take over with progression of the abuse reactions

Incorporating this insight into a cell-level model will help improve predictive capability to determine the location of cell failure. For instance, Figure III.E.7-3 shows results from a purely mechanical approach to simulating cell failure. In this case, literature values report the force exertion point to be the point of failure as well, which is true in the case of cells with no significant contribution to the pressure term from reaction heat (i.e., only the last term of our pressure balance equation is significant).

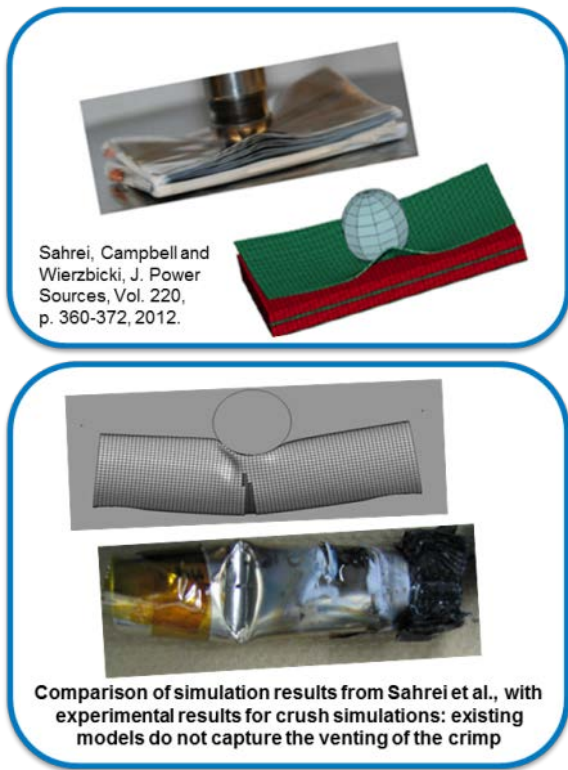


Figure III.E.7-3: Failure point of fully-discharged cell coincides with the point of test, whereas that for fully-charged cell is significantly different

Similar results for a prismatic cell subjected to venting, obtained using the model equations reported above, are shown in Figure III.E.7-4.

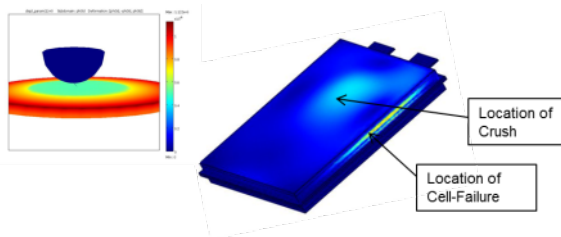


Figure III.E.7-4: NREL cell venting simulation results show that, for propagation purposes, the location of cell failure does not always coincide with the location of crush

Conclusions and Future Directions

Using a rigorous model that captures the contribution of kinetic, thermal, and mechanical properties of cell components is critical to identifying the failure mode of individual cells during abuse testing and the direction of failure propagation within a module. Subsequent work will consider propagation mechanisms based on understanding developed from these models.

Simultaneously, it is pertinent to develop a set of parameters from independent experiments to characterize the rate constants and transport coefficients for abuse kinetics reactions, as well as the mechanical constants that are used in these models. Toward this end, we have started measurement of heat generation rates for cell components, such as the cathode at different states of lithiation, the electrolyte, and combinations thereof. These results are currently being compared with similar measurements made at the cell level to identify the most appropriate experimental technique to measure these parameters. These results will be documented in a future report.

FY 2013 Publications/Presentations

1. Ahmad Pesaran, Shriram Santhanagopalan, and Gi-Heon Kim; "Addressing the Impact of Temperature Extremes on Large Format Li-Ion Batteries for Vehicle Applications"; Presented at 30th International Battery Seminar, Ft. Lauderdale, FL; March 11-14, 2013. NREL Report No. PR-5400-58145.
2. Ahmad Pesaran, Matt Keyser, Gi-Heon Kim, Shriram Santhanagopalan, and Kandler Smith; "Tools for Designing Thermal Management of Batteries in Electric Drive Vehicles"; Presented at the Large Lithium Ion Battery Technology & Application Symposia Advanced Automotive Battery Conference; Pasadena, CA. February 4-8, 2013. NREL Report No. PR-5400-57747.
3. Ahmad Pesaran, Gi-Heon Kim, Kandler Smith, Shriram Santhanagopalan; "Accelerating Development of EV Batteries Through Computer-Aided Engineering"; Presented at the 2012 Automotive Simulation World Congress, Detroit, MI; October 30-31, 2012

IV.D.4 Evaluate Impact of ALD Coating on Li/Mn-rich Cathodes

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David King, Karen Buechler, ALD Nanosolutions

Start Date: June 2012

Projected End Date: Projected September 2013

- Build capabilities to directly coat electrode sheets up to 6" x 6" in size

Accomplishments

- In FY12, NREL initiated collaborative work with LGCPI and obtained commercial samples of manganese-rich cathode materials
- These samples were coated with alumina using the ALD technique, in collaboration with ALD NanoSolutions, a leading company for coating ALD on battery materials

FY13 accomplishments include:

- Coating large batches of cathode material powders (several tens of kg)
- Coating sheet electrode samples in modified reactor built in the previous year
- Demonstration of cell performance using pouch cells

Objectives

- Assess the technical viability of atomic layer deposition technique on commercial battery active material, such as Li/Mn-rich cathode materials
- Mitigate durability and abuse tolerance issues associated with high-capacity Li-manganese-rich cathodes

Technical Barriers

- Rapid fade in capacity of high voltage Li-manganese-rich cathode, particularly at high temperatures (45°C)
- Lack of uniform data from large batches of commercial active material treated with ALD technique to overcome durability issues
- Ineffectiveness in coating sheets of electrodes directly with ALD to achieve results similar to coating powders of active material

Technical Targets

- Demonstrate capacity loss of less than 20% at C/2 rate over 500 cycles at 45°C for high-voltage manganese-rich cathode
- Demonstrate scalability of ALD process by coating batches up to 500g of manganese-rich cathodes with alumina to reproduce cell-level performance observed at lab scale

Introduction

Extending the driving range of PHEVs requires the use of high-voltage cathodes that offer consistent performance over 5000 cycles, or 15 years of battery life, without compromising safety. The Mn-rich cathode is an excellent choice of material for these specifications, and has been shown to have the potential to be stable over a wide voltage window between 4.5 and 2.7 V. Preliminary work at the lab scale, between NREL and LGCPI, indicated that while ALD coating of the cathode improved its cycling performance, no enhancements were observed on coating carbon-based anodes. This effort was initiated in June 2012. In this report, we show findings from the preliminary study, using large-format pouch cells.

Approach

Powders

- Coat 200-500g batches of Mn-rich cathode powders in pilot-scale reactors at subcontractor facility
- Optimize coating conditions to minimize rate capability losses, if any, by building cells using several batches of ALD-coated cathode material and testing them at NREL

- Evaluate optimized coatings by building and testing pouch cells at LGCPI

Electrodes

- Modify ALD reactors to hold sheet electrodes
- Develop process to coat electrodes uniformly across the thickness of the sample
- Characterize and test samples at NREL and LGCPI
- Refine coating process based on initial results

Results

In FY13, the focus was on evaluating cycling performance of cells fabricated using ALD-coated powders. Cathode powder samples were subjected to different ALD coating profiles to assess uniformity of the coating and resistance as a function of the number of cycles. Based on these results, the samples with the coating that best suited the requirements of cycling and resistance buildup were used to build pouch-format cells and cycled at different temperatures. The coating procedure was the same as adopted last year.

ALD Coating

Pre-processing included drying overnight, and no unusual off-gassing or decomposition reactions were observed. The coating process involved the following steps:

- Loading the bed of powders into the fluidized bed reactor (shown in Figure IV.D.4-1)
- Fluidizing the powders at coating temperature and pressure
- Introducing the ALD precursors sequentially; each cycle comprised the routine A-purge-B-purge, and the process was repeated for the desired number of cycles



Figure IV.D.4-1: Fluidized bed reactor to coat powders with ALD cycles; the existing reactor at ALD Nanosolutions can process up to 8L of powder per batch

Coating was carried out at the ALD Nanosolutions facility in Broomfield, CO, which has the capability to process ALD-coated battery materials in multiple batch sizes, from tens of grams to tens of kilograms. Samples were fluidized at 10 cm³ per minute after initial drying, and coating time per batch was about 2.5 hours. Initial trials focused on alumina coatings, since we had demonstrated the proof-of-concept with alumina on the Mn-rich cathode material.

Cell Evaluation

Sample results from cycling at 25 and 45°C are shown in Figure IV.D.4-2.

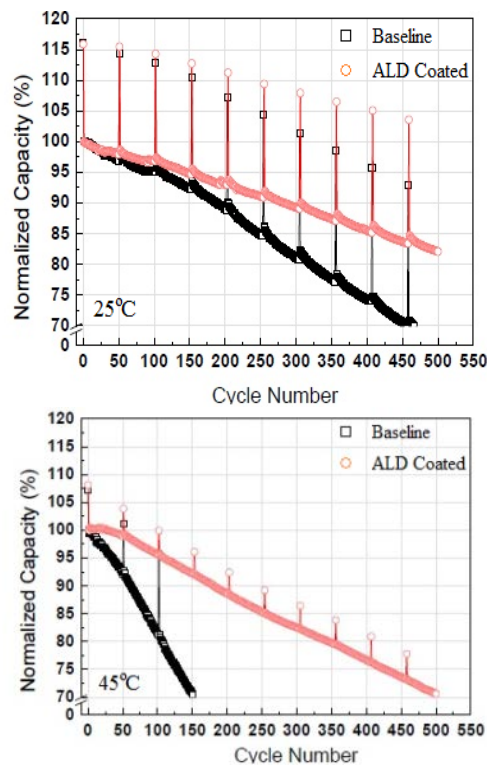


Figure IV.D.4-2: Cycling performance of ALD-coated Mn-rich cathodes

Cell evaluation results indicate that cycling performance at 25°C shows a fade of less than 20%. At 45°C, the cycle life is considerably improved with the coating built under the present effort; however, the performance mark of less than 20% fade was reached around cycle 350.

Conclusions and Future Directions

The scalability of the ALD technique for coating battery materials is attractive. In fact, this technique has now become popular with several materials vendors, who are actively pursuing cathode coating to improve high-temperature performance. A roll-to-roll coating option has also been explored separately for

large-scale manufacturing. Future work will consider tailoring the composition of the coatings to improve functionality. For example, the coatings can be used as a means to improve the processing ability of cathode particles during the cell fabrication process by expanding the range of temperatures over which the performance of the material is stable.

FY 2013 Publications/Presentations

1. Shiram Santhanagopalan, Mohamed Alamgir, Karen Buechler, David King and Ahmad Pesaran, "Evaluate ALD Coatings of LGCPI Cathode Materials or Electrodes", Milestone Report #55894, Submitted September 2012
2. Shiram Santhanagopalan – AMR presentation

IV.E.3 Development of Industrially Viable Battery Electrode Coatings

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Subcontractor:
University of Colorado at Boulder

Start Date: January 2012
Projected End Date: September 2013

Objectives

- The ABR program is focused on improving cycle life and abuse tolerance, and reducing cost for PHEV battery technologies
- Previous work conducted by NREL and the University of Colorado at Boulder has demonstrated that thin, conformal coatings of lithium-ion battery electrodes formed by 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 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

- Limited calendar and cycle life
- Abuse tolerance
- High cost

Technical Targets

- Design and construct prototype in-line ALD coater for deposition on porous substrates

Introduction

In previous work, NREL, in partnership with the University of Colorado, has shown that extremely thin, conformal coatings 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 FY13, NREL and the CU team 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.

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 in a mild vacuum, as shown in Figure IV.E.3-1. 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 that 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 the key to

achieving the excellent conformal film deposition on highly-textured substrates for which the ALD technique is known.

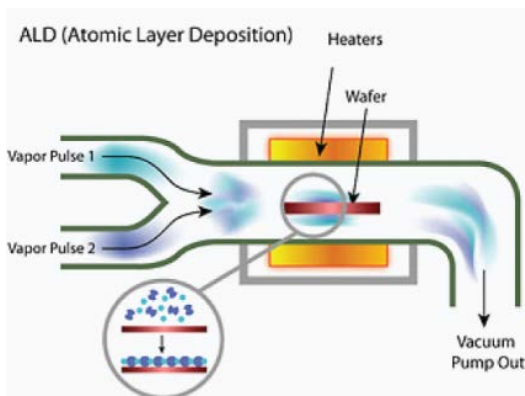


Figure IV.E.3-1: Typical ALD chamber with sequentially separated precursor exposures that draws out overall processing time

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 IV.E.3-2 shows a simplified conceptual schematic of our proposed apparatus.

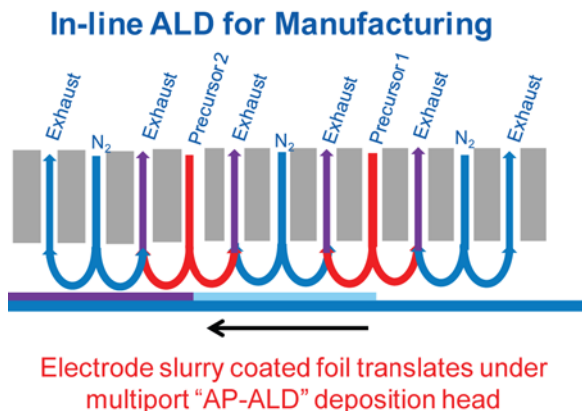


Figure IV.E.3-2: Simplified schematic demonstrating the in-line spatial ALD concept

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

A crucial factor for successful coating of battery 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 penetration of precursor gases into the film, while low local pressures (molecular flow conditions) allow 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 concept is shown in Figure IV.E.3-3. In addition to precursor introduction and exhaust channels, the system is also designed with a nitrogen gas window that is pressured higher 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.

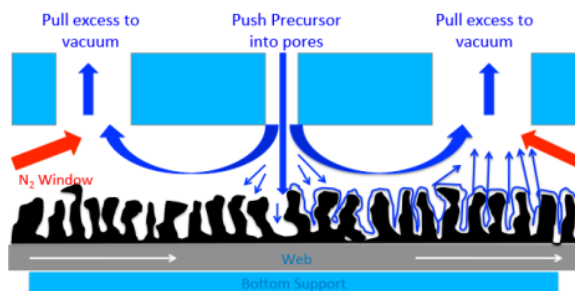


Figure IV.E.3-3: Simple schematic demonstrating alternate high and low pressure regimes present in the “push-pull” reactor concept

Digital Modular Roll-to-Roll System Design

As shown schematically earlier, a linear translational roll-to-roll (R2R) design was initially considered for our push-pull deposition system. However, it was determined through earlier results and discussions with additional 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 IV.E.3-4. 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.

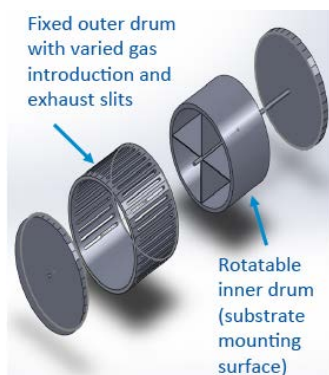


Figure IV.E.3-4: Diagram of drum-in-drum reactor format

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 IV.E.3-5 shows a more detailed schematic of the drum-in-drum reactor 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 experimentation across a broad range of deposition conditions in order to optimize performance.

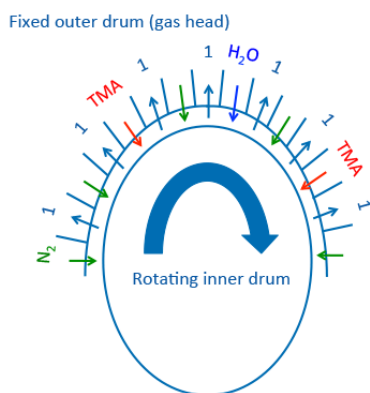


Figure IV.E.3-5: Schematic representation of digital modular concept

Module Design

Computational flow dynamics 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 IV.E.3-6 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.

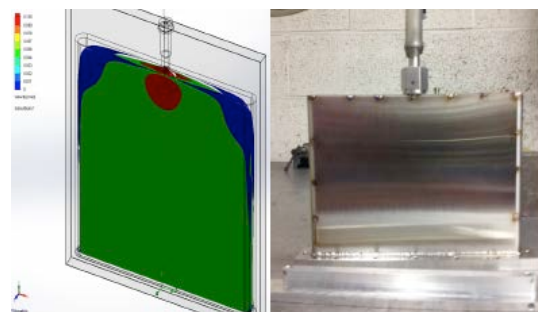


Figure IV.E.3-6: CFD simulation of gas flow through precursor introduction module and final construction

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. For example, additional modules are being designed that will allow 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 and assembled, and are currently under test. Figure IV.E.3-7 shows the final fabricated internal and external drum units, including the faceted slits for process module interfacing, as well as the full reactor at different stages of completion. Note that a portion of the external drum has been left intact. This was left unmodified to enable later integration of the unit within existing R2R processing units, as will be briefly described in the next section.

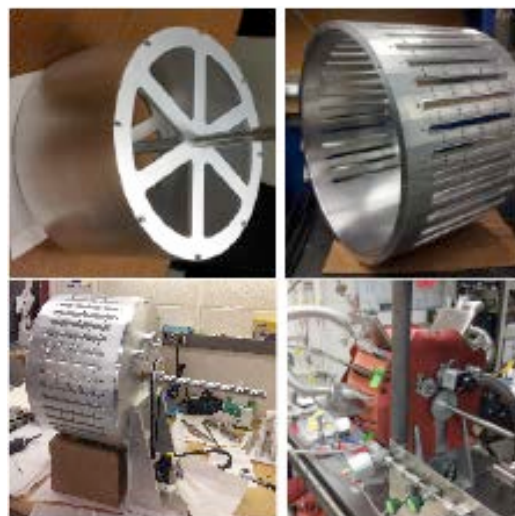


Figure IV.E.3-7: Fabricated and final assembly of drum-in-drum in-line reactor

Conclusions and Future Directions

In FY13, the NREL/CU team designed and completed construction of a new in-line ALD-based electrode coating reactor. Initial testing of the unit is currently underway. If additional funding can be obtained for a continuation of this effort into FY14, 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 NREL/CU laboratories as well as within collaborating labs.

It is anticipated that at a later stage, the NREL/CU team will partner with battery manufacturers and other laboratories 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. Figure IV.E.3-8 shows an early stage schematic for integration of the digital modular reactor design into an R2R system. The unmodified sidewall of the outer

drum of the reactor will be modified to include roller designs to bring an electrode foil into the reactor and into contact with the inner drum. The roller integration is shown on the left side of the Figure IV.E.3-8 schematic.

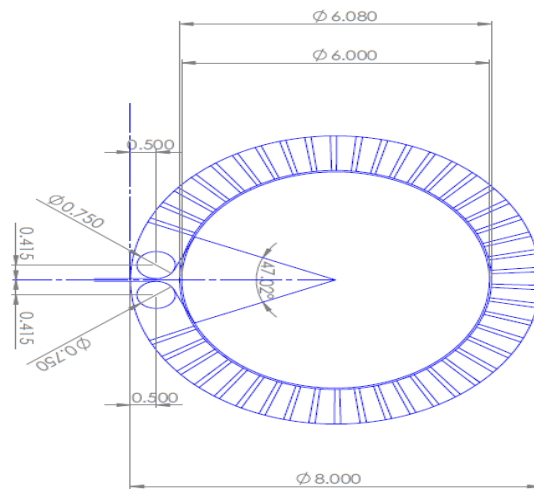


Figure IV.E.3-8: Initial schematic of roller integration within the drum-in-drum reactor design

FY 2013 Publications/Presentations

1. 2013 DOE Annual Merit Review Presentation

V.C.7 Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

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Start Date: October 2010
Projected End Date: September 2014

Objectives

- Develop a low-cost, thick, high-capacity silicon anode with sustainable cycling performance, by advanced surface modification
- Synthesize novel stable and elastic coatings for Si anodes using ALD and 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 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 addressed include:

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

Technical Targets

- Stabilize high-capacity silicon anodes by employing advanced surface coating techniques
- Demonstrate stable high-rate cycling performance of Si anodes
- USABC goals: 200Wh/kg (EV); 96Wh/kg, 316W/kg, 3000 cycles (PHEV-40)
- Calendar life: 15 years
- Improved abuse tolerance

Accomplishments

- Growth of an aluminum alkoxide polymer (alucone) film using sequential reactions of trimethylaluminum (TMA) and ethylene glycol (EG)
- Achieved durable cycling (>100 cycles) of MLD-engineered thick Si anodes (>15 μ m) using optimized MLD coating reactions and conditions
- Demonstrated specific capacity of ~ 900 mAh g⁻¹ at the 150th cycle for alucone-coated Si anodes, whereas uncoated Si electrode undergoes rapid degradation
- Characterized the effect of MLD alucone coatings on the morphology and structure of silicon anodes during cycling
- Investigated the cyclization of polyacrylonitrile (PAN) coating for Si composite anode to address Si expansion and enable greatly-improved cycling performance

Introduction

Significant advances in both energy density and rate capability for Li-ion batteries will be critical for their implementation in the next generation of EVs. Due to the high theoretical capacity of Si, 3579 mAh g⁻¹ for Li15Si4, 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 then leads to the interruption of electronic transport pathways and the electrochemical isolation of pulverized particles. In this project, new conformal nanoscale coatings with desirable elastic properties and conductivity are being developed via ALD and MLD to accommodate volumetric expansion, protect the surface from reactive electrolytes, and ensure electronic paths through composite electrodes.

Greatly improved performance has been achieved for both ALD-coated nano-MoO₃ anodes and cathodes. The effect of Al₂O₃ ALD coatings on structure and SEI composition was studied via in-situ synchrotron x-ray diffraction (XRD), ex-situ x-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). Results showed that ALD coatings mitigated side reactions on the electrode surface and preserved structure during severe cycling. This suggests that new ALD coatings with improved mechanical properties and conductivity can help accommodate volumetric expansion in electrodes and ensure their electronic paths.

Higher rates and more durable cycling of Si may be achieved by employing ALD and new elastic (polymer-like) coatings with low-elastic moduli (MLD coating). The successful completion of this project will enable coated Si anodes to have significantly improved cycling stability and high CE. In the end, the development of new flexible and conductive MLD films will enable the BATT program to achieve durable, high-rate capability with both anodes and cathodes.

Approach

Metal-organic hybrid films have been developed and grown on Si electrodes by using MLD, with the aim of accommodating volumetric changes in Si particles. The growth of alucone has been demonstrated using sequential exposures of trimethylaluminum and ethylene glycol. In addition to aluminum-based precursors, other metal precursors are also being investigated to enhance the conductivity of MLD flexible coatings.

Chemical vapor deposition via silane decomposition on a hot filament was used to synthesize

silicon thin films with different degrees of crystallinity. A nanocrystal radio-frequency plasma reactor successfully synthesized silicon/alloy nanocrystals with uniform size and shape, and the size may be tuned from <10 to ~100 nm by varying the plasma conditions, which will allow the study of how Si nanocrystal size affects electrochemical performance. Additionally, commercially-available silicon particles were used to identify coating effects. Conventional electrodes containing active material, conductive additive, and binders were fabricated to evaluate cycling properties.

Results

Development of Elastic Coatings using MLD

A new metal-organic hybrid coating, aluminum alkoxide (alucone), was grown based on reactions of inorganic trimethylaluminum (Al(CH₃)₃) and organic glycerol polyol (HOCH₂CH(OH)CH₂OH) precursors. The sequential exposure of Al(CH₃)₃ and HOCH₂CH(OH)CH₂OH in AB cycles resulted in the evolution of alucone coatings with growth rates of about 3-5 Å per AB cycle at substrate temperatures of 100-140°C.

Figure V.C.7-1 shows a schematic of the controlled layered chemistry structure of the aluminum alkoxide alucone polymer used in this work.

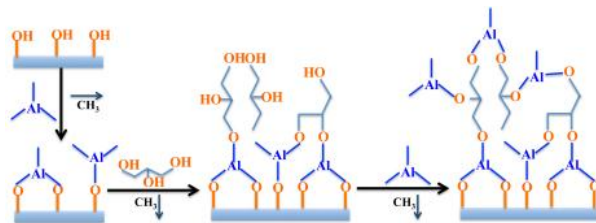


Figure V.C.7-1: Schematic depicting alucone MLD reaction

The growth of the alucone MLD coating occurs via the reaction of hydroxyl groups on the alcohol with AlCH₃. More than two hydroxyl groups on the alcohol results in a greater probability that unreacted hydroxyl groups will remain after polyol reactions with AlCH₃ surface species. These unreacted hydroxyl groups can produce additional crosslinking between growing polymer chains that can strengthen alucone films and lead to higher fracture resistance.

Despite the success of elastic MLD coatings, the technique presents challenges with high-surface-area nano-Si electrodes with tortuous architecture. Two different reaction modes, static reactant exposure and viscous flow, were used during MLD to address these challenges in fabricating conformal coating. Static reactant exposure allows the precursor gas to reach more surfaces of the electrode and enhance completion of the self-limited reaction on the surface. High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), which is highly sensitive

to atomic number contrast (Z-contrast imaging), was used to further clarify MLD coating conformity. The HAADF-STEM image in Figure V.C.7-2a shows that the alucone layer is a thin (~5 nm), dense, and conformal coating adhered to the Si particles. Electron energy loss spectroscopy (EELS) was also used to characterize the microstructure of MLD-coated electrodes. The conformal, thin coating of metal-alkoxide film MLD (red mapping) can be seen on the nano-Si particles (cyan mapping), as displayed in Figure V.C.7-2b. Note that the alucone MLD was coated on laminated electrodes, rather than powdery silicon. Static reactant exposure facilitates surface reactions through the entire electrode, providing an intimately-linked conductive network.

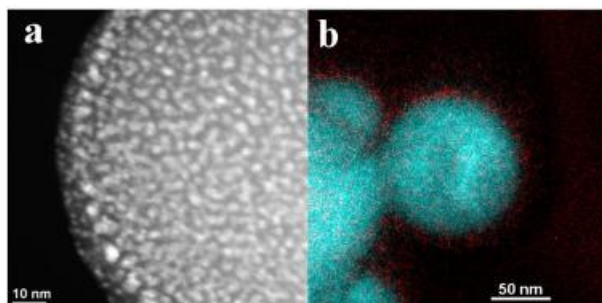


Figure V.C.7-2: (a) HAADF-STEM image of alucone MLD-coated particle; (b) EELS elemental mapping (Si in cyan, Al in red), confirming conformal alucone MLD coating on Si composite electrode

Improvement of Electrochemical Performance with Alucone MLD Coating

Electrochemical cycling performance of alucone-coated Si electrodes was investigated in a coin cell configuration with Li-metal as a counter electrode. The Si electrodes were prepared with 60% Si nanoparticles (purchased from Alfa without further treatment), 20% acetylene black, and 20% polyvinylidene difluoride (PVDF) binder. All of the cells were first cycled at 175 mA/g (C/20), and then cycled at 350 mA/g (C/10) in the voltage window between 0.05-1V.

Figure V.C.7-3 shows significantly-improved cycling stability for the alucone MLD-coated Si electrodes. The capacity obtained at a cycling rate of 0.1C has been stabilized for the static-coated Si electrode, while the slow fade in capacity is observed for the viscous flow-coated Si electrode. The static-coated Si electrode has higher CE for the first cycle, which further confirms conformal enhancement of the tortuous electrode structure. In contrast, bare silicon anode capacity decays to nearly zero after 28 charge-discharge cycles.

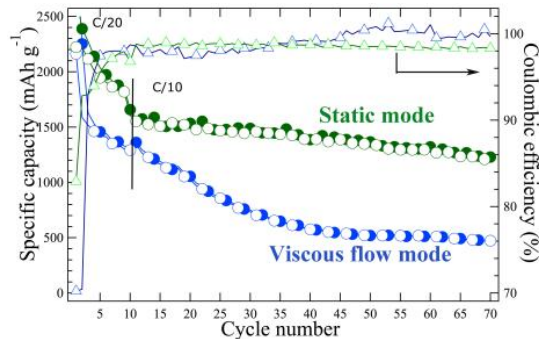


Figure V.C.7-3: Cycling performance of alucone-coated Si anodes by static and viscous flow modes

Figure V.C.7-4 displays the impact of different coating thicknesses on cycling performance. The highest capacity was obtained for both thicker MLD-coated Si anodes. We expect that better conductivity in conformal alucone coatings may lead to higher capacity and better cycling performance than bare electrodes.

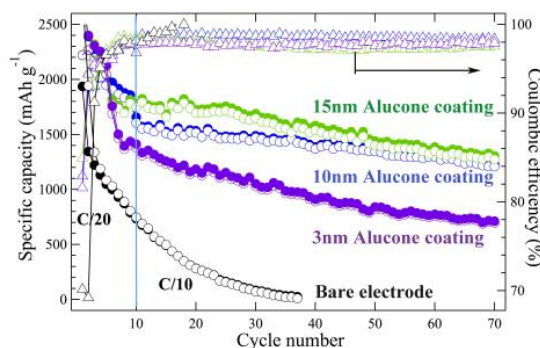


Figure V.C.7-4: Cycling performance and coating thickness

Cycling stability has been demonstrated for alucone-coated Si anodes, as indicated in Figure V.C.7-5. Rapid capacity decay was observed in the bare Si electrode, but the alucone-coated Si anode exhibited sustainable cycling over hundreds of cycles with CE in excess of 99%. Specific charge capacity of 900 mAh/g at the 150th cycle corresponds to volumetric capacity of 569 mAh/cm³ with an initial electrode thickness of 12.74 μm. That level of cycle life and CE for thick electrodes is evidence that alucone MLD coating provides favorable mechanical properties, accommodating volumetric changes of the Si electrode and preserving the structural integrity of the electrode network throughout deep cycling.

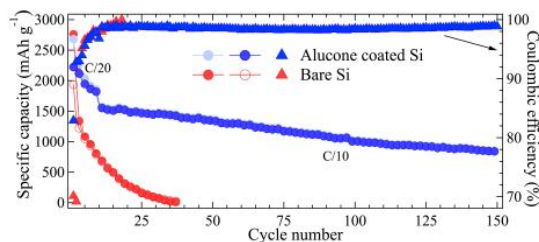


Figure V.C.7-5: Greatly enhanced cycling stability in alucone MLD-coated Si anodes

SEM Characterization of Resilience of Alucone MLD Coating

Cross-section SEM images at different stages of cycling are shown in Figure V.C.7-6. The fresh bare and alucone-coated electrodes have an initial thickness of 12.15 μm and 12.74 μm , respectively. Figure V.C.7-6b and V.C.7-6e correspond to the first lithiation of the bare and coated electrode with thickness of 20.34 μm and 23.06 μm . Volume expansion in the thickness direction was observed for both bare and coated electrodes. Similar volume expansion on the coated electrodes indicates that the alucone coating allows volume expansion in the coated electrodes to complete full lithiation. Cross-sections after the 20th delithiated electrodes, as shown in Figure V.C.7-2c and V.C.7-2f, show that the uncoated and coated electrodes have a thickness of 18.13 μm and 14.97 μm , respectively. A nearly full recovery from the massive volumetric expansion was observed for the alucone-coated electrodes. On the contrary, the bare electrode remains almost fully expanded after the 20th delithiation. This indicates that the bare electrode may lose its original electrical contact and structural integrity, resulting in the rapid capacity degradation observed in the uncoated Si anodes. These findings imply that the resilience of the alucone coatings provides sufficient mechanical support to accommodate the major volumetric changes experienced by Si anodes, as well as aid in the recovery and preservation of the whole composite network upon delithiation.

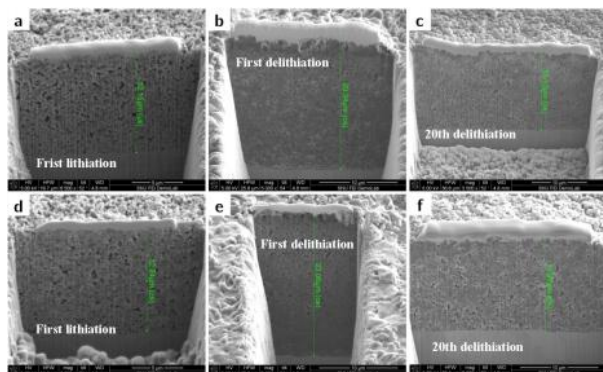


Figure V.C.7-6: SEM images showing cross-sections of bare electrodes (a, b, c) and alucone-coated electrodes (d, e, f)

Conclusions and Future Directions

Growth of flexible metal-organic coatings on Si electrodes has been accomplished by using the MLD technique. Using sequential reactions of TMA and EG precursors, we have been able to coat Si electrodes with aluminum alkoxide films. In order to enhance coating conformity for tortuous electrodes, optimized static reactant exposure has been used in MLD.

Significantly-improved performance has been demonstrated for alucone-coated nano-Si electrodes,

and coated Si anodes exhibit sustainable cycling over hundreds of cycles with CE in excess of 99%. Specific charge capacity of 900 mAh/g at the 150th cycle corresponds to electrode volumetric capacity of 569 mAh/cm³. Thin and conformal coating, observed via advanced microscopy, accommodates complete volume expansion during lithiation, and also helps preserve structural integrity during delithiation.

Observed electrochemical and spectroscopic data suggests that alucone MLD coating provides a mechanically robust, resilient and conductive network for Si composite electrodes, allowing for long cycle life and remarkable stability. Alucone coating on conventional nano-Si composite electrodes provides significant improvement in stability, rate, and CE.

In FY14, research efforts will focus on developing conformal elastic coatings with enhanced ionic and electronic conductivity. In order to better understand the effects of these coatings, our FY14 objectives include in-situ characterization of coating impact on structural and morphological evolution during cycling, and exploration of the importance and mechanism of various coatings through the BATT coating group.

FY 2013 Publications/Presentations

1. D. M. Piper, T. A. Yersak, S-B. Son, S. C. Kim, C. S. Kang, K. H. Oh, C. Ban, A. C. Dillon, and S.H. Lee, "Conformal Coatings of Cyclized-PAN for Mechanically Resilient Si nano-Composite Anodes", *Adv. Energy Mater.* 2013. doi: 10.1002/aenm.201200850
2. D. M. Piper, J. J. Travis, M. Young, S-B Son, S. C. Kim, K. H. Oh, S. M. George, C. Ban, S-H Lee, "Reversible High Capacity Si Nanocomposite Anodes enabled by Molecular Layer Deposition", *Adv. Mater.* Under review.
3. C. Ban, M. Xie, X. Sun, J. J Travis, G. Wang, H. Sun, A. C Dillon, J. Lian and S. M George, "Atomic layer deposition of amorphous TiO₂ on graphene as an anode for Li-ion batteries" *Nanotechnology*, 24, 424002, 2013, doi:10.1088/0957-4484/24/42/424002
4. A. I. Abdulagatov, K. E. Terauds, J. J. Travis, A. S. Cavanagh, R. Raj, and S. M. George, "Pyrolysis of titanocene molecular layer deposition films as precursors for conducting TiO₂/Carbon composite films" *J. Phys. Chem. C*, 2013, 117 (34), pp 17442–17450 DOI: 10.1021/jp4051947
5. Atomic Layer Deposition of Al₂O₃ for Highly Improved Performance in Li-ion Battery Electrodes (Invited talk), 2012 Fall MRS, Boston, MA, USA.
6. Nanoscale Interface Engineering for Improved Li-ion Batteries (Invited talk), 2013 Spring MRS, San Francisco, CA, USA.
7. 2013 DOE Annual Merit Review Presentation