FY2011 Annual Report for NREL Energy Storage Projects

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Technical Report
NREL/TP-5400-54491
April 2012

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NATIONAL RENEWABLE ENERGY LABORATORY

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Foreword

The Energy Storage Team within the Center for Transportation Technologies and Systems at the National Renewable Energy Laboratory performed the work detailed in this report under the Energy Storage Research & Development (R&D) activity of the Vehicle Technologies Program, which is managed by David Howell within 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 2011, NREL identified several R&D projects in its Annual Operating Plan submitted to DOE on materials, 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 the Energy Storage FY11 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 Vehicle Technologies Program of the U.S. Department of Energy for funding support and guidance. We also wish to thank Taeyoung Han of General Motors, Steve Hartridge of CD-adapco, and Christian Schaffer of EC Power for their contributions to the CAEBAT program.

Executive Summary

The National Renewable Energy Laboratory (NREL) supports energy storage R&D under the Vehicle Technologies Program at the U.S. Department of Energy (DOE). 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)]*
- *Testing, Design and Analysis (TDA)*
- *Applied Battery Research (ABR)*
- *Focused Fundamental Research, or Batteries for Advanced Transportation Technologies (BATT)*

In FY11, DOE funded NREL to make technical contributions to all of these R&D activities. This report summarizes NREL's R&D projects in FY11 in support of the USABC, TDA, ABR, and BATT program elements. In addition, we continued the enhancement of NREL's battery testing facilities funded through the American Reinvestment and Recovery Act (ARRA) of 2009.

The FY11 projects under NREL's Energy Storage R&D program are briefly described below. Each of these is discussed in depth in the main sections of this report.

ARRA – Battery Thermal Test Facility: With investment from ARRA, the size of our battery doubled, significant pieces of equipments for thermal testing of batteries were added, and several jobs were created.

Battery Ownership Model: We completed the enhancement of the software and then used it to answer several questions regarding the impact and sensitivity of electric drive vehicle economics on various parameters such as drive pattern.

PEV Battery Second Use: We continued our collaboration with our second-use subcontractor to continue analysis of the battery second-use opportunities and to plan for testing of used batteries.

Battery Life Trade-Off Studies: We used the previously developed life model for nickel-cobalt-aluminum chemistry to analyze the impact of more "real world" drive cycles for plug-in hybrid electric vehicles (PHEV10 and PHEV40) for multiple cities.

Low Energy Hybrid Electric Vehicle Requirements Analysis: We continued refining the requirements for the lower energy, energy storage system for a power-assist hybrid electric vehicle for USABC.

Battery Thermal Analysis and Characterization Activities: We continued thermal testing and characterization of energy storage systems from several USABC battery developers using our calorimeters and thermal imaging equipment

Development of an On-Demand Internal Short Circuit: We continued our development of NREL's on-demand internal short circuit device for emulating lithium (Li)-ion field failures due to latent defects.

Computer-Aided Engineering of Batteries – CAEBAT (NREL): We entered into subcontract agreements with three industry teams (EC Power, General Motors, and CD-adapco) to develop CAEBAT tools. Good technical progress has been made.

Development of CAEBAT Design Tools (GM Subcontract): GM and its subcontractors started the project by identifying the end-user needs, developing physical models and mathematical equations and solution techniques, developing strategies for reduced order modeling, and validation of the models.

Development of CAEBAT Design Tools (CD-adapco Subcontract): An initial spiral cell method was established, providing an extensible framework into which future electrode performance models can be added.

Development of CAEBAT Design Tools (EC Power Subcontract): The baseline version of the large-format software tool "Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model" was completed.

NREL Multi-Scale Multi-Dimensional (MSMD) Framework and Modeling Activities: We developed several electrochemical-thermal sub-models for wound cylindrical and wound prismatic cells for incorporation into the MSMD framework. The MSMD modeling framework of Li-ion batteries was documented in a publication in the *Journal of Electrochemical Society*.

Lithium-Ion Abuse Model Development: We developed an overcharge model that incorporates a mechanism for dendrite growth.

Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes: We explored a variety of electrochemical systems, including full cells, to achieve a better understanding of atomic layer deposition coating and its impact on improving amorphous silicon anodes. We collaborated with BATT's *Coating Group*, Marca Deoff, and Stan Whittingham.

List of Acronyms and Abbreviations

A123	A123 Systems
AB	acetylene black
ABR	Applied Battery Research
Al_2O_3	aluminum oxide
ALD	atomic layer deposition
ARRA	American Recovery and Reinvestment Act
a-Si	amorphous silicon
BATT	Batteries for Advanced Transportation Technologies
BDS	Battery Design Studio
BOM	Battery Ownership Model
BTM	battery thermal management
CAEBAT	Computer Aided Engineering of Automotive Batteries
CAE	computer-aided engineering
CD	charge depletion
CFD	computational fluid dynamics
CPI	Compact Power Incorporated
CS	charge sustaining
CT	counter tab cell design
CU	University of Colorado at Boulder
DK	Dow Kokam
DOE	U.S. Department of Energy
ECT3D	Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model
EDV	electric drive vehicle
EES TT	Electrochemical Energy Storage Technical Team
ESS	energy storage system
EV	electric vehicle
FVLSM	Finite Volume Linear Superposition Method
GM	General Motors
HEV	hybrid electric vehicle
HWCVD	hot wire chemical vapor deposition
ISC	internal short circuit
JCI	Johnson Controls Inc.
JCS	Johnson Controls-Saft
K2	K2 Energy Solutions, Inc.
LCPM	levelized cost per mile
LEESS	lower-energy energy storage system
$LiCoO_2$	lithium cobalt oxide
Li-ion	lithium-ion
MCMB	mesocarbon microbead
MoO_3	molybdenum trioxide
MPPC	multiple potential-pair continuum
MSMD	multi-scale, multi-dimensional
nano-Si	nano-silicon
NCA	nickel-cobalt-aluminum
ND	nominal design (cell)
NG	natural graphite
NREL	National Renewable Energy Laboratory
OAS	open architecture software
ORNL	Oak Ridge National Laboratory
P2D	Pseudo-2D Model by John Newman
PA-HEV	power-assist hybrid electric vehicle
PEV	plug-in electric vehicle
PHEV	plug-in hybrid electric vehicle
PVDF	polyvinylidene difluoride
R&D	research & development
RED	rolled electrode design
regen	regenerative braking
RFP	request for proposals
ROM	reduced order modeling
SED	stacked electrode design
SEM	scanning electron microscope
Si	silicon
SK	SK Innovation
SOC	state of charge
SPPC	single potential-pair continuum
ST	small tab cell design

TCS	Traffic Choices Study of the Puget Sound Regional Council
TTF	Thermal Test Facility
UDDS	Urban Dynamometer Driving Schedule
USABC	United States Advanced Battery Consortium
U.S. DRIVE	United States Driving Research and Innovation for Vehicle efficiency and Energy sustainability
WPPC	wound potential-pair continuum
WS	wide stack-area cell design

Synopsis

The National Renewable Energy Laboratory (NREL) supports Energy Storage R&D for the Vehicle Technologies Program of the U.S. Department of Energy (DOE). 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 to reduce dependence on imported oil and gaseous pollutants. 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.

As described in the DOE Energy Storage R&D Annual Progress Report:

> *The energy storage research and development effort within the VT Program is responsible for researching and improving advanced batteries and ultracapacitors for a wide range of vehicle applications, including HEVs, PHEVs, EVs, and fuel cell vehicles (FCVs). Over the past few years, the emphasis of these efforts has shifted from high-power batteries for HEV applications to high-energy batteries for PHEV and EV applications. The energy storage effort includes multiple activities, from focused fundamental research, to applied R&D, to testing and analysis, to hardware development with industry. The activities begin by establishing technical requirements for the energy storage technologies in cooperation with industry. Next, commercially available batteries are evaluated against those requirements. If requirements are unmet, additional R&D takes place, which involves either short-term directed research (applied research) by commercial developers and national laboratories, or exploratory research, generally spearheaded by the national laboratories. Thus, there are four major inter-related and complementary program elements, namely:*
>
> - *Advanced Battery Development (through United States Advanced Battery Consortium - USABC)*
> - *Testing, Design and Analysis (TDA)*
> - *Applied Battery Research (ABR)*
> - *Focused Fundamental Research, or Batteries for Advanced Transportation Technologies (BATT)*

This report provides a summary of NREL's research and development projects in support of the USABC, TDA, ABR, and BATT program elements. Furthermore, the enhancement of NREL's battery testing facilities through the American Reinvestment and Recovery Act (ARRA) of 2009 continued through FY11. This report also summarizes NREL's continued efforts to maximize the $2M received in 2010 to enhance and upgrade its battery thermal testing facility.

The FY11 highlights of the NREL Energy Storage R&D tasks are described below. Each of these is discussed in depth in subsequent sections of this report.

ARRA – Battery Thermal Test Facility

- Following the addition of 1,000 ft^2 of new battery laboratory space, all battery testers and environmental chambers acquired with ARRA funds are operational, calibrated, and in use.
- ARRA fund-purchased thin film and bulk thermal conductivity meters as well as the coin cell calorimeter are now in use. The fabrication of all components for the new custom-designed cell calorimeter is now complete, and assembly of the final product has begun.
- An electrochemical impedance spectroscopy unit that will aid NREL in developing new battery materials was purchased.
- Many component pieces for the battery thermal management test loop have been acquired.

Battery Ownership Model

- The software architecture of the Battery Ownership Model was restructured around NREL's high-fidelity battery life model, enabling the incorporation of NREL's battery second use model and a preliminary vehicle-to-grid services model.
- Longitudinal drive pattern data from the Puget Sound Regional Council's Traffic Choices Study (TCS) were acquired, illustrating the high sensitivity of electric vehicle (EV) economics to drive pattern.

PEV Battery Second Use

- A team of utility companies, university research centers, and hardware providers led by the California Center for Sustainable Energy was subcontracted to support analyses, acquire aged lithium (Li)-ion automotive batteries, and perform long-term testing.
- A preliminary analysis of second-use battery value and likely second-use applications was completed and accepted for publication in the *Journal of Power Sources*.
- Numerous aged Li-ion automotive batteries were acquired, and significant acceptance testing was completed.

Battery Life Trade-Off Studies

- The previously developed graphite/nickel-cobalt-aluminum chemistry life model was applied to analyze 782 "real world" plug-in hybrid electric vehicle (PHEV10 and PHEV40) drive cycles in multiple climates.
- Differences in battery life under nightly and opportunity charging scenarios were compared.
- Worst-case PHEV duty cycles and quantified benefits of possible life-extending controls were identified.

Low Energy HEV Requirements Analysis

- Concerns that the 10-sec, 30-kW charge target and the 2-sec, 55-kW discharge power target were dominating lower-energy energy storage system (LEESS) sizing and cost were addressed.
- Analysis was performed to show that relaxing the 10-sec charge requirement to 20 kW and the 2-sec discharge requirement to 40 kW would have minimal impact on hybrid electric vehicle (HEV) fuel economy, so adjusting the targets could be worthwhile if significant cost savings would be achieved.
- After consulting with two lower-energy energy storage system (LEESS) developers, it was determined that the cost savings would not actually be very significant, so the USABC decided not to relax the power targets after all and left them as they were.
- Working with an automaker, a power-assist HEV test platform was selected and a conversion plan developed to enable in-vehicle LEESS demonstration and evaluation in FY12.

Battery Thermal Analysis and Characterization Activities

- Thermal and electrical evaluations of energy storage systems from A123 Systems, LG Chem Power Inc., K2 Energy Solutions, Johnson Controls Inc., and SK Innovation were conducted.

Development of an On-Demand Internal Short Circuit

- Progress was made toward the development of an on-demand internal short circuit for Li-ion batteries that does not affect battery performance while under test and that can be activated without puncturing or deforming the battery.

Computer-Aided Engineering of Batteries – CAEBAT (NREL)

- Three CAEBAT subcontracts were placed, and each team was assigned a different NREL technical monitor.
    - **EC Power** (teamed with Pennsylvania State University, Johnson Controls Inc., and Ford Motor Company) [NREL Technical Monitor; Shriram Santhanagopalan]
    - **General Motors (GM)** (teamed with ANSYS and ESim) [NREL Technical Monitor: Gi-Heon Kim]
    - **CD-adapco** (teamed with Battery Design LLC, Johnson Controls-Saft and A123 Systems) [NREL Technical Monitor: Kandler Smith]
- The three teams held their kick-off meetings in June 2011, followed by regular monthly conference calls, and the first quarterly meetings were held in October 2011.

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

- End user needs have been defined, including a comprehensive set of model inputs and outputs, geometry requirements, meshing requirements, graphical user interface requirements, and performance requirements; CPU time; and turnaround time. Standard input parameters were shared with the Open Architecture Software (OAS) Work Group.

- Mathematical equations and physical models to describe mass transport, electron, and Li-ion transport and heat generation based on John Newman's Pseudo-2D (P2D) model have been implemented in code using a coupled solver with adaptive time stepping.
- Battery pack simulation applications, from a coarse level to a fine level, with the potential to replace various tests in the product development cycle have been identified. GM's CAEBAT team members have scheduled meetings with potential vehicle program customers to further understand end user needs.
- A strategy involving reduced order modeling, solver accelerators, and co-simulation is under development to overcome computational limitations.

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

- An initial spiral cell method has been established, providing an extensible framework into which future electrode performance models can be added.
- An automatically created 3D representation of a spiral cell within a finite volume modeling package was developed.
- An approach to simulating aging within Li-ion cells has been formulated that considers solid-electrolyte interphase layer growth and will be included in the cell-level analysis.

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

- The baseline version of the large-format software tool "Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model" (ECT3D) is now complete.
- An exhaustive literature review was performed, and preliminary experimental efforts toward the development of a materials database for ECT3D were completed.

NREL Multi-Scale Multi-Dimensional (MSMD) Framework and Modeling Activities

- The Single Potential-Pair Continuum (SPPC) model was enhanced and further developed as an option of the cell domain model to resolve cell domain physics, and the model was applied to simulate large format stacked prismatic cell behavior.
- The Wound Potential-Pair Continuum (WPPC) model was developed as an option of the cell domain model to resolve cell domain physics in wound cell formats, and the model was applied to simulate large-format cylindrical cell behavior.
- The Multiple Potential-Pair Continuum (MPPC) model was developed as an option of the cell domain model to resolve cell domain physics in alternatively stacked cells.
- The Finite Volume Linear Superposition Method (FVLSM) was developed as a fast solution method to achieve enhanced computation speed without compromising accuracy.
- Development of the MSMD framework was documented in an article published in the *Journal of the Electrochemical Society.*

Lithium-Ion Abuse Model Development

- Software was developed to generate meshable geometries from scanning electron microscope images with a lever to control surface morphologies.
- An overcharge model was built that incorporates a mechanism for dendrite growth and relates the detailed electrolyte composition to the size, shape of the dendrites, and the growth rate of the surface film.
- The overcharge model was used to compare factors that limit cell performance over a wide range of temperatures and identified material modifications that will increase the operating range of the cell.

Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

- A new *Coatings Group* has been formed to better understand the importance of coatings in next-generation material.
- A variety of systems, including full cells, were explored internally to achieve a better understanding of atomic layer deposition coating.
- Collaborations were established with external BATT partners via the *Coatings Group* to better understand coatings.
- NREL techniques were employed to enable high-capacity cathodes via collaboration within BATT.
- Collaboration was established with Marca Deoff for spray deposition of spinel structures.
- In collaboration with Stan Whittingham, NREL helped demonstrate that $LiNi_yMn_yCo_{1-2y}O_2$ has inherent high rate capabilities.

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ARRA – Battery Thermal Test Facility

Introduction

To facilitate and accelerate the commercialization of advanced energy storage technologies by U.S. industry, the U.S. Department of Energy (DOE) awarded the National Renewable Energy Laboratory (NREL) \$2M to expand and upgrade its battery thermal test facility under the 2009 American Recovery and Reinvestment Act (ARRA). Proper thermal design and performance are critical in achieving desired battery life, performance, and cost targets. In this facility, NREL will perform thermal evaluation and characterization for batteries developed by U.S. battery developers to aid them in understanding the thermal characteristics of batteries to improve thermal design.

NREL performs thermal testing, analysis, and modeling for two purposes: 1) to assist DOE and the United States Advanced Battery Consortium (USABC) battery developers in designing battery cells, modules, and packs for improved thermal performance; and 2) to benchmark and validate the thermal performance of cell, module, and pack deliverables from DOE/USABC battery developers and suppliers.

Benchmarking cells, modules, and packs under development has been a critical effort for integrating battery systems in advanced vehicles. NREL's current thermal test facilities identify areas of thermal concern as well as characterize the efficiency and heat generation of cells (with different chemistries) and sub-modules under various drive profiles and at various temperatures. NREL's equipment can also benchmark how changing the design of the cell using a different cathode, anode, current collector, electrolyte, or separator affects the overall performance of the cell.

The information garnered from these tests helps battery and car manufacturers design thermal management systems that reduce the life-cycle cost of battery systems in advanced vehicles. Because DOE's energy storage program has expanded over the past year, we have a backlog in thermal characterization and testing of prototypes, particularly in heat generation measurement. With the anticipated growth in the DOE program and an increase in the number of batteries coming from domestic battery manufacturing facilities under ARRA funding, we plan to add capacity and enhanced capability by adding new equipment and additional space in our existing facilities. We will add calorimeters, thermal conductivity measuring instruments, pack thermal evaluation equipment, environmental chambers, and high-power cell and module battery cyclers.

- Total value of award: \$2 million
- Percent of funds expended: 82% – End of FY11

Progress and Current Status

Thermal Test Facility Laboratory Facility

NREL identified 1,000 ft^2 of space adjacent to the existing energy storage test laboratory in the Thermal Test Facility (TTF) for a large portion of the new equipment purchased under the ARRA program. The additional laboratory space needed to be modified to house the new equipment. In particular, the space required electrical, chilled water, and safety modifications before it could be used for energy storage activities. NREL, in conjunction with DRG

Construction (a commercial contractor), modified the space and completed all facility modifications by the end of March 2011. Since the completion of the new laboratory, all the battery cyclers and environmental chambers acquired with ARRA funds are operational, calibrated, and in use. The ABC-150 battery cycler is being used to test the A123Systems (A123)/USABC plug-in hybrid electric vehicle (PHEV10) pack as well as the Johnson Controls-Saft (JCS)/USABC PHEV20 pack. The newly acquired Bitrode cyclers are being used for testing USABC cells from A123, JCS, K2 Energy Solutions (K2), and SK Innovation (SK). We have begun using the ARRA-purchased thin film and bulk thermal conductivity meters as well as the coin cell calorimeter. Furthermore, we have completed fabrication of all the component pieces for the new custom-designed cell calorimeter and are presently assembling the pieces into the final product. We filed U.S. Provisional Patent Application 61/532,869 entitled "Calorimeters for Testing Energy Storage Systems and Power Electronics" (NREL ref. 11-102) that outlines the innovative features of the cell calorimeter developed with ARRA funds. Finally, we have purchased an electrochemical impedance spectroscopy unit that will aid NREL in developing new battery materials and have purchased many of the component pieces for the battery thermal management test loop.

- Construction complete: 100%
- Equipment Installed: 90%
- Production Started: 90%
- Jobs: One regular employee was hired at NREL for specifying, purchasing, installing, and operating the equipment. We anticipate this position to continue for testing batteries in the coming years.
- Construction Jobs: We estimate that four temporary/construction jobs were created over the two years of the project so far.

Pictorial Overview

Photographs of the new NREL laboratory space and equipment purchased under the ARRA program are shown below. (All photos taken by Dirk Long, NREL.)

TTF laboratory before construction

Workers installing chilled water and electrical components in TTF laboratory

TTF laboratory after construction and equipment installation

TTF laboratory environmental chambers (3/5) with JCS & A123 PHEV battery packs under test

TTF laboratory Bitrode battery testers

Thin film thermal conductivity meter, coin cell calorimeter, and bulk thermal conductivity meter (clockwise from upper left)

NREL-designed/fabricated cell calorimeter

Planned Work for FY 2012

The NREL Battery TTF, including the purchase and installation of equipment, will be finished by June 2012. The remainder of the work for FY12 will concentrate on completing the fabrication of the battery thermal management test loop and the custom-designed cell calorimeter. We will also be vetting these two systems to determine how well they perform and adjust the design as necessary.

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

Objective

- Identify cost-optimal electric vehicle (EV) use strategies capable of achieving national oil displacement goals.

Technical Barriers

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

Accomplishments

- Applied the FY10 Battery Ownership Model (BOM) to a comparison of the costs of operating EVs and presented the results at the 25th Electric Vehicle Symposium. This work highlighted the need for a more efficient model that considered battery degradation more precisely.
- Restructured the software architecture around NREL's high-fidelity battery life model. This has not only resulted in faster computational times and more realistic results, but has also enabled additional features such as the incorporation of NREL's battery second use model and a preliminary vehicle-to-grid services model.
- Acquired longitudinal drive pattern data from the Puget Sound Regional Council's Traffic Choices Study (TCS). Preliminary analysis of the data has illustrated that each individual vehicle drive pattern is unique, that EV economics are highly sensitive to drive pattern, and that the use of cross sectional drive patterns typically overestimates battery electric vehicle costs.

Introduction

Wide-scale consumer acceptance of alternatives to conventional gasoline-powered vehicles such as HEVs, PHEVs, and battery electric vehicles will depend on their cost-effectiveness and their functionality, including driving range and ease of refueling.

A number of technical and business strategies have been proposed and/or deployed to enable the transition to these alternative powertrain technologies, including the electric utility's 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 electric vehicles while parked, fast-charge and/or battery swap stations that effectively extend EV range, and alternative car ownership models that allow users to own an EV but rent other vehicles for long-distance excursions. Each strategy has unique implications to the vehicle design, operating characteristics, and battery life. Accordingly, it can be challenging to compare different system options on a consistent basis.

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

Approach

The purpose of the BOM is to calculate the 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. The vehicle economics 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. A simplified illustration of the BOM architecture is shown in Figure 1. The model is currently written in Microsoft Excel.

There are many reasons why an individual car buyer chooses one vehicle over another. The economic factor is important for individual consumers, but there are many other factors that impact the purchasing decision as well. For end-users such as fleet owners, economics is one of the top factors for purchasing. In addition, the economics of technologies can aid policy makers in decision-making. Thus, there is a strong motivation to look at the economics of vehicle technologies to see how they compare against each other. As such, the primary output of the BOM is an economic indicator of end-user net present costs called "levelized cost per mile" (LCPM). The LCPM economic metric is defined as follows:

$$LCPM = \frac{\sum_{i=1}^{N} c_i \cdot d_i}{\sum_{i=1}^{N} vmt_i \cdot d_i}$$

The variable c is the cost to the end user during the given period, i. The discount factor for the given period is d. Finally, the vehicle miles traveled for the given period is vmt. The total number of periods is represented by N.

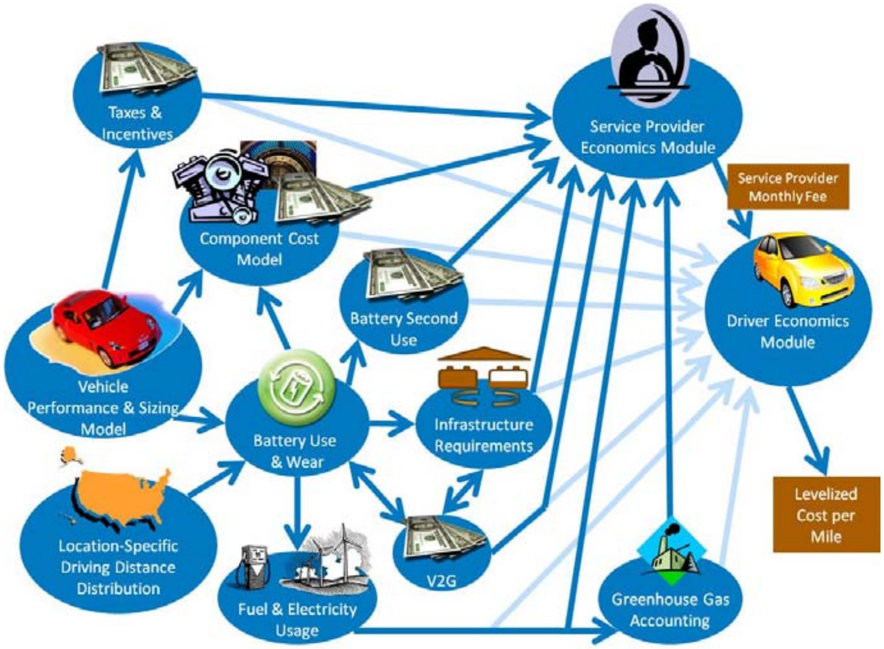

Figure 1: Overview of Battery Ownership Model

Results

Results of FY10 analyses (made prior to the integration of the NREL high-fidelity degradation model and acquisition of TCS drive pattern data) were presented at the 25th Electric Vehicle Symposium in Shenzhen, China, in early FY11. This study identified that battery life has a major impact on overall vehicle economics, as the sensitivity of the vehicle levelized cost ratio to several design variables in Figure 2 shows.

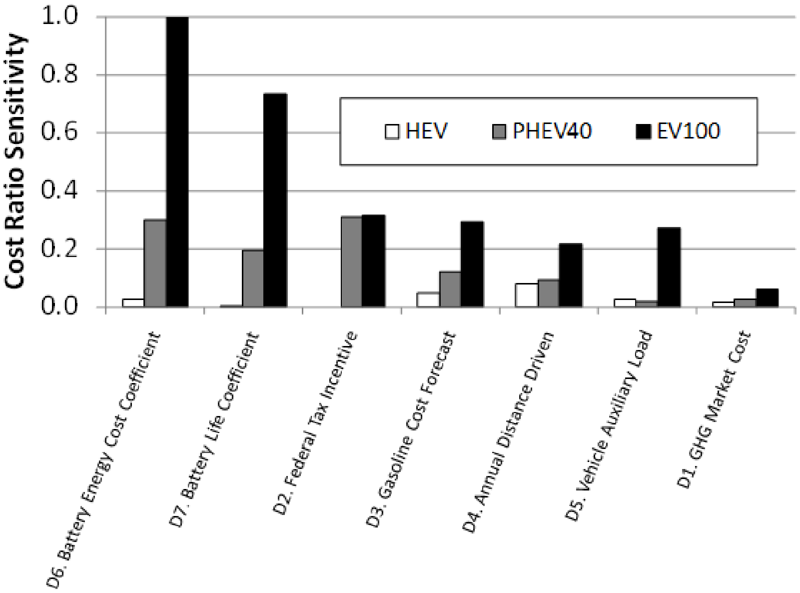

Figure 2: Sensitivity of vehicle levelized cost ratio to design variables

In response to this finding, NREL developed and integrated the battery use and wear module to the BOM software in FY11. This element is built around NREL's higher-fidelity degradation model, capable of considering complex battery duty cycles and accurately capturing the impact of depth of discharge, temperature, and state of charge (SOC). As integrated into the BOM, the degradation model calculates capacity loss and resistance growth at the end of each service year, based on the selected drive pattern, charge strategy, and vehicle-to-grid service, which is used in turn to both compute the achievable vehicle miles traveled each year and determine the end of automotive service life. In addition, the use and wear module also calculates the second use service life achievable by the battery after its extraction from automotive service. Although the model framework is expandable to any chemistry type, at present we are restricted to a nickel-cobalt-aluminum (NCA) cathode, graphite anode Li-ion chemistry due to the public availability of life test data upon which to build the model.

In addition to making these model upgrades, we acquired and analyzed longitudinal drive pattern data from the Puget Sound Regional Council's TCS. The TCS placed global positioning systems in 445 vehicles from 275 volunteer Seattle metropolitan area households that recorded driving patterns over an 18-month average per household period. We extracted three months of data from each of 398 of these vehicles to create 398 vehicle-specific discrete probability distribution functions of daily vehicle miles traveled for use in the BOM. Analysis of battery electric vehicle costs for each of these drive patterns revealed a large sensitivity to the daily vehicle miles traveled distribution of a given vehicle. Further, we found that employing cross sectional drive patterns overestimates battery electric vehicle costs relative to most vehicle-specific longitudinal drive patterns. Thus, we have concluded that proper application of drive pattern data—specifically, the use of longitudinal datasets—is critical to accurate techno-economic EV analysis.

Conclusion and Future Directions

Significant upgrades have been made to the BOM in FY12, including the integration of a high-fidelity battery degradation model and the acquisition of high-quality longitudinal drive pattern data for future analyses. Both of these additions have proven to have a large impact on cost calculations from preliminary investigations.

In future work, we plan to leverage these additions via multiple studies. After developing methods and metrics to efficiently manage the simulation and results of hundreds of drive patterns, we plan to analyze the effects of vehicle range and multiple charge strategies on EV economics, exercising the new capabilities of the upgraded battery degradation model. Investigation of the impacts of battery swapping, vehicle-to-grid service, and battery second use will follow.

FY2011 Publications/Presentations

- J. Neubauer, "The Impact of Lithium Availability on Vehicle Electrification." Plug-In 2011, July 2011. Raleigh, NC.

PEV Battery Second Use

Objectives

- Identify, assess, and verify profitable applications for the second use of PEV Li-ion traction batteries after their end of useful life in a vehicle to reduce cost and accelerate adoption of PEVs.

Technical Barriers

- Currently, the cost of batteries is too high for mass production of electric drive vehicles (EDVs). Re-using PEV batteries in secondary applications and avoiding sending them to recycling prematurely is of considerable interest.
- Applications best suited for used PEV batteries, their value, and their market potential have not yet been identified. Grid-based applications—those typically discussed as most appropriate—are often complicated by uncertain electrical demands, complex and difficult-to-assess revenue streams, and regulatory structures prohibitive to energy storage technology.
- Battery degradation, both in automotive and secondary service, is notoriously difficult to ascertain, yet has a strong impact on the potential profitability of secondary use strategies. Further, it is envisioned that accurate degradation forecasting will be necessary to meet warranty requirements on second use batteries. However, sufficiently capable and accurate degradation models have yet to be developed, representative testing has not yet been performed, and used automotive batteries for such testing are in extremely short supply at present.
- Profitable second use applications may require significant reconfiguration of automotive batteries, and/or the integration of a large number of disparate (both in design and age) automotive batteries into a single system. Further, it is as yet unclear what thermal and electrical management systems from the donor automobile will be supplied with each used battery. Thus, identifying the hardware and approach necessary to meet performance and safety targets while minimizing cost is a significant challenge.

Technical Targets

- Identify profitable and 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 prevent premature recycling of otherwise useable batteries.

Accomplishments

- Contracted a team of utility companies, university research centers, and hardware providers led by the California Center for Sustainable Energy to support analyses, acquire aged Li-ion automotive batteries, and perform long-term testing.
- Completed a preliminary analysis of second use battery value and likely second use applications accepted for publication in the Journal of Power Sources.
- Acquired numerous aged Li-ion automotive batteries and completed significant acceptance testing.

Introduction

Accelerated market penetration of PEVs is presently limited by the high cost of Li-ion batteries. In fact, it has been estimated that a more than 50% reduction in battery cost is necessary to equalize the current economics of owning PEVs versus conventionally fueled vehicles.

One means of reducing battery cost is to recover a fraction of the battery cost via reuse in other applications after it is retired from service within the vehicle, where it may still have sufficient performance to meet the requirements of other energy storage applications. 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.

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. Such application of used and new automotive traction batteries has been investigated before, but due to the use of outdated application and battery assumptions, these studies are in need of revision.

Approach

This effort investigates the application of new and used Li-ion PEV batteries to modern utility and other applications with the goal of reducing the cost to automotive consumers. The major technical barriers to the success of such efforts have been identified as second use application selection, long-term battery degradation, and cost and operational considerations of certifying and repurposing automotive batteries.

To address these barriers, NREL is conducting a detailed techno-economic analysis to develop optimal use strategies for automotive batteries, inclusive of second use application identification. The results of this analysis will, in part, be verified via the acquisition of used automotive batteries and their long-term testing in second use applications. Success of the project is measured by the completion of long-term testing and the determination of used battery value. To facilitate and accelerate these efforts, we identified interested second use partners by issuing a request for proposals (RFP) for a collaborative project.

Results

Preliminary Analysis

Assuming that second use battery applications of sufficient value are present in the future, it is reasonable to assume that the value of used batteries will be set not by the value of the application, but of competing technology. Further assuming the competition for used Li-ion batteries to be new Li-ion batteries, second use value then becomes a strong function of future battery prices. Accounting for the anticipated future decline in battery prices, degraded battery health at automotive retirement, the cost of repurposing, a used product discount factor, and the time value of money, the possible first purchase discount and second use battery sale price was calculated and is presented in Figures 3 and 4. The possible variations in health factors, repurposing costs, etc., lead to significant uncertainty in the results, but in all cases the expected cost of second use batteries to grid or other applications is low. However, the potential for second use to reduce cost to the automotive consumer is also generally low.

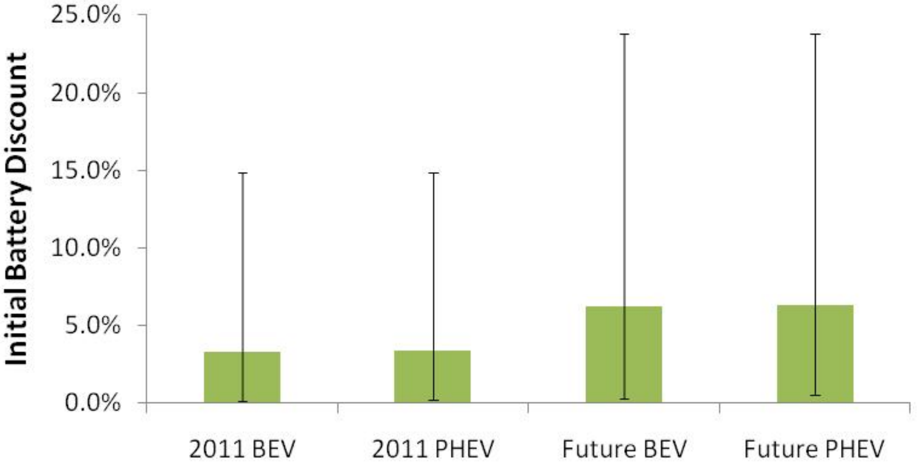

Figure 3: Projected initial battery discount due to second use

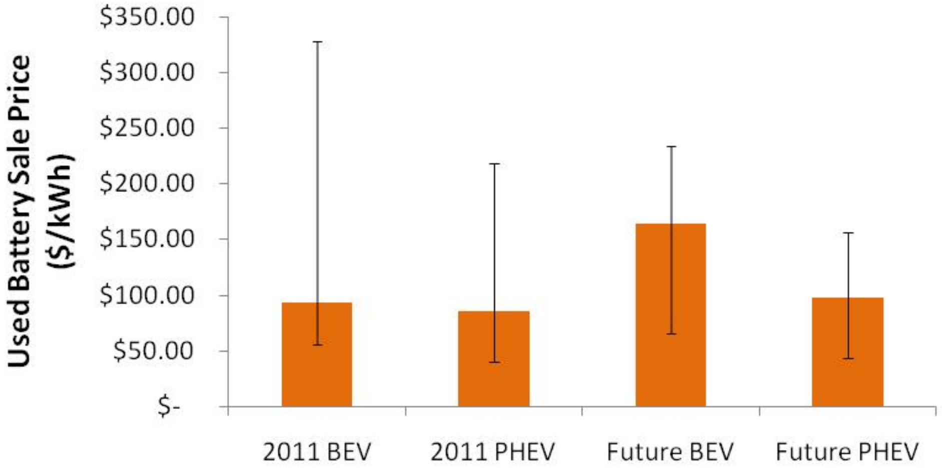

Figure 4: Projected second use battery sale price

Next, we assessed the value and market potential of possible grid-based secondary use applications. This analysis combined the results of Eyer and Corey's 2010 Sandia National Laboratories report titled "Energy Storage for the Electricity Grid: Benefits and Market Potential Assessment Guide" with the limitations of typical Li-ion batteries to provide the revenue possible on a dollars per kilowatt-hour basis. After subtracting expected balance of systems costs, these results suggest that area regulation, electric service power quality and reliability, and transmission and distribution upgrade deferral offer considerable value, as seen in Figure 5. However, the scale of such markets is important to note. Utilizing market potential forecasts from the same Sandia National Laboratories report, along with an average of PEV deployment forecasts found in the literature, we illustrate in Figure 6 that the supply of second use batteries has the potential to saturate the total *ten-year* market potential for these three high-value applications prior to 2030.

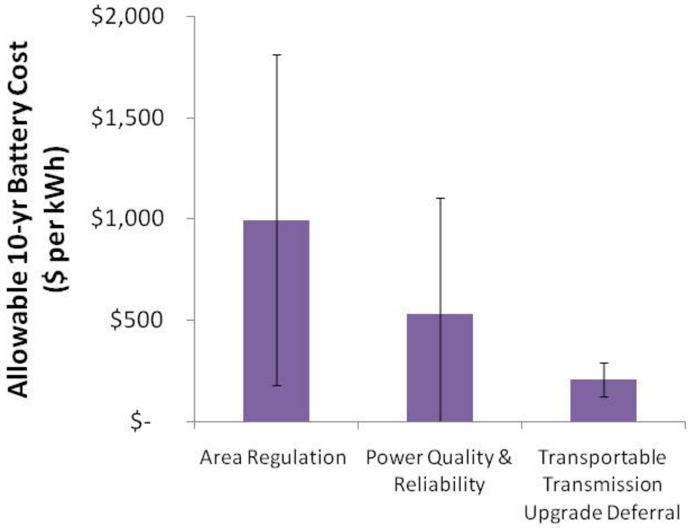

Figure 5: Projected second use battery sale price

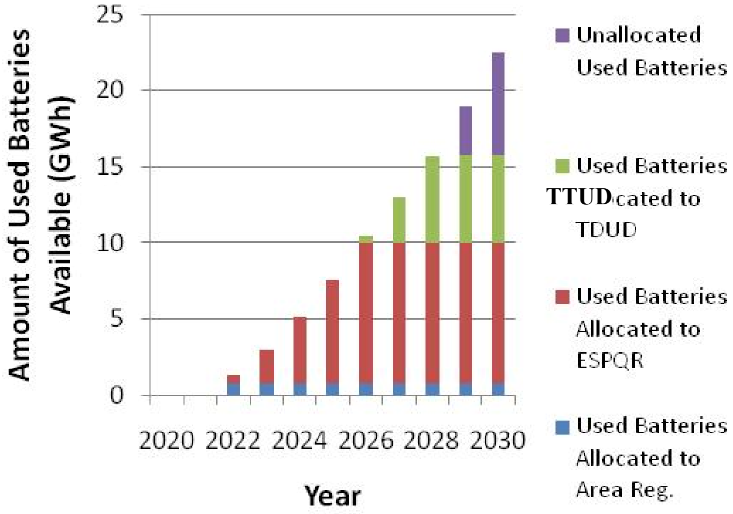

Figure 6: Allocation of second use batteries by year and application [Unallocated, Transportable Transmission Upgrade Deferral (TTUD)], Energy Storage Power Quality & Reliability (ESPQR), Area Regulation)

Battery Acquisition and Testing

Our subcontracted partners, led by the California Center for Sustainable Energy, have acquired numerous aged automotive battery packs. These packs include multiple Li-ion chemistries, including iron phosphate, nickel manganese cobalt, and manganese oxide cathodes, and graphite, hard carbon, and lithium titanate anodes. Acceptance test plans and procedures to support our analyses and down-selection of packs for long-term testing were finalized, and significant acceptance testing has been completed.

The design of our long-term test located on the University of California San Diego microgrid has also been completed. All permits and permissions have been acquired and construction will commence in early FY12. This should allow the initiation of long-term grid-connected testing on four battery packs by January 2012.

Conclusions and Future Directions

NREL has completed a preliminary analysis on the second use of PEV Li-ion traction batteries. The results of this study indicate that a few grid-based energy storage applications capable of bearing the expected cost of second use batteries exist today, although the size of their markets relative to the expected available supply of second use batteries is questionable. Further analysis in early FY12 in collaboration with NREL's subcontracted research partners will build upon these results, refining assumptions on costs and performing more detailed revenue calculations to reduce uncertainty in second use value projections and identify probable second use battery duty cycles.

These duty cycles will then be applied to the long-term testing of four aged automotive Li-ion battery packs connected to the University of California San Diego's microgrid. This testing will demonstrate both the feasibility and potential revenue of second use battery operation. Importantly, continuation of these tests over several years will provide critical information on the longevity of second use batteries serving grid-connected applications.

FY 2011 Publications/Presentations

- Neubauer, Jeremy, and Pesaran, Ahmad, "The Ability of Battery Second Use Strategies to Impact Plug-In Electric Vehicle Prices and Serve Utility Energy Storage Applications," *Journal of Power Sources,* Vol. 196, Issue 23, 1 December 2011, pp, 10351–10358.

Battery Life Trade-Off Studies

Objectives

- Develop techno-economic models that quantify battery degradation over a range of real-world temperature and duty-cycle conditions.
- Develop physically based, semi-empirical battery life prediction models for the life trade-off studies.
- Identify systems solutions and controls that can reduce the overall lifetime cost of EDV batteries.

Technical Barriers

- Achieving 10- to 15-year battery life in disparate thermal/geographic environments and duty cycles.
- Appreciable cost of PHEVs and EVs driven by conservative battery designs employed to reduce warranty risk.
- Lack of models and methods to perform economic and engineering analyses related to battery life.

Technical Targets

- Ten- to 15-year calendar life for batteries used in EDVs such as HEVs, PHEVs, and EVs.
- Develop strategies to enable 10- to 15-year PHEV and EV battery life in challenging thermal and duty-cycle environments.
- Develop models and analysis tools to understand impact of real-world duty cycles and scenarios on battery life.
- Validate battery life models using both accelerated laboratory and real-world data.

Accomplishments

- Applied previously developed graphite/ NCA chemistry life model to analyze 782 "real world" PHEV10 and PHEV40 drive cycles in multiple climates.
- Compared differences in battery life under nightly and opportunity charging scenarios.
- Identified worst-case PHEV duty cycles and quantified benefits of possible life-extending controls.
- Initiated development of graphite/iron-phosphate chemistry life model and validation study based on real world automotive data.

Introduction

EDVs offer the potential to reduce reliance on fossil fuels; however, the fuel displacement of EDVs will be elusive until they achieve meaningful market penetration. Batteries are often the most expensive component of the EDV, and further cost reduction is required to make the vehicles more attractive in the marketplace. To compete with conventional vehicles, EDVs and their batteries must achieve 10- to 15-year life in a variety of climates and possible duty cycles.

A battery's aging behavior directly impacts applications and environments to which it is suited and to what degree the battery must be oversized to achieve desired service life. Unlike batteries for consumer electronics, automotive batteries face large variability in thermal environment and duty cycle. Worst-case aging conditions drive the need to conservatively size batteries and it is important to explore degradation impacts for a range of possible duty cycles to identify and understand such worst cases. Systems design and control strategies that extend battery life are important to reduce the market cost of EDVs.

Approach

From the systems perspective, significant stressors to a Li-ion battery include exposure to high temperature, exposure to high charge voltages, calendar age, depth of discharge, and frequency of charge/discharge cycles. Based on aging datasets for the Li-ion NCA chemistry, NREL previously developed a physically justified semi-empirical model that can be used to interpolate from simple laboratory test conditions to arbitrary duty cycles likely to be encountered in real-world environments. NREL's life-predictive model is suitable for battery systems engineering and techno-economic analysis of Li-ion batteries.

To explore a range of possible light-duty vehicle duty cycles, NREL conducted vehicle simulations of two PHEV configurations (Table 1) using as inputs 782 speed-versus-time profiles collected in GPS travel surveys by the Texas Department of Transportation (M. Earleywine, J. Gonder, T. Markel, M. Thornton, IEEE-VPPC, September 2010). Vehicle simulation of the 782 single-day driving cycles thus provides a distribution of possible battery power profiles for PHEV10 and PHEV40 applications. Those power profiles together with battery thermal and life simulations generate a distribution of possible battery life outcomes for multiple drive cycles and consumer charging behaviors.

Table 1: Vehicle and Battery Model Parameters

		PHEV10	PHEV40
Vehicle	All-electric range, km	16.7	67
	Total vehicle mass, kg	1714	1830
	Electric motor power, kW	40	43
	IC engine power, kW	77	80
Battery Electrical[1]	Useable power, kW	44	48
	Useable energy, kWh	2.67	11.48
	Maximum SOC	80%	90%
	Minimum SOC at BOL	30%	30%
	Minimum SOC at EOL	13%	10%
	Excess energy at BOL	100%	67%
	Excess power at BOL, 10% SOC	43%	43%
Battery Thermal[2,3]	Heat transfer area - cells-to-coolant, m^2	1	3
	Heat transfer area - pack-to-ambient, m^2	1.2	2.9
	Heat transfer coeff. - pack-to-ambient, W/m^2K	2	2

The complete analytic matrix of scenarios considered in the NCA battery life analysis (K. Smith, M. Earleywine, E. Wood, A. Pesaran, 220th ECS Meeting, 2011) are:

- PHEV10 and PHEV40 midsize sedans

- Hot and cold geographic regions (represented by Phoenix, Arizona, and Portland, Maine, with effective ambient temperatures of 28°C and 10°C, respectively)
- Nightly and opportunity charge scenarios
- Isothermal, limited, and aggressive thermal management scenarios.

Results

Figure 7 shows statistics of typical NCA battery remaining capacity after 8 years of repeated battery cycling under each of the 782 driving cycles. (One rest day is assumed for each 6.8 days driving, such that the average annual miles traveled for the dataset is same as the U.S. national average, 12,375 miles/year) In an actual pack, individual cells may age slower or faster due to manufacturing variability at beginning of life and temperature variation throughout the pack. Neither effect is considered here. A worst-case cell in the pack may thus age at a somewhat faster rate than predictions given here.

In Figure 7, the PHEV10 and PHEV40 have similar mean aging behavior, with around 80% capacity remaining on average after 8 years. The shapes of the distributions differ, however. Slightly more of the PHEV10 outcomes are grouped at the lower end of the histogram, in the 75% to 78% remaining capacity range. This is because 86% of PHEV10 drivers will use their battery's entire charge depletion (CD) available energy each day compared to 34% of PHEV40 drivers. (Note that the distribution of daily driving distances for the 782 drive cycles used here reasonably mirrors the U.S. national distribution of distances)

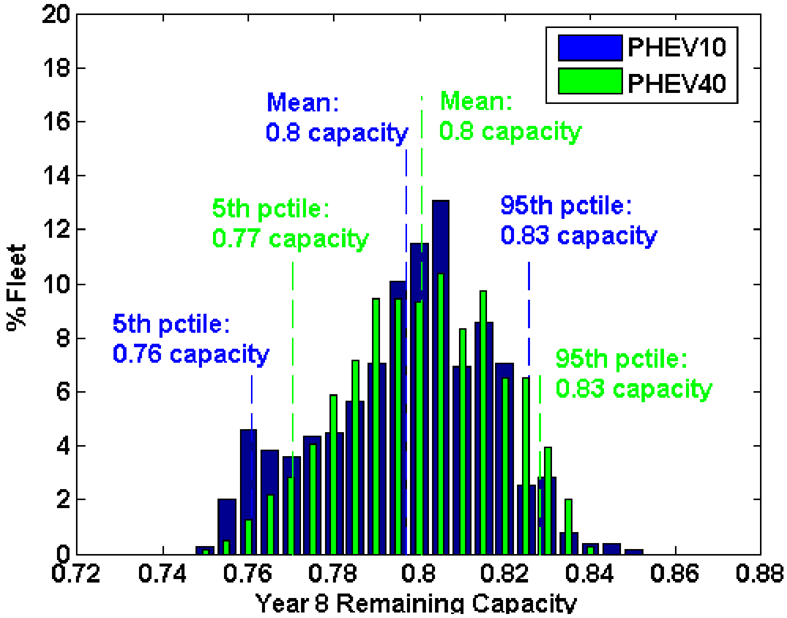

Figure 7: Battery remaining capacity at Year 8 for hot-climate geographic scenario with battery temperature fixed at 28°C ambient and nightly charging.

Moving on to the complete analytic matrix of scenarios considered, Figure 8 shows statistics of remaining capacity after 8 years for the various geographic regions, charging scenarios, and thermal management scenarios. Considering geography first, the hot climate isothermal case (28°C ambient) shows almost double the capacity loss of the cold climate (10°C ambient) temperature.

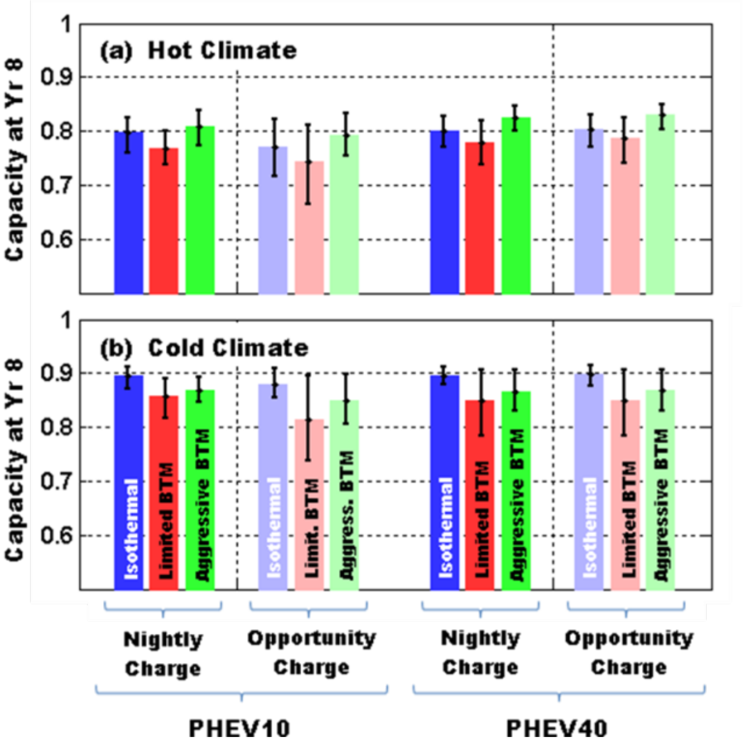

Figure 8: Remaining capacity at the end of 8 years for various battery thermal management and charging scenarios. Colored bars show average result for all 782 drive cycles; error bars show result for 5th and 95th percentile drive cycles.

Differences between hot and cold climates narrow slightly when more realistic battery temperature evolution with time is considered in the "limited" and "aggressive" battery thermal management (BTM) scenarios. Here, the limited BTM system assumes forced ambient air cools the battery, resulting in temperature rise above ambient and shorter battery life relative to the isothermal case. The aggressive BTM system assumes 20°C chilled fluid cools the battery that, in the hot climate, results in slightly longer life relative to the isothermal case. In Figure 8, error bars denoting degradation for 5th and 95th percentile drive cycles show that aggressive BTM can reduce sensitivity of battery life to drive-cycle, a desirable outcome.

As shown Figure 9, the PHEV10 and PHEV40 generally experience similar degradation trends. The impact of charging behavior is an exception. The PHEV10's battery life is far more sensitive to opportunity charging than the PHEV40's. As mentioned before, the PHEV10 battery's available CD energy is more often completely used compared to the PHEV40's battery due to the high percentage of driving trips longer than 10 miles. If the driver charges the battery whenever the vehicle is parked, the PHEV10 battery's available CD energy may be utilized two, three, or even four times per day. The aggressive BTM design accommodates the extra heat generation of additional charge/discharge cycles due to opportunity charging and keeps the battery at a lower average temperature.

Frequent charging behavior can result in a worst-case cycle-life requirement on the battery, especially for high-mileage drivers and for vehicles with small electric range such as the PHEV10. But for PHEV40 drivers with short-to-moderate daily driving distance, frequent charging can actually improve battery life.

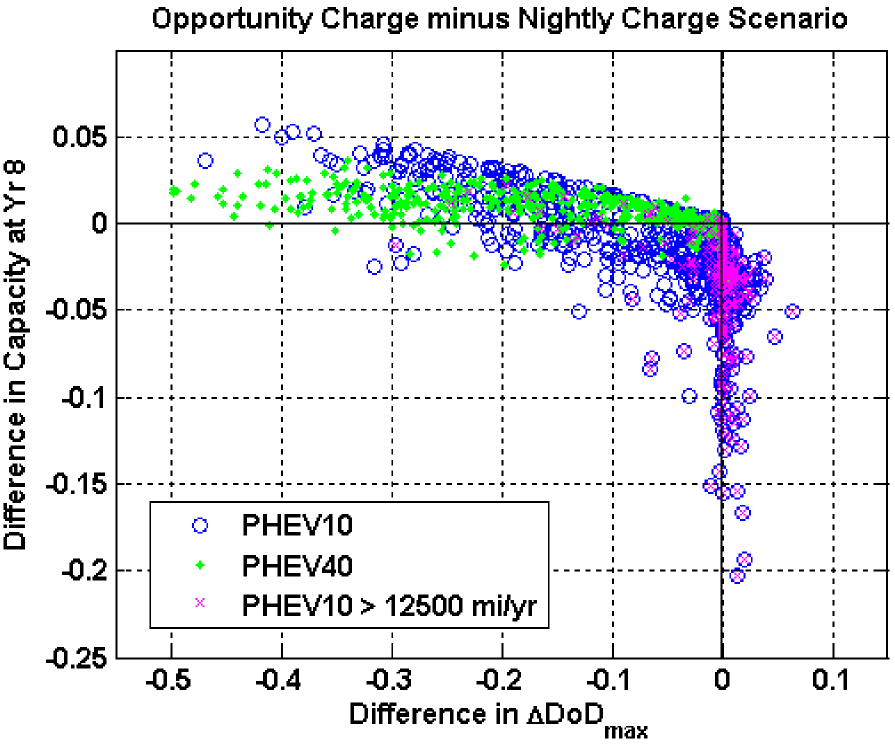

Figure 9: Difference in life outcomes for opportunity charging behavior versus nightly charging behavior (aggressive-cooling, hot-climate scenario). A slight majority of PHEV40 drive cycles benefit from frequent charging, owing to shallower cycling.

Shown with green "diamond" symbols in Figure 9, the PHEV40 8-year capacity may improve by as much as 4% or worsen by as much as 3% when a driver's behavior changes from nightly charging to opportunity charging. The majority of PHEV40 drivers, however, will realize longer life from their batteries by opportunity charging as the more frequent charging favorably results in shallower CD cycles that cause less damage. (Note that these results do not consider fast charging and depend on the battery useable energy window assumptions given in Table 1) In contrast, a significant portion of the PHEV10 population will experience shorter life from opportunity charging, with as much as 20% additional capacity fade at 8 years. In Figure 9, the purple "×" symbol denotes PHEV10 drive cycles with annual mileage greater than 12,500 miles/year. Those high-mileage drive cycles account for many of the worst life outcomes for the PHEV10 vehicle when opportunity-charged.

Conclusions and Future Directions

Thermal management system design is shown to be effective in extending battery life for the most severe duty cycles and reduces sensitivity in battery aging to drive cycle. Use of a refrigerated or chilled-fluid cooling system extends life in hot climates. Worst-case battery life has some correlation with high annual miles traveled, although charging behavior also has significant impact. This means that battery state of health cannot be directly determined from the vehicle's odometer.

Future work will include extension of the life model to capture battery degradation mechanisms specific to fast charging, extension of the model to additional chemistries within the Li-ion family, and validation of the life model with real-world automotive data.

FY2011 Publications/Presentations

- K. Smith, T. Markel, G.-H. Kim, A. Pesaran, “Design of Electric Drive Vehicle Batteries for Long Life and Low Cost,” IEEE Workshop on Accel. Stress Test. & Reliability, Denver, October 6–8, 2010.
- E. Wood, J. Neubauer, J. Gonder, A.D. Brooker, K. Smith, “Variability of Battery Wear in Light Duty Plug-In Electric Vehicles Subject to Ambient Temperature, Vehicle Design and Consumer Usage,” submitted.
- K. Smith, M. Earleywine, E. Wood, A. Pesaran, “Prediction of Li-ion Battery Life under Real-World Automotive Duty-Cycles,” 220th Electrochemical Society Meeting, Boston, October 11, 2011.

Low Energy HEV Requirements Analysis (NREL)

Objectives

- Support development of a cost-effective HEV energy storage system (ESS), with the overall goal of maintaining high HEV fuel economy with a smaller/lower-cost ESS. Increased market penetration of such systems would lead to larger aggregate petroleum savings.
- Evaluate potential adjustments to the lower-energy ESS (LEESS) targets established by the USABC in FY10. Consider results of cost analysis based on the LEESS targets, and opportunities to further the goal of cost-effective HEV energy storage.
- Identify a power-assist HEV (PA-HEV) test platform for in-vehicle demonstration and evaluation of LEESS operation.

Technical Barriers

LEESS technical barriers include the need to optimally design the device to achieve high HEV fuel economy, without including excessive capabilities that will increase cost. Other important considerations include the need to build confidence in the capability of LEESS devices and the need to identify unforeseen system integration issues, both of which will be addressed by the in-vehicle demonstration and evaluation effort.

Technical Targets

Previous NREL analysis, conducted in collaboration with USABC and an Electrochemical Energy Storage Technical Team (EES TT) workgroup, led to the creation of the following LEESS technical targets:

- 2 sec | 10 sec discharge pulse power: 55 kW | 20 kW (previous minimum PA-HEV target was 25 kW for 10 sec).
- 2 sec | 10 sec charge pulse power: 40 kW | 30 kW (previous minimum PA-HEV target was 20 kW for 10 sec).
- Energy over which both power requirements simultaneously met: 26 Wh (previous minimum PA-HEV target was 300 Wh).
- Energy window for vehicle use: 165 Wh (previous minimum PA-HEV target was 425 Wh).
- Selling system price @ 100k/yr: $400 (previous minimum PA-HEV target was $500).

Accomplishments

- Responded to concerns that the 10-sec, 30 kW charge target and the 2-sec, 55 kW discharge power target were dominating LEESS sizing and cost. Noted that the EES TT workgroup chose to use the most demanding US06 drive cycle case as the basis for setting the LEESS targets.
- Performed analysis to show that relaxing the 10-sec charge requirement to 20 kW and the 2-sec discharge requirement to 40 kW would have minimal HEV fuel economy impact. Small impacts would occur on the aggressive US06 cycle and little to no impact would occur on more moderate cycles, so adjusting the targets could be worthwhile if significant cost savings would be achieved.

- After consulting with two LEESS developers, it was determined that the cost savings would not actually be very significant, so USABC decided not to relax the power targets after all and left them as they were.
- Worked with an automaker to select a PA-HEV test platform and developed a conversion plan to enable in-vehicle LEESS demonstration and evaluation in FY12.

Introduction

Previous NREL analysis, conducted in collaboration with the USABC and an EES TT workgroup, led to creation of the LEESS goals summarized under the above Technical Targets section. NREL was asked in FY11 to revisit two pulse power targets (10-sec, 30 kW for charge and 2-sec, 55 kW for discharge), because a cost analysis by Tiax[1] had suggested that these two targets were driving LEESS sizing and cost higher than necessary. NREL was asked to study the impact of lowering the two power targets on the fuel economy of a PA-HEV.

Approach

Originally, the EES TT workgroup selected the most demanding US06 drive cycle case from the previous set of analyses as the basis for setting the LEESS targets. To evaluate the fuel economy impact of relaxing the 10-sec charge power target, NREL performed additional processing and analysis on the previous simulation results. To examine the impact of relaxing the 2-sec discharge power target, NREL modified the midsize HEV model used in the previous analyses and performed new simulations.

Results

The investigation that helped set the LEESS power targets included an analysis of all the pulse power events that occur during a given drive cycle. The irregular demands of a drive cycle on an HEV powertrain result in irregular charge/discharge power pulses to/from the HEV ESS. As a result, there is no single perfect way to uniformly characterize all of the pulses that occur. A few options include: 1) dividing the energy of each pulse by its total duration to determine the average pulse power, 2) dividing the energy of each pulse by its peak power to determine the effective duration at that power, and 3) dividing the energy of each pulse by a fixed time interval to determine the equivalent power for the given interval. Figure 10 shows a power pulse analysis incorporating each of these methods, including three different fixed time intervals (0.5, 2 and 10 sec).

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[1] http://www1.eere.energy.gov/vehiclesandfuels/pdfs/merit_review_2011/electrochemical_storage/es001_barnett_2011_o.pdf

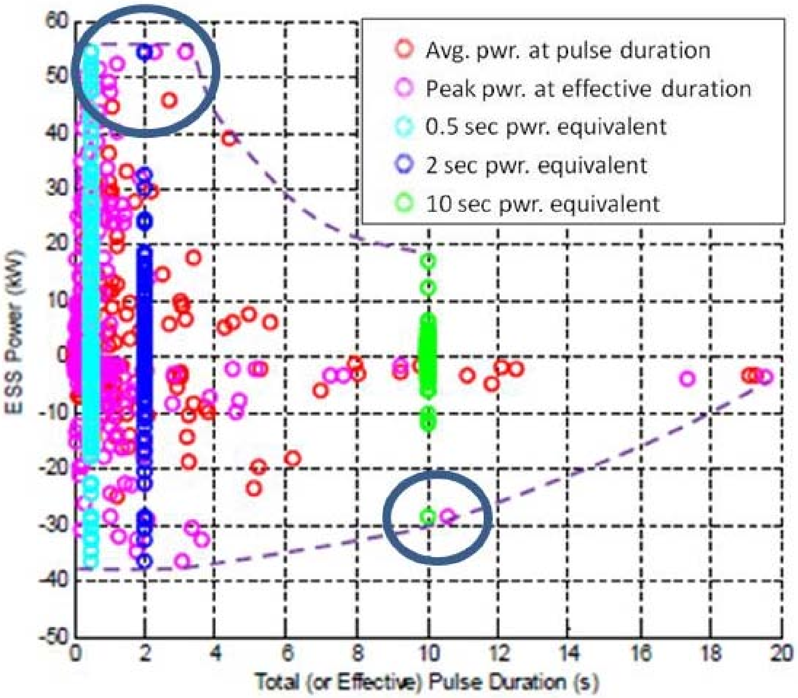


Figure 10: Analysis results of simulated HEV ESS power pulses over the US06 drive cycle (corresponding to an in-use ESS energy window of roughly 165 Wh).

The power pulse analysis in Figure 10 reflects the largest considered ESS case from the LEESS target setting analysis over the aggressive US06 drive cycle. This scenario was selected as the basis for setting the official LEESS targets. The circle in the negative (charge) power region around 10 seconds indicates the one regenerative braking (regen) pulse that would be cut off by reducing the corresponding power target to 20 kW. The circle in the positive (discharge) power region around two seconds indicates those pulses that would be cut off by reducing the corresponding power target to 40 kW.

The results in Figure 11 show that the power pulses for the same vehicle simulated over the standard Urban Dynamometer Driving Schedule (UDDS) already fall within the reduced power levels under consideration. Therefore, there would be no UDDS fuel economy impact from reducing the power targets, unless an automaker wished to increase the engine size (to make up for any loss in acceleration performance resulting from reducing the 2-sec discharge power capability). A UDDS simulation with a larger-engine HEV would be expected to have a similar power pulse envelope as shown in Figure 11, but worse fuel economy.

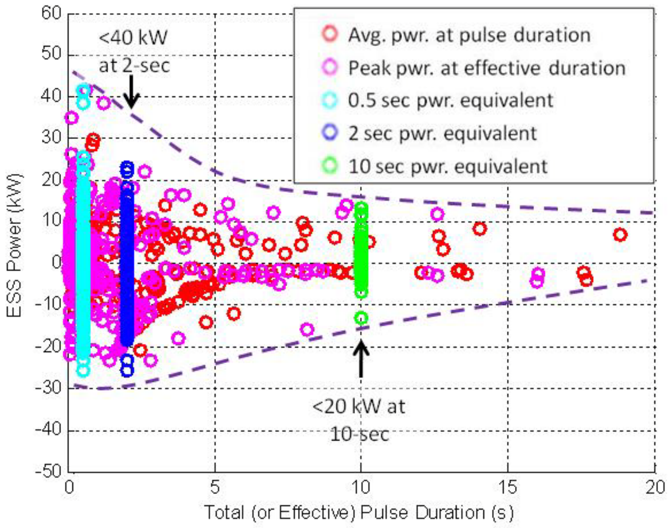


Figure 11: HEV ESS power pulses over the UDDS already fall within the reduced power levels under consideration.

The following two sections focus on the US06 cycle fuel economy impact of the two power target reductions under consideration.

Impact of Relaxed Charge/Regen Power

Figure 12 highlights the exact amount of the circled power pulse in Figure 10 that would be cut off by capping the 10-sec charge power at 20 kW. The amount of regen energy that would no longer be captured only totals about 6 Wh. NREL estimated that an additional 0.001 gal of fuel would be required to instead use the engine to return this amount of energy into the ESS. Therefore, the estimated US06 fuel economy improvement over a comparable conventional vehicle for the reduced-charge power HEV would be 20.0%, as opposed to 20.4% for the higher charge power case.

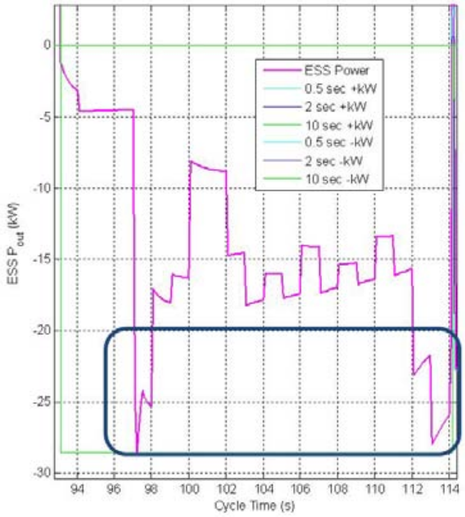


Figure 12: Indicates the amount of the large US06 regen power pulse that would cut off by capping the 10-sec charge power level at 20 kW.

Impact of Relaxed Discharge Power

To evaluate the US06 fuel economy impact of eliminating the high-power, short-duration pulses circled in the top left of Figure 10, NREL modified the HEV motor model to reduce its discharge/assist power capability by nearly 20%. NREL also increased the HEV's engine power by about 20% to maintain comparable acceleration performance with the baseline conventional vehicle. Figure 13 shows the power pulse analysis from the modified HEV simulated over the US06 drive cycle.

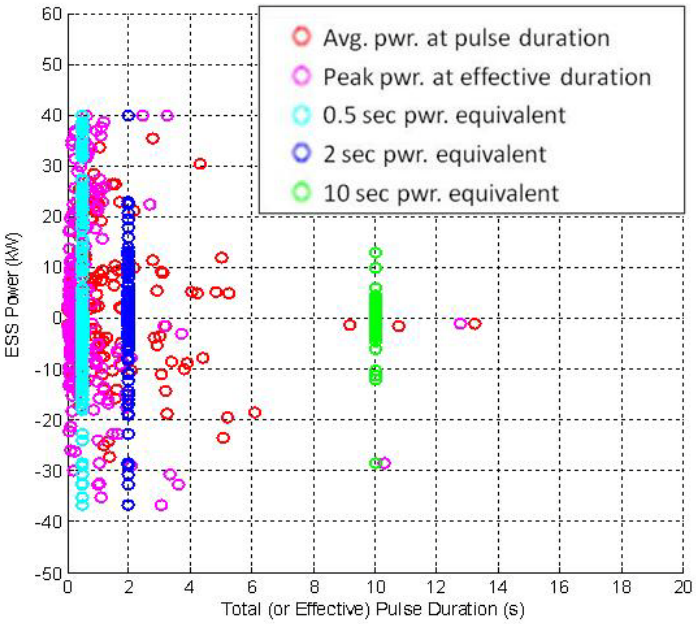


Figure 13: ESS power pulse analysis over the US06 cycle for the restricted discharge power HEV model.

Note that the power pulse analysis shown in this figure is identical to that in Figure 10, with the exception of the eliminated short-duration discharge/assist pulses above 40 kW. The elimination of these pulses and, more importantly, the reduced amount of engine down-sizing relative to the conventional vehicle results in lower relative US06 cycle fuel savings. As opposed to the 20.4% simulated US06 fuel economy improvement relative to the baseline conventional, the reduced ESS discharge power HEV achieves an estimated 19.1% US06 fuel economy improvement.

Impact on Energy Requirement

Of the two power target changes that were considered, relaxing the 10-sec charge/regen power requirement requires no engine re-sizing and produces a miniscule overall fuel economy impact. Reducing this power target to 20 kW, however, would change the calculation of the required energy over which the charge and discharge power targets must be simultaneously met. This is because a smaller amount of energy from the 10-sec, 20 kW pulse (as opposed to the larger 10-sec, 30 kW pulse) would be subtracted from the top end of the 165 Wh energy window for vehicle use. As illustrated in Figure 14, this would result in a goal of 53 Wh (as opposed to 26 Wh) for the energy over which both power requirements must be simultaneously met.

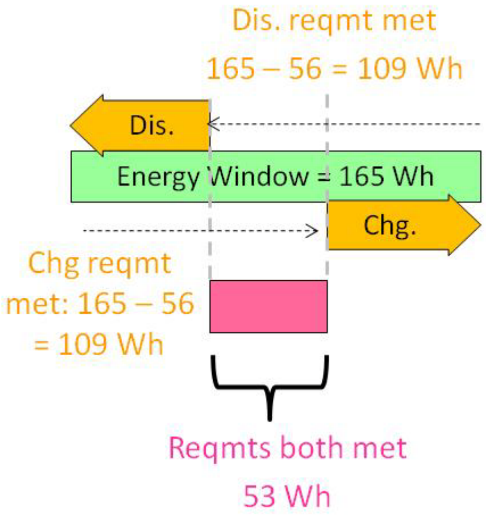


Figure 14: Calculating the goal for the energy over which both power targets must be simultaneously met, based on a reduced 10-sec charge power target of 20 kW.

Cost Target Implications of Lower Power

The USABC program managers discussed the impact of changing the power targets with the two USABC LEESS developers. The response from the developers (A123 and Maxwell Technologies) was that lowering the 10-sec charge power target from 30 kW to 20 kW and the 2-sec discharge power target from 55 kW to 40 kW would not have any significant impact on the $400 total target cost of the system. Based on this input and the NREL analysis, the EES TT decided to not modify the targets and keep the 10-sec charge power target at 30 kW and the 2-sec discharge power target at 55 kW.

Test Platform Progress

As discussed previously, an additional area of effort in FY11 was to identify a PA-HEV test platform for in-vehicle demonstration and evaluation of LEESS operation. To this end, NREL developed a technical plan in collaboration with an automaker that will support conversion of a production HEV to operate on a LEESS instead of its existing ESS. Once completed, the HEV test platform will enable demonstration and evaluation of multiple LEESS device types, including very high power batteries, electrochemical double-layer capacitors and/or asymmetric devices possessing some battery and some ultracapacitor characteristics (very high power, low energy, and long cycle life).

Conclusions and Future Directions

NREL's analysis, in collaboration with an EES TT workgroup and USABC, helped establish LEESS targets for HEVs. In response to concerns raised by an initial cost analysis, NREL conducted the further analysis described above to evaluate the potential fuel economy impact of relaxing two of the LEESS power targets. The analysis showed negligible fuel economy impact, particularly for relaxing the 10-sec charge power target from 30 kW to 20 kW (although this change would require also changing the goal for energy over which both power requirements are simultaneously met). Reducing the 2-sec discharge power target from 55 kW to 40 kW would also have little fuel economy impact, but the impact would be larger than that of the 10-sec charge power change because of the need for less engine downsizing relative to the baseline conventional vehicle (in order to maintain comparable acceleration capability).

Potentially, only the US06 cycle fuel economy would be impacted for both the prospective charge and discharge power target changes, because the power pulses on other cycles such as the UDDS already fall within the reduced power levels. Having no impact on other test cycles would serve to dilute the overall negative impact on composite fuel economy. However, if it was decided that the discharge power change would require re-running every test cycle with less engine downsizing, then a larger fuel economy impact would occur. Accepting a small fuel economy penalty (particularly for the 10-sec charge power reduction) could be worth considering if the change(s) led to significant cost savings. However, after USABC program managers discussed the impact of changing the power targets with the two USABC LEESS developers, it was decided that the changes would not produce significant cost savings after all. Therefore, the ESS TT and USABC decided to leave the LEESS power targets unchanged.

Future project efforts will focus on completing development of the HEV test platform, and performing in-vehicle demonstration and evaluation of actual LEESS devices. This activity will help to validate and build confidence in the overall LEESS approach, and may help identify important system integration issues. If the various barriers can be overcome, LEESS technology could help improve HEV ESS cost effectiveness, increase HEV market penetration, and lead to large aggregate petroleum savings.

FY 2011 Publications/Presentations

- 2011 DOE Annual Merit Review Meeting Poster, May 2011.
- Presentations to USABC and FreedomCAR/U.S. DRIVE Electrochemical Energy Storage Technical Team, May, August, and November 2011.

Battery Thermal Analysis and Characterization Activities

Objectives

- Thermally characterize cell and battery hardware and provide technical assistance and modeling support to U.S. Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE)/USABC and developers to improve system design and performance of ESSs.
- Quantify the impact of temperature and duty cycle on ESS life and cost.

Technical Barriers

- Decreased energy storage life at high temperatures.
- High energy storage cost due to cell and system integration.
- Cost, size, complexity, and energy consumption of thermal management systems.
- Inadequate energy density and specific energy to meet the "charge-depleting" energy requirement.
- Insufficient cycle life stability to achieve the 3,000 to 5,000 "charge-depleting" deep discharge cycles.

Technical Targets

- Energy storage operation temperature of -30°C to 52°C.
- Develop a high-power battery technology that has a 50 Wh cycle life exceeding 300,000 cycles.
- Calendar life at 35°C exceeds 15 years.

Accomplishments

- We have been thermally and electrically evaluating ESSs from A123, Compact Power Incorporated (CPI), K2, JCS, and SK.

Introduction

The operating temperature is critical in achieving the right balance between performance, cost, and life for both Li-ion batteries and ultracapacitors. At NREL, we have developed unique capabilities to measure the thermal properties of cells. We also use our electrothermal finite element models to analyze the thermal performance of battery systems 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 U.S. DRIVE program manufacturers and other industry partners. NREL supports the EES TT by participating in various work groups such as the JCS, CPI, A123, K2, and SK Work Groups.

Results

Calorimeter Testing

NREL's calorimeters provide critical heat generation and efficiency data for the battery under test. A typical heat generation and efficiency curve produced by the calorimeter for a PHEV battery is shown in Figure 15. The figure shows how the heat generation is dependent on the ambient temperature conditions and the magnitude of the current applied to the battery. Understanding how much heat is produced by the battery allows car manufacturers to operate the vehicle battery within a range that extends the life and operational safety of the battery. In the past, battery manufacturers could only estimate the round-trip efficiency of a battery—the battery would be discharged and then charged back to its original SOC. The limitation of this technique is that the discharge and charge efficiency cannot be determined independently. By using NREL's calorimeters to directly measure heat, the efficiency of the battery can be determined independently for both charge and discharge currents rather than a combination of the two—a necessary data point when outlet charging batteries for PHEV applications.

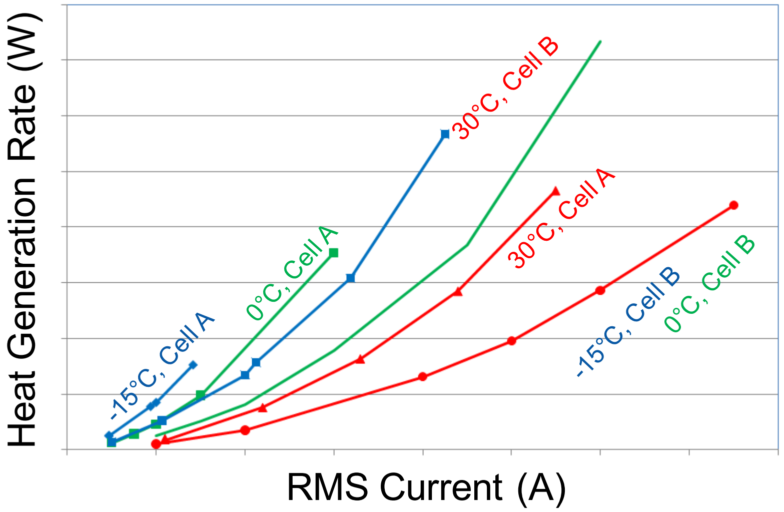


Figure 15: Heat generation from a PHEV cell

NREL's calorimeters are designed to be accurate enough to measure the electrochemical response from batteries under test. As car manufacturers progress from HEVs to PHEVs and EVs, the design of the battery pack will also change. For instance, an HEV battery pack is cycled within a very narrow band, typically within a window encompassing 10% of the overall energy window of the pack. For example, the Toyota Prius battery pack is primarily used within a 10% SOC window from 55% to 65% SOC. Batteries used in EVs and PHEVs are cycled over a much wider range—typically from 95% SOC to 25% SOC. Over this SOC range, the battery goes through several crystalline phase transitions as shown in Figure 16. The battery in this figure was cycled from 100% SOC to 0% SOC at a very low current. As shown in the figure, the battery undergoes an endothermic transition at about two hours, which is the equivalent of 80% SOC. With any phase transition (crystalline or other), the material going through the phase transition expands and contracts. Observing the phase transition requires an extremely accurate calorimeter with a very stable baseline.

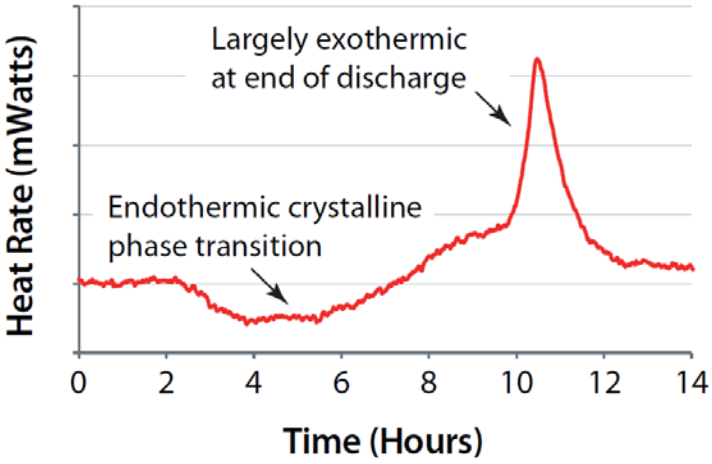


Figure 16: Heat generation from a PHEV cell under low current discharge

Advanced vehicles are being developed to increase the Corporate Average Fuel Economy for an automobile manufacturer. Since most advanced vehicles rely on an ESS to realize this benefit, it is imperative that the ESS function at an optimal level during U.S. Environmental Protection Agency testing for fuel economy. Figure 17 compares the efficiency curves for an ESS at the beginning of its life and after the ESS has gone through limited cycling. The efficiency of the ESS increased substantially, in particular at the higher root-mean-square currents, after being cycled. By cycling the ESS prior to U.S. Environmental Protection Agency testing, the fuel economy of the vehicle can be positively affected—a key understanding provided by the calorimeter. The overall fuel economy benefit for a vehicle varies depending on many factors, but understanding that the ESS requires a break-in period to realize optimal efficiency could save the vehicle manufacturer from incurring fines due to the upcoming Corporate Average Fuel Economy standards.

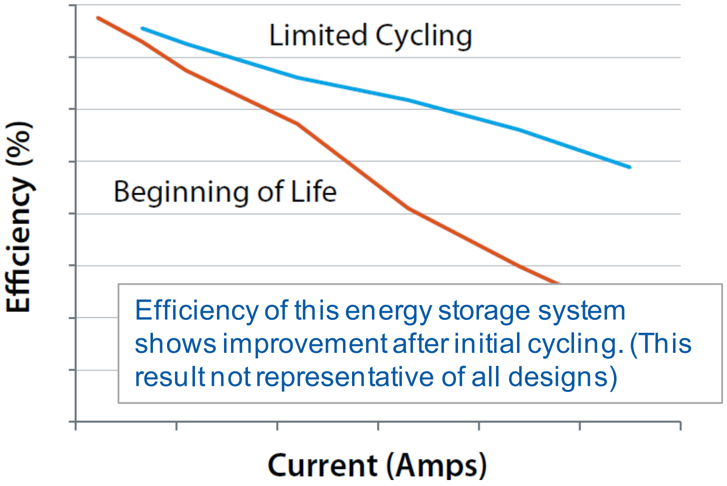


Figure 17: Efficiency curve for an ESS at the beginning of life and after limited cycling

Infrared Imaging

NREL has performed infrared imaging of battery manufacturers' cells to determine areas of thermal concern, as shown in Figure 18. NREL combines the infrared imaging equipment with a battery cycler to place the cells under various drive cycles, such as a US06 CD 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.

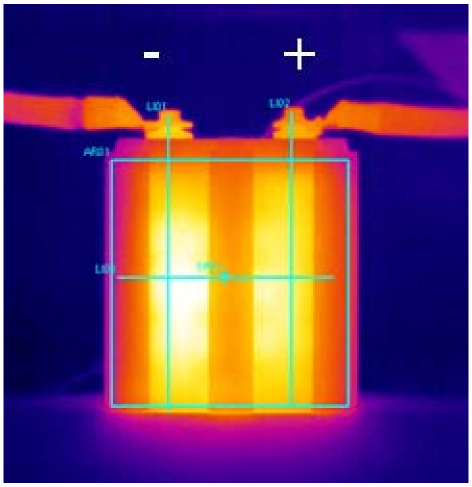


Figure 18: Infrared image of a cell under constant current discharge

Pack Thermal Studies

NREL is presently evaluating air-, liquid-, and vapor compression-cooled packs for USABC. We measure the temperature rise and difference between corresponding cells as well as the voltage of each cell within the pack. Testing is performed at temperatures between -20°C and 30°C with drive cycles pertinent for the battery under test—PHEV or EV. It has been shown that a 2%–3% difference in cell temperature can have a 2%–3% effect on fuel economy. Also, the higher-temperature cells within a pack are typically more efficient and therefore work harder than the cells at lower temperatures; higher temperature cells typically provide more power. When different cells within the pack provide different amounts of energy over time, then the cells age differently, possibly causing imbalances within the pack, and warranty issues may result. Figure 19 shows the temperature spreads of various cells in a pack during cooldown.

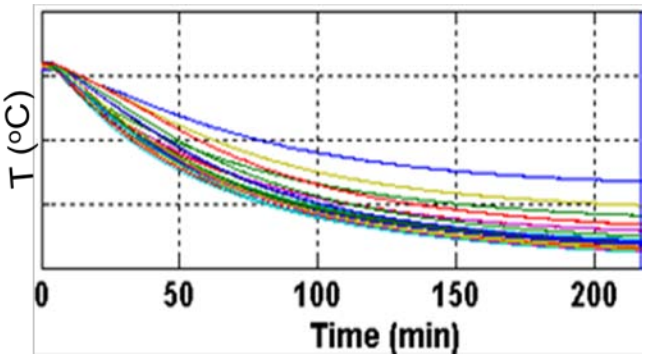


Figure 19: Thermal management system performance during higher temperature soak conditions

Conclusions and Future Directions

NREL has thermally tested cells, modules, and/or packs from A123, CPI, JCS, K2, and SK. We have provided critical data to the battery manufacturers and original equipment manufacturers that can be used to improve the design of the cell, module, pack and their respective thermal management systems.

In FY12, NREL will continue to thermally characterize cells, modules, and packs for USABC, DOE, and U.S. DRIVE.

FY 2011 Publications/Presentations

- 2011 DOE Annual Merit Review Poster.
- Data were shared with the EES TT and each of the individual battery manufacturers' work groups.

Development of an On-Demand Internal Short Circuit

Objectives

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

- Simulates an emergent ISC that replicates catastrophic field failure behavior due to a latent cell defect.
- Is capable of triggering the four types of cell internal shorts.
- Produces consistent and reproducible results.
- Allows the cell to behave normally until the short is activated—the cell can be aged before activation.
- Establishes test conditions for the cell—SOC, temperature, power, etc.
- Provides relevant data to validate ISC models.

Technical Barriers

Safety is a major impediment in transitioning to Li-ion batteries in advanced vehicles. The electrode/electrolyte in Li-ion cells makes them prone to catastrophic thermal runaway under some rare ISC conditions. The cost and size of the Li-ion cell is impacted by making the occupants of advanced vehicles safe from an internal short.

Technical Targets

It is critical for any new vehicle technology (including advanced ESSs) to operate safely under both routine and extreme conditions, which can include conditions of high temperature, overcharge, or short circuit.

Accomplishments

NREL has made progress towards the development of an on-demand ISC for Li-ion batteries that does not affect the performance of the battery under test and can be activated without puncturing or deforming the battery.

Introduction

A very small fraction of the Li-ion cells sold for consumer use, mainly in portable electronic devices, have exhibited safety failures in the field. The cells in question are normally of designs that have successfully passed a wide variety of safety tests, such as those required by governmental shipping regulations and by many certification organizations. These failures typically occur after the cell has been in use for several months with no previous, obvious problems. When these failures do occur, they can result in the cells getting very hot; some cells will go into thermal runaway and can burn or ignite the device in which they are installed. Failures of this type are often reported in the media as a “burning laptop” and have resulted in the recall of thousands of batteries. Many members of the technical community believe that these failures are caused by a latent flaw that results in an ISC between the electrodes after significant use. Some reports have suggested that the latent flaw takes the form of a very small piece of foreign material, such as metallic particles from manufacturing.

Battery manufacturers have found it very difficult to study this mode of failure. Therefore, a method is being sought to simulate this type of ISC in Li-ion cells and to develop methods to prevent such failures and/or mitigate their effects. The ideal method would be applicable to both spirally wound and flat-plate cells containing any of the common Li-ion electrochemical systems. Approaches of interest must 1) develop a method to introduce an appropriate latent flaw into a Li-ion cell; 2) "activate" the flaw to produce an ISC after representative in-field testing; and 3) compare the behavior of a cell that fails because of an ISC with the behavior of a similar, unflawed cell that is subjected to one of the standard abuse tests (such as nail penetration) that has been designed to simulate an internal short caused by a latent flaw.

Approach

NREL has developed an ISC device that can be placed anywhere within the battery and may be used with both spirally wound and flat-plate cells. The internal short device is small compared to other shorting techniques being developed by industry and does not rely on mechanical pressure deforming the battery to activate the short as do most of the other "internal shorts" being developed. The battery can be used and cycled within normal operating conditions without activating the internal short device. This allows for the battery to be aged prior to activation of the internal short. Another unique feature of NREL's internal short device is that 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 the ISC begins.

Results

In FY10, NREL conceived the idea of developing a thermal circuit to connect individual components within a Li-ion cell to simulate an ISC. The original idea was to use a metal with a low melting point to complete a circuit between any two of the following four components within a cell—copper current collector, aluminum current collector, anode, and cathode. NREL had limited success in the activation of this short, and the impedance of the internal short was not consistent, making it difficult or impossible to use as a standard test methodology for battery manufacturers and original equipment manufacturers. At the end of FY10, 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 and an illustration of how the ISC can be used between the anode and cathode is shown in Figure 20.

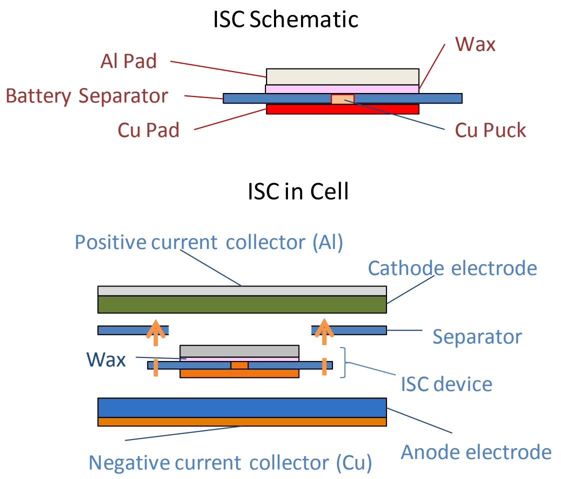


Figure 20: ISC schematic (top) and ISC placed in a cell (bottom)

In laboratory testing in FY10, the wax ISC activated 100% of the time and the resistance across the short was very consistent: within ±10%.

In FY11, NREL incorporated the wax ISC in pouch cells from Dow Kokam (DK). NREL found that the wax ISC was flexible enough to survive bend radii less than 0.050 in. without damage to the ISC or to its initial inactivated impedance. Furthermore, the implanted ISC did not affect the performance of the DK cell; the capacity and discharge/charge voltage curves of the cells with the ISC matched the control DK cells. The wax ISC was placed in DK cells to assess an internal short between:

- Cathode and anode
- Anode and aluminum current collector
- Copper and aluminum current collectors.

During testing of the wax ISC in the DK cells, it was determined that:

- The amount of wax needs to be controlled or limited.
- For a low-impedance short to exist, the contact resistance between the aluminum and copper pads of the ISC and the battery components needs to be minimized.
- When the short displaces active battery material, the copper and aluminum pad thicknesses need to be chosen so as to account for the swelling of the surrounding active material due to electrolyte filling.

Due to the aforementioned limitations, we had partial success with the wax ISC. For instance, the anode-to-cathode short increased the cell temperature by 55°C when activated, and the heat effect from the ISC caused four 1–in. holes to develop in the z-fold separator; even with the holes that developed in the separator due to the short activation, the cell did not go into thermal runaway. To address the issues outlined above, NREL conceived of various coating techniques that limit the amount of wax and create a consistent thickness of wax on the ISC. We are presently running a series of experiments to determine the optimum coating method. We have also been experimenting with different coatings (indium, carbon, etc) on the ISC to limit the contact resistance between the ISC and the battery component materials.

Conclusions and Future Directions

In summary, the final goal is to develop an ISC that:

- Is small and has a low profile that can be implanted into a Li-ion cell, preferably during assembly.
- Is triggered by heating the cell above the phase change material (wax) melting temperature.
- Can handle currents in excess of 200 amps—this has already been proven in laboratory testing.
- Has impedance that is consistent and can be selected to simulate a hard or soft short.
- Can short between any of the battery components within a cell.

NREL's ISC is the only ISC being developed that can be selectively used 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 then 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—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. If the ISC is shown to be consistent, then the internal short can be used to verify abuse models being developed by battery manufacturers and national laboratories.

In FY12, NREL will complete the design of experiments to optimize the parameters necessary for spin coating the wax on the ISC. Furthermore, we will continue to develop techniques to lower the contact resistance between the ISC and the battery component materials. The improved wax ISC will be tested in pouch cells and in 18650 cylindrical cells—all four possible shorts will be tested in pouch and cylindrical cells. Finally, the improved wax ISC will be characterized and incorporated into cells to verify NREL's abuse models.

FY 2011 Publications/Presentations

- 2011 DOE Annual Merit Review Poster.
- 2010 NASA Aerospace Battery Workshop, Huntsville, AL.
- Advanced Automotive Battery Conference (AABC) 2011, Pasadena, CA.
- 83rd Li Battery Technical/Safety Group Meeting, Key West, FL.
- Data were shared with the EES TT and each of the individual battery manufacturers' work groups.

Computer-Aided Engineering of Batteries – CAEBAT (NREL)

Objectives

- Develop battery cell, pack, and system modeling tools to enhance understanding of battery performance, life, and safety to enable development and manufacture of cost-effective batteries for EDVs.
- Coordinate with other national laboratories to support the CAEBAT project with battery performance, cost, and life and safety models with respect to materials, components, and packs.
- Support the U.S. 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 Oak Ridge National Laboratory (ORNL) in their development of an Open Architecture Software (OAS) to link material and battery models developed under the DOE Energy Storage R&D.

Technical Barriers

- Cost, life (calendar and cycle), high performance at all temperatures, and safety are barriers for widespread adoption of Li-ion batteries in EDVs.
- Large investment and long lead time in cell and pack research, design, prototyping, and testing cycle (repeating the cycle many times changes) increase production costs.

Technical Targets

- Develop a linked suite of software tools that enable automobile manufacturers, battery developers, pack integrators, and other end-users to simulate and design cells and battery packs to accelerate development of ESSs that meet the requirements of the EDV.

Accomplishments

- NREL supported DOE with further definition and refinement of scope, elements, and project plan for CAEBAT.
- We interacted with other national laboratories involved or interested in battery modeling on the progress of the CAEBAT project.
- As mentioned in the FY10 annual report, NREL received several proposals after issuing a request for proposals; we selected the top three proposals for consideration of award.
- In the first quarter of FY11, NREL entered into negotiations with the top three teams for placing subcontracts to develop battery computer-aided design tools with 50%–50% cost-sharing.
- NREL placed three subcontracts and assigned a different technical monitor for each:
    - **EC Power** (teamed with Pennsylvania State University; Johnson Controls, Inc.; and Ford Motor Company). Subcontract signed May 2, 2011; NREL technical monitor: Shriram Santhanagopalan
    - **General Motors** (teamed with ANSYS and ESim). Subcontract signed June 1, 2011; NREL technical monitor: Gi-Heon Kim

  - **CD-adapco** (teamed with Battery Design LLC, Johnson Controls-Saft, and A123). Subcontract signed July 1, 2011; NREL technical monitor: Kandler Smith
- The three teams had their kick-off meetings in June 2011, followed by regular monthly meetings.
- GM and CD-adapco held their first quarterly meetings in October 2011.
- Each team has made progress according to the work plan in the statement of work.
- NREL close collaborated with ORNL on the vision, definition, and strategy of the OAS through regular meetings and a site visit.
- NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT.

Introduction

In April 2010, DOE announced a new program activity called Computer-Aided Engineering of Electric Drive Vehicle Batteries (CAEBAT) to develop software tools for battery design, R&D, and manufacturing. The objective of CAEBAT is to incorporate existing and new models into battery design suites/tools with the goal of shortening design cycles and optimizing batteries (cells and packs) for improved performance and safety, long life, and low cost. The objective was to address the existing practices under which battery and pack developers operate: tedious experimentation 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. By introducing battery simulations and design automation at an early stage in the battery design life cycle, it is possible to significantly reduce the product cycle time and cost and thus significantly reduce the cost of the battery. There have been extensive modeling efforts going on at national laboratories, universities, private companies, and other institutions to capture the electrochemical performance, life, thermal profile, and cost of batteries. NREL has been developing an electrochemical-thermal model of Li-on cells with three-dimensional geometries. However, these tools were not integrated into a 3D computer-aided engineering approach, which automotive engineers routinely use for other components. In many industries, including automotive and combustion engine development, CAE tools have been the proven pathway to:

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

The CAEBAT project was initiated by DOE to provide battery CAE tools and is broken down into four elements, as shown in Figure 21:

- Material- and component-level models [mostly developed under the Batteries for Advanced Transportation Technologies (BATT) and Applied Battery Research (ABR) program elements of DOE Energy Storage R&D],
- Cell-level models,
- Pack-level models, and
- OAS for interfacing and linking all models, particularly from national laboratories.

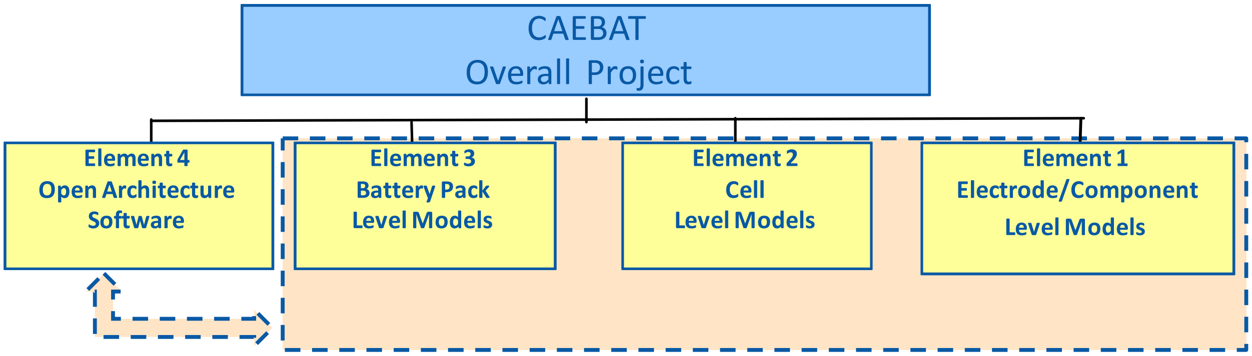


Figure 21: Four elements of the CAEBAT activity

The goal of the CAEBAT activity is to "develop suites of software tools that enable automobile manufacturers, battery developers, pack integrators, and other end-users the ability to simulate and design cells and battery packs in order to accelerate development of energy storage systems that meet the requirements of the electric drive vehicle." Involvement of industry (car makers, battery developers, and pack integrators) in CAEBAT activity, particularly for Elements 2 and 3 (Development of Cell and Pack Models), was essential. DOE's major strategy was to solicit active participation of industry in developing cell and pack software suites for the design of batteries. In support of this goal, NREL issued a Request for Proposals in FY10 to seek proposals for development of cell and pack battery design tools for a period of three years with 50%–50% cost sharing. Several proposals were received in the fourth quarter of FY10 and a Source Evaluation Team consisting of internal and external reviewers from DOE, Argonne National Laboratory, ORNL, and Lawrence Livermore National Laboratory was assembled to review and recommended the top proposals that best met the objectives and requirements of the RFP. The review process ended in October 2010 with the Source Evaluation Team selecting the top three proposals for negotiation and award. We continued working on developing and further improving NREL 3D electrochemical-thermal models that will be further detailed later in this report. We also collaborated with ORNL in their development of the OAS as part of Element 4.

Approach

For several years, the DOE Energy Storage R&D program has supported battery modeling and simulation through Focused Fundamental Research (i.e. BATT), ABR, and Battery Development activities at national laboratories and universities. Battery modeling under the BATT program has been focused on understanding the behavior of material, electrochemical, electrolyte, stress propagation, and degradation physics. Battery modeling under ABR has been focused on life prediction and cost projects. Due to program priorities, these modeling activities will be mostly continued under the BATT and ABR activities, but will interface with CAEBAT activities through ORNL's OAS. Battery modeling under the CAEBAT program activity will be focused on thermal, electrical, and abuse reaction-thermal models, ISC simulations, electrothermal and electrochemical modeling of cells with 3D geometries, and thermal and fluid flow analysis of multi-cell modules and packs using CAE design tools. The scale of these models varies from nanometers to meters, as shown in Figure 22. The links between various physics (electrochemistry, chemistry, thermal, electrical, mechanical, etc) and scales (material, cell, module, pack) have been limited and only for specific cases. DOE has focused the CAEBAT project on linking the relevant battery models, and to initiate stronger collaborations between laboratories and industry and academia, and to make these simulation tools readily and commercially accessible and available as design tools for the industry and other end-users.

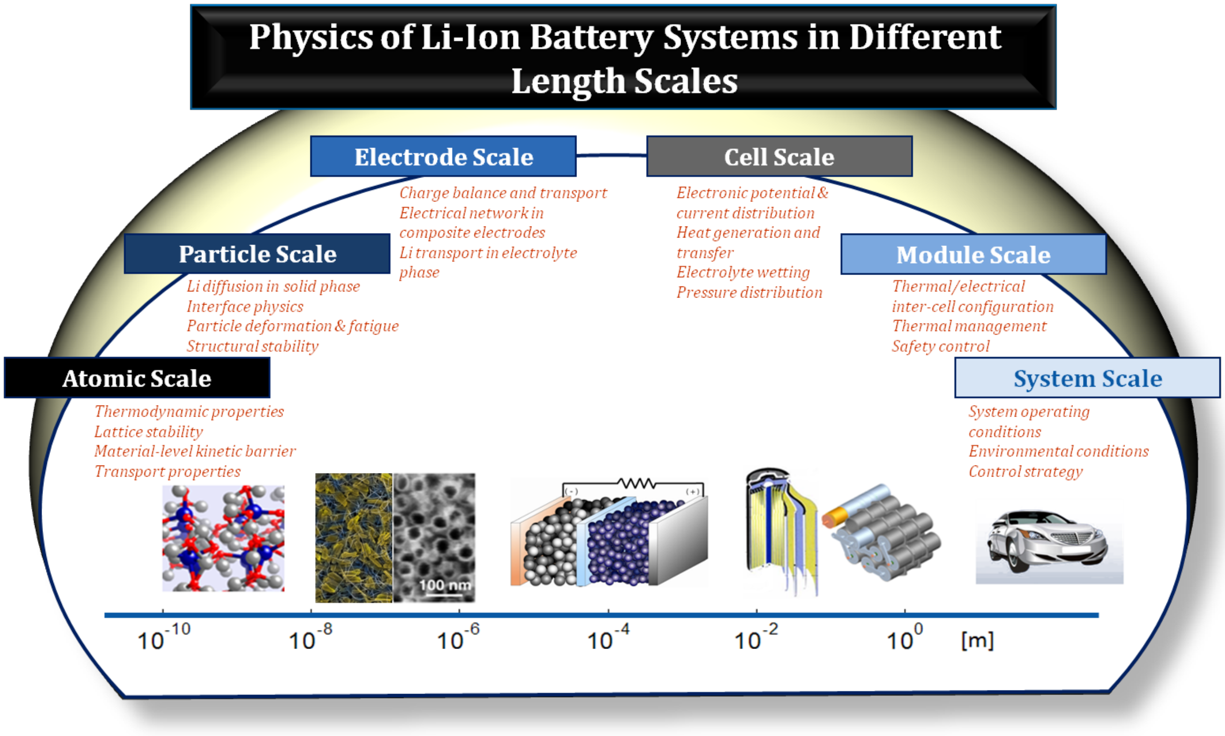


Figure 22: Multi-scale physics in battery modeling from molecular modeling to pack- and system-level modeling

To oversee the successful execution of the CAEBAT program, DOE has designated NREL as the Overall Project Coordinator. Cell level modeling and pack level modeling will be performed by industry, national laboratories, and academia, coordinated through NREL. The OAS element will be performed by the national laboratories, to be coordinated by ORNL. Cell level modeling and pack level modeling by the industry will be conducted by subcontractors chosen through a competitive procurement process. ORNL and NREL will collaborate with Argonne National Laboratory, Lawrence Berkeley National Laboratory, and other national laboratories to incorporate and interface with models developed under BATT and ABR.

Results

Subcontracts with Industry

In first quarter of FY11, NREL staff (Contract and Business Services, Legal, and the Center for Transportation Technologies and Systems) have discussed, reviewed, and negotiated technical, financial, contractual, and legal contents of all three proposals with the three winning teams. Different NREL technical monitors were assigned to each team. Some of the terms and conditions imposed by NREL’s prime contract with DOE, particularly the intellectual property ownership and data/software rights for the government, proved to be challenging and time consuming to resolve. However, after intense negotiations, all issues were resolved, agreements were reached and signed, subcontracts were placed, and work began. The three winning subcontracts were:

- **EC Power (**teamed with Pennsylvania State University, Johnson Controls, Inc., and Ford Motor Company). The subcontract with EC Power was signed on May 2, 2011, with Dr. Shriram Santhanagopalan as the NREL technical monitor.
- **General Motors (**teamed with ANSYS and ESim). The subcontract with GM was signed on June 1, 2011, with Dr. Gi-Heon Kim as the NREL technical monitor.
- **CD-adapco** (teamed with Battery Design LLC, JCS, and A123). The subcontract with CD-adapco was signed on July 1, 2011, with Dr. Kandler Smith as the NREL technical monitor.

Each of the subcontractors has proposed a plan to develop computer-aided design tools for automotive batteries, with the following tasks:

Task 1. Battery Cell Level Modeling
    Subtask 1.1 Identify what End-Users Need in a Cell CAE tool
    Subtask 1.2 Enhance Physics Linkage—Expandability
    Subtask 1.3 Enhance Solver Modules—Flexibility
    Subtask 1.4 Validation, Verification, and Demonstration
    Subtask 1.5 User Interface Development

Task 2. Battery Pack Model Development
    Subtask 2.1 Identify End-Users' Need for a Pack CAE Tool
    Subtask 2.2 Model, Code, and Algorithm Development
    Subtask 2.3 Validation, Verification, and Demonstration
    Subtask 2.4 User Interface Development

Task 3. Interface Development to Interact with CAEBAT Open Architecture Software
    Subtask 3.3.1 Interaction with CAEBAT OAS Workgroup
    Subtask 3.3.2 Develop Interface for CAEBAT OAS

The kickoff meeting for the EC Power subcontract was held on June 20, 2011, at Ford Motor Company in Dearborn, MI. The kickoff meeting for the GM subcontract was held at General Motors in Warren, MI, on June 21, 2011. The kickoff meeting with CD-adapco was held at NREL in Golden, CO, on June 29, 2011. NREL technical monitors have been working closely with the subcontractors through weekly or monthly progress reviews to make sure progress is made according to the timeline set by the technical and contractual agreements. Significant progress has been reported by each subcontractor according to the agreed-upon timetable.

Collaboration with ORNL on Open Architecture Software

NREL and ORNL held monthly meetings to discuss the best approach and strategy for the OAS. We had monthly conference calls to discuss the definition, environment, structure, and timeline planning of the OAS. We also participated in the OAS kickoff meeting held at Oak Ridge, TN, with representatives from GM, ESim CD-adapco, and EC Power. ORNL has identified and adapted the Python-based Integrated Plasma Simulation framework developed for fusion, and SWIM (Simulation of RF Wave Interactions with Magnetohydrodynamics) for the CAEBAT OAS. ORNL has added two components (DualFoil for Electrochemistry and AMPERES for thermal) to create the Virtual Integrated Battery Environment (VIBE) to solve a loosely coupled demonstration cell problem. They have arrived at initial specifications for the modeling inputs and battery state (output for exchange among the models). The specifications have been discussed with the partners and there is ongoing work to refine these based on their input.

Development of Multi-Physics Battery Models at NREL

NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional platform for CAEBAT. The GM team is working with NREL to incorporate the MSMD Li-ion battery modeling framework into their CAEBAT tools.

Conclusions and Future Directions

We selected three teams for further negotiation and finally awarded them with subcontracts. The three teams included GM (with ANSYS and ESim), CD-adapco (with Battery Design, JCI, and A123) and EC Power (with Pennsylvania State University, JCI, and Ford). Kickoff meetings were held in June of 2011, and the projects have been on track. We also collaborated with ORNL on its development of the OAS to link the developed and existing models.

In FY12, we will continue to monitor the technical progress of each team through monthly and quarterly meetings to ensure success. We anticipate models to be developed and solution techniques to be chosen by each subcontractor. We expect a major part of each subcontractor's activity to be collection of validation data for the first version of each CAEBAT tool. We will also continue collaborating with ORNL on development of the OAS and performing example problems. We plan to coordinate a conference on the computer-aided engineering of batteries.

FY 2011 Publications/Presentations

- A.A. Pesaran, G.-H. Kim, K.A. Smith, S. Santhanagopalan, "Negotiate and Place Subcontracts with CAEBAT RFP Winners." *NREL Milestone Report, June 2011.*
- G.-H. Kim, K.A. Smith, S. Santhanagopalan, K.-J. Lee, A.A. Pesaran, "Progress Review on the Work for the CAEBAT–NREL Program." *NREL Milestone Report, July 2011.*
- A.A. Pesaran, G.-H. Kim, K.A. Smith, "Accelerating Design of Batteries Using Computer-Aided Engineering Tools," Presented at the 25th Electric Vehicle Symposium, Shenzhen, China, November 5–9, 2010.

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

Objectives

- Develop integrated multi-scale, multi-physics design and analysis tools to evaluate Li-ion battery cell and pack designs for EDVs. These simulation tools will shorten the product development cycle for EDVs, reduce costs associated with the current build-test-break design evaluation approach, and enable incorporation of quality metrics at the earliest phases of design.
- Validate the design tools using GM's six-step math model verification and validation approach in conjunction with production cell and pack experimental data.
- 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 operating under the CAEBAT umbrella.

Technical Barriers

- Existing design tools are not practical for realistic battery design and optimization.
- Various cell physics sub-models exist, but they have not been integrated in a single framework in the commercial code.
- Current engineering workstations do not have the computational power required to simulate integrated pack-level physics. Reduced order modeling (ROM) is required to simulate integrated pack-level physics. ROM approaches for battery packs are not well understood.
- No single organization has all the personnel and data required to develop battery design tools. Collaboration to date has been difficult to achieve because software developer commercial code, automaker electrification strategies, and battery developer cell designs and chemistry are all well-guarded intellectual property.

Technical Targets

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

- Predict capacity utilization due to current distribution associated with tab size and location.
- Predict optimum cell energy capacity in terms of electrical performance, cooling requirements, life, safety, and cost.
- Predict cell degradation due to non-uniform utilization and heat generation within the cell.
- Predict optimum SOC range for maximum life and safety.
- Predict power requirements at low-temperature operations.
- Evaluate battery pack thermal management.

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

- Ability to predict maximum intra- and inter-cell temperature differences for any arbitrary drive cycle.
- Ability to predict peak temperatures and their locations during hot and cold soak under various ambient conditions. Turnaround time should be less than 12 hours.
- Ability to create a meshed computational fluid dynamics (CFD) model that simulates a steady-state fluid flow to predict the total pressure drop of the pack cooling system for a given flow rate and temperature, as shown in Figure 23. Turnaround time should be less than 12 hours.

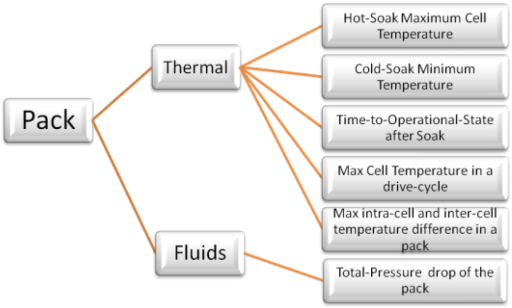


Figure 23: CFD model simulating a steady-state fluid flow

Introduction

To accelerate the production of safe, reliable, high-performance, and long-lasting Li-ion battery packs, the automotive industry requires CAE design tools that accurately represent cell and pack multi-physics phenomena occurring across a wide range of scales. In response to its own urgent demand for this technology, GM has assembled a CAEBAT Project Team composed of GM researchers and engineers, ANSYS Inc. software developers, and Professor Ralph E. White and his ESim staff. This team will develop a flexible modeling framework that supports multi-physics models. GM will provide end-user requirements, physical validation of the models, and focused leadership commensurate with the GM vision for vehicle electrification. Professor White and his ESim team will provide coupled thermal-electrochemical modeling expertise, along with cell aging and degradation characterization capabilities. ANSYS will provide a state-of-the-art framework for multi-physics simulation. At the conclusion of the project, ANSYS will make new developments available in commercial software.

Approach

The GM CAEBAT project has two main tasks, namely cell- and pack-level design tool development. The principal objective of each task is to produce an efficient and flexible simulation tool for prediction of multi-physics battery response. In partnership with DOE and NREL, the Project Team will interact with the CAEBAT working groups to identify end-user needs and establish requirements, integrate and enhance existing sub-models, develop cell- and pack-level design tools, and perform experimental testing to validate the tools. In a third task, the team will create interfaces to enable these new tools to interact with current and future battery models developed by others.

The emphasis in software integration will be to provide a flexible array of modeling choices that can support several categories of battery researchers—cell manufacturers, pack integrators, and vehicle manufacturers—while enabling a controllable balance between model fidelity and computational cost. The Project Team expects to make maximum use of existing battery models, while also leveraging ANSYS' large technology investment in established commercial CAE software tools. The design tools will capture the relevant physics, including electrochemical, thermal, fluid, and structural response, focusing on the intra-cell and inter-cell non-uniformities that critically impact battery performance and life.

The Project Team will incorporate the latest advances in battery modeling research with software tools that are unsurpassed in their ease of use. At the pack level, significant advances will be made by the development of innovative ROMs, derived and calibrated from cell-level models and carefully validated through experimentation, as shown in Figure 24. With a strong plan for rapid deployment to industry, these project results will contribute to accelerate the pace of battery innovation and development for future EDVs.

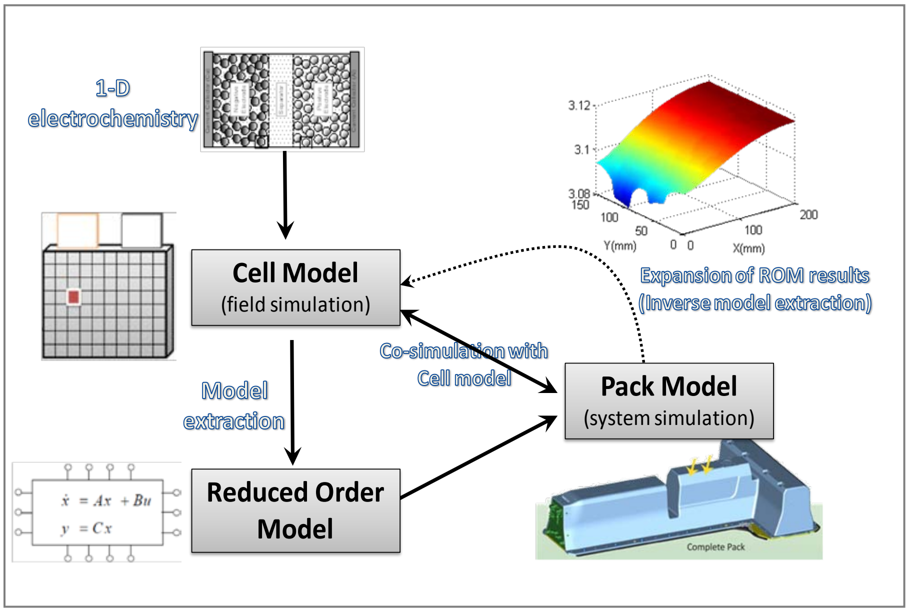


Figure 24: Relationship between models, calibration, and validation through experimentation

Results

Accomplishments toward the development of a battery cell design and analysis tool:

- End user needs have been defined. These include a comprehensive set of model inputs and outputs, geometry requirements, meshing requirements, graphical user interface requirements, performance requirements, CPU time, and turnaround time. Standard input parameters were shared with the OAS Work Group.
- A survey of potential cell-level models has been completed, and the team has identified key electrode- and particle-level models based on accuracy and computational efficiency.
- The cell-level framework has been defined based on NREL's MSMD model.
- Mathematical equations and physical models to describe mass transport, electron and Li-ion transport and heat generation based on John Newman's Pseudo-2D (P2D) model have been implemented in code using a coupled solver with adaptive time stepping.

- A P2D and an equivalent circuit model have been implemented in code, tested, and validated.
- A development plan has been laid out to incorporate P2D, equivalent circuit model, and a third electrode-level model (Newman-Tiedman-Gu-Kim) into each finite volume in the ANSYS FLUENT computational domain.
- A test plan for collecting empirical data from production cells to validate the cell design tool has been created.

Accomplishments toward the development of a battery pack design and analysis tool:

- Battery pack simulation applications, from coarse to fine levels, with the potential to replace various tests in the product development cycle have been identified. GM CAEBAT team members have scheduled meetings with potential vehicle program customers to further understand end user needs.
- End user requirements for CFD/thermal have been defined. There is consensus agreement among team members that current industrial computing resources are inadequate to support the brute force expansion of the cell-level model for the pack-level. Therefore, the GM Team is developing new pack-level strategies: 1) ROM for flow and thermal equations as well as electrochemical reaction equations; 2) co-simulation approach with the cell-level model; and 3) system-level simulation approach based on the linear time invariant method.
- A current battery CAE capability matrix has been defined for specific pack-level applications in the automotive industry, and the desired CAE capabilities at the completion of the CAEBAT project have been defined. ROM requirements in terms of turnaround time and memory have been defined to meet the future CAE capability matrix. Accuracy requirements are being investigated for each pack-level application area.
- A strategy involving ROMs, solver accelerators, and co-simulation is being developed to overcome computational limitations.

Conclusions and Future Directions

Future directions for the development of a battery cell design and analysis tool:

- Solicit input for end user requirements and tool validation from battery manufacturers.
- Develop and deliver the alpha version of the cell-level tool.
- Implement ROM for electrochemistry models.
- Build test setup and perform tests to validate the cell-level tool.
- Develop cell-level computational model, including mesh and physical boundary conditions.

Future directions for the development of a battery pack design and analysis tool:

- Demonstrate the porous-media approach for a production-level pack.
- Develop ROM strategy for fluid flow and heat transfer.
- Evaluate linear parameter variable method for systems approach and explore co-simulation.
- Identify existing pack test data suitable for the pack-level validation.

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

Objectives

- Provide simulation tools that will accelerate the inclusion of advanced Li-ion battery systems for ground transportation.
- Specifically develop a numerical simulation model that can resolve the appropriate phenomena required to create a coupled thermal and electrochemical response of Li-ion spirally wound cells.
- Apply advanced numerical techniques to expedite the solution of the governing fundamental equations within Li-ion battery cells to enable advanced electrochemical models to be used in module and pack simulations.

Technical Barriers

One of the challenges of this project is including all of the important advances of the rapidly maturing Li-ion battery simulation field in an easy-to-use, widely accepted CAE tool. The implementation needs to be flexible and extensible to ensure the methods can move forward as the level of understanding in the fundamental physics evolves. To achieve mass acceptance, the technology must also be available in an easy-to-use form.

Another significant challenge is the creation of a modeling concept for cylindrical cells and their underlying architecture. Spiral cells can be grouped into several categories, and therefore flexible templates are created. The user then provides appropriate data to populate these templates, creating a complete cell model. This includes specification of jelly roll properties, physical dimensions of electrodes within the jelly roll, tabbing details, and finally the outer can dimensions. The creation of such electrical and thermal templates and the overall method for doing so are a significant part of this project.

Technical Targets

- Create a spiral cell analysis framework that includes two electrodes that are wound together to create a spiral. This method should resolve planar gradients along the length and height of the electrodes as well as the overall performance of the electrode pair through the use of an electrochemistry model.
- Validate the created cell simulation models against test work provided by subcontractors for both cylindrical and prismatic forms of spiral cells.
- Use the validated methods within a larger framework to create simulations of battery modules that include such cells. These results should include electrical and thermally conducting components that link cells together and the appropriate physics within these components.
- Compare the results of the simulations with relevant test work using subcontractors' cells.

Accomplishments

- Since beginning this project three months ago, an initial spiral cell method has been established. In a demonstration problem, the impact of tab position on the positive electrode was investigated and is reported below. The simulation architecture was created in such a way as to allow a range of numerical models of a cell electrode's performance to be used. This provides an extensible framework into which future electrode performance models can be added. Figure 25 shows a schematic of how the one-dimensional electrochemistry model, shown as cubes, has been combined with a two-dimensional electrode model, shown as resistors, to capture the required physical phenomena.

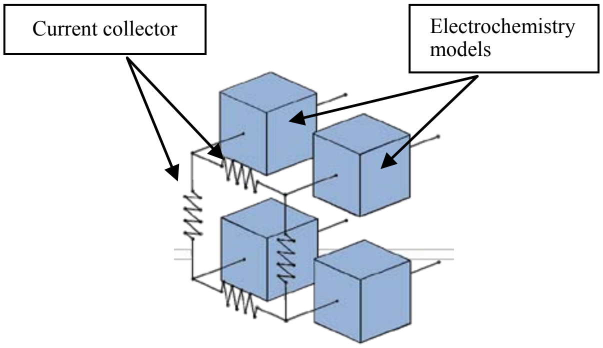


Figure 25: Schematic of the underlying modeling abstraction

- An automatically created 3D representation of a spiral cell within a finite-volume modeling package was developed. This 3D representation uses previously defined cell data to operate a cell model within a combined thermal and electrochemical solution. The repetition of this cell model to create modules or packs is possible using STAR-CCM+ software.
- An approach to simulating aging within Li-ion cells has been formulated that considers solid-electrolyte interphase layer growth. This model is based on the work of Ploehn, Ramadass and White [*J. Electrochem. Soc*. A456-A462 (2004)] and will be included in the cell-level analysis.

Introduction

Under solicitation from DOE's CAEBAT program, CD-adapco proposed to extend its class-leading CAE code, STAR-CCM+, to analyze the flow, thermal, and electrochemistry occurring within spirally wound Li-ion battery modules and packs. This development will create additional coding and methods that will focus on the electrochemical analysis of spirally wound electrodes. This coding will be developed in collaboration with Battery Design, LLC, a subcontractor to CD-adapco, which has considerable experience in the field of electrochemistry modeling. The contract, awarded in July 2011, is funded 50% by DOE (managed by NREL) and 50% by CD-adapco and its industry partners Battery Design, LLC, JCI, and A123.

The aim is to create a new piece of analysis coding that will embody a method to produce electrochemical and thermal understanding using state-of-the-art electrochemistry models based on the work of Fuller, Doyle, and Newman [*J. Electrochem. Soc.*, 141, 1 (1994)]. The methods will use a matrix of electrochemistry unit cell models that communicate through the metallic current collectors, shown in Figure 25. Current ultimately enters and leaves the spiral electrodes via the tabs, which are also integral to the problem and are included in the simulation.

Once created, the modeling approach will be validated using test results from JCI and A123, both of which are subcontractors for this project. The test work will be carried out on the following cell:

Table 2: Test Cell Specifics

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

The inclusion of a pouch cell in this project provides a control through which to validate the results for analysis methods on components around the cell itself. The A123 test work will include considerable measurements from conducting components around the cells to ensure their thermal and electrical effects are also included.

Approach

A prototype spiral cell template has been created that is being used and tested with 26650-sized cylindrical cell parameters. The electrode shapes are presented in Figure 26, and the images are taken from Battery Design Studio (BDS), which is being used as a host for this development until a stable standalone code is achieved.

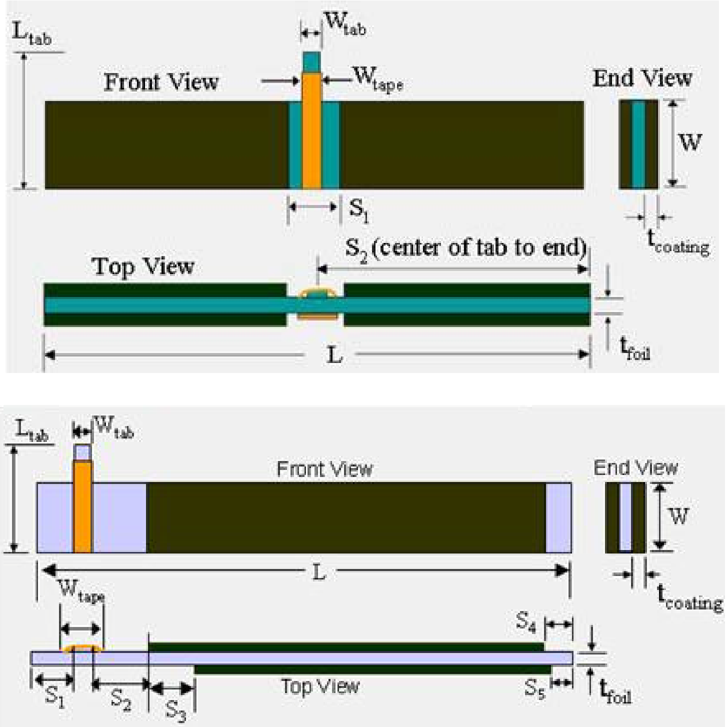


Figure 26: Parameters used to describe the positive and negative electrodes in the host BDS code

In parallel with this cell-level development, work on the automatic creation of a 3D geometry to represent the spiral cell has been ongoing in STAR-CCM+. The images in Figure 27 show several cells that have been created by reading in a setup file that contains the required shapes.

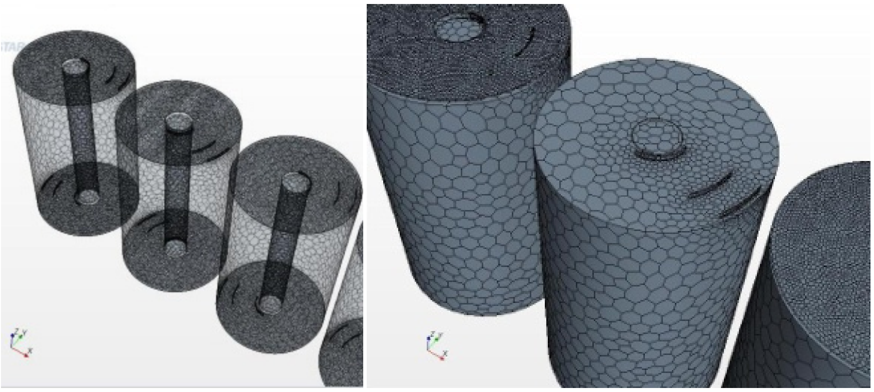


Figure 27: Screenshots of spiral cells within STAR-CCM+ showing resolved current-carrying tabs

The concept resolves the spiral electrodes, commonly known as the jelly roll, as a homogeneous material with anisotropic quantities and resolves the tabs, tab collection mechanisms, outer can, and end caps as separate bodies. These are resolved as they will contribute to the overall heating and thermal distribution within the cell. The ohmic heating may be considerable in high power cells.

Results

Cell Development

The created model has been used to carry out a study investigating the effect of positive tab location along the length of the positive electrode to the overall resistance of the cell. These results are presented in Figure 28 with the horizontal axis being position relative to the core and the vertical axis displaying the resistance drop for a given discharge.

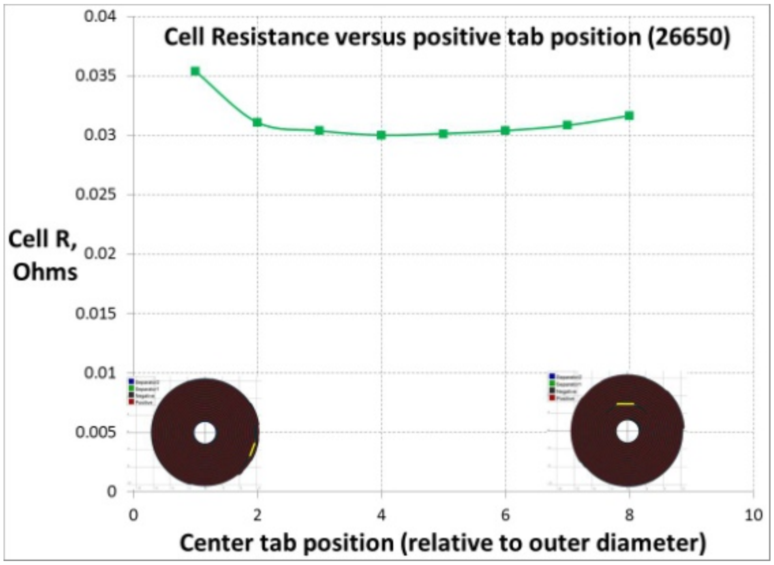


Figure 28: Cell resistance results for a study of positive tab position

The graph shows that the ideal location for this cell design is around 40% along the length of the positive electrode for this case. This computation includes all aspects of the cell design, including collector resistance, electrochemistry resistance, temperature dependence, and tab width. The model shows clear insight into the ideal location of the tab and can be used within a multi-dimensional optimization to improve overall cell performance.

Figure 29 shows the results of distributed quantities along the negative electrode, highlighting the complexity of the calculation. The electrode is coated on both sides, but with differential length to match the opposing positive electrode. This ensures optimal use of the active material and is an input requirement for any analysis method.

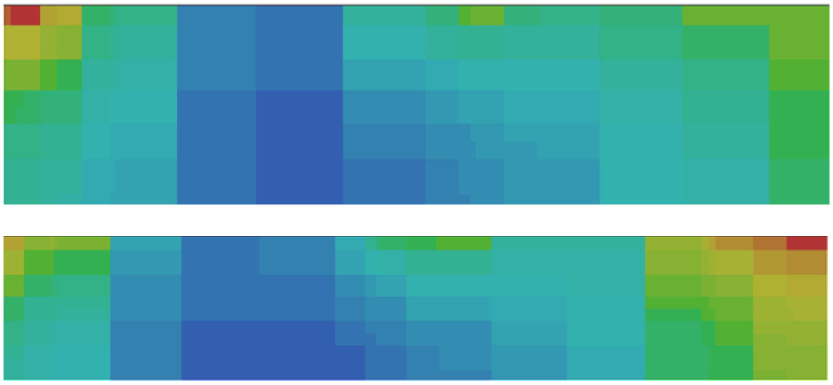


Figure 29: Current density on the inner (top) and outer (bottom) sides of the negative current collector

Module & Pack Development

No module- or pack-level analysis has been run at this point, although considerable software architecture has been created to allow multicell computations within STAR-CCM+. It is now possible to read in definition files of spiral cells and appropriate computer-aided design shapes created within STAR-CCM+. This is a first step to linking the thermal and electrochemical behavior of a single cell, shown above, to a number of neighboring cells to form a module.

Conclusions and Future Directions

Significant steps have been taken to reach the objectives listed above with current focus on the development of cell-level coding. In the near term, this coding will be validated against the cell-level test work due to start in early 2012. In parallel with this validation, the module- and pack-level coding will be completed before the more complex module-level validation can begin. A future goal of this project is to integrate a state-of-the-art electrochemistry model with a widely accepted 3D finite-volume code, STAR-CCM+, to enable detailed simulation of Li-ion battery modules and packs.

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

Objectives

- Develop an electrochemical-thermal coupled model and associated computer code for large-format automotive Li-ion batteries for both cells and packs.
- Create a novel computational framework and fast solution algorithms spanning several length scales ranging from particle size, to an electrochemical unit cell, to a 3D battery with wound or stacked geometry, and finally to a battery pack.
- Develop a comprehensive materials database that is required for accurate modeling and simulation of large-format Li-ion batteries.
- Validate the developed large-format Li-ion cell and pack models over a wide range of operating conditions relevant to automotive use, such as low-temperature operation, complex power profiles, etc.

Technical Barriers

The large-format nature of automotive Li-ion cells presents a unique set of challenges that are not as appreciable in applications such as cell phones and laptops. For example, in automotive applications, the large format of the cell and the high rates of charge and discharge lead to significant temperature non-uniformity in the batteries and packs. This temperature non-uniformity causes severe issues, including poor battery performance, shorter battery life, potential safety issues, and the inability to fully utilize the active material in the battery. Creating new cell and pack devices is time consuming and expensive, which makes an efficient, high-fidelity model highly desirable. However, due to the strongly coupled electrochemical and thermal physics, the wide-ranging relevant scales of a battery cell or pack (from sub-microns to meters), and a great deal of uncertainty in the materials properties required to model Li-ion batteries, the creation and development of such a model and software tool pose a unique challenge.

Technical Targets

- Development of an extensive database of materials properties for accurate model input.
- Creation of a multi-dimensional electrochemical-thermal coupled model.
- Development of a set of fast, scalable numerical algorithms enabling near real-time simulation of batteries on a single PC and of packs with thermal management systems on a small computer cluster.
- Experimental validation of the model and software created.

Accomplishments

In the first six months of the project, our team has accomplished the following major items:

- Completed the first (baseline) version of our large-format software tool, “Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model” (ECT3D).
- Performed an exhaustive literature review and completed preliminary experimental efforts towards development of materials database for ECT3D.

Introduction

To curb greenhouse gas emissions and reduce U.S. dependence on foreign oil, the accelerated development of HEVs, EVs, and PHEVs is extremely important. The use of Li-ion batteries and battery packs in these vehicles is critically important in the effort to reduce the weight and size of the battery packs.

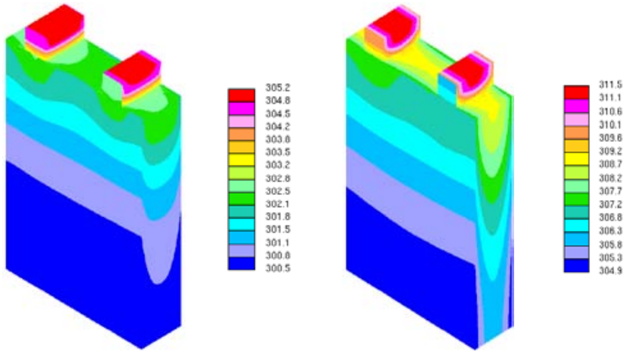
However, the design, build, and testing of batteries and packs is extremely time consuming and expensive. EC Power's code, ECT3D, directly addresses technical design and engineering issues related to these cells and packs. While many technical characteristics critically important to good battery performance are difficult or impossible to measure experimentally, these characteristics are easily analyzed using ECT3D. Thus, we anticipate that ECT3D will be an invaluable tool for the design engineer, facilitating the design of large-format cells and packs with significant improvements in attributes such as energy density and cycle life, among others. The digital design environment will facilitate significantly cheaper and shorter battery and pack design-build-test cycles.

Approach

EC Power is developing the large-format Li-ion battery simulation software, ECT3D, to analyze battery cells and packs for electrified vehicles (EV, PHEV, HEV, etc.). Project team member Pennsylvania State University will be primarily responsible for performing diagnostic experiments that will supply data for an extensive properties database, to be incorporated into ECT3D. Industrial partners Ford Motor Company and Johnson Controls, Inc. will test and validate ECT3D to ensure its utility for industrial use. The overarching goal of the project is to produce a world-class large-format Li-ion cell and pack design tool that greatly accelerates the research and design process for electric vehicle batteries.

Results

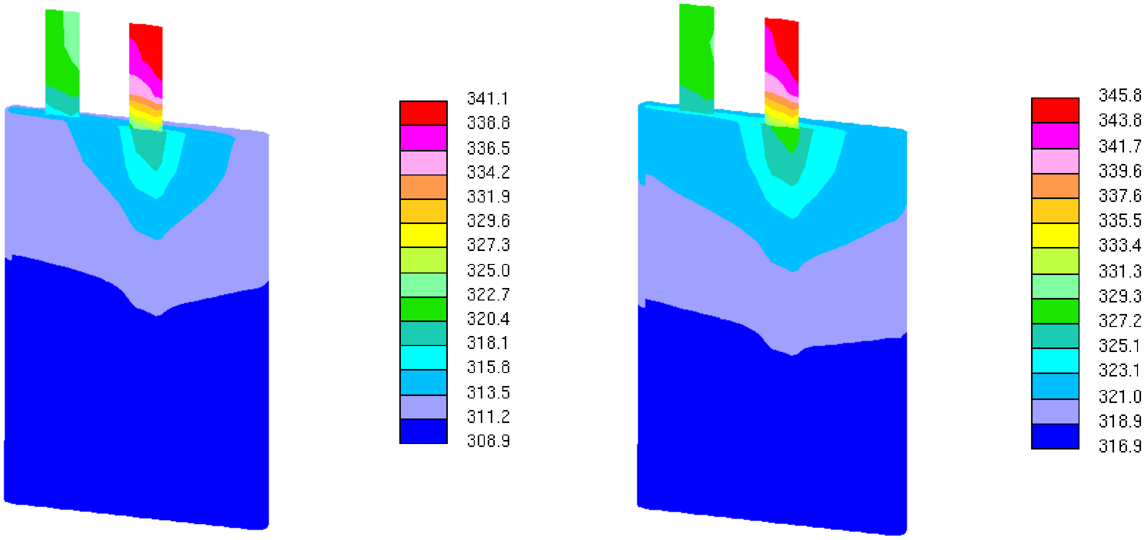
Figure 30 was generated for a 15-Ah prismatic stacked electrode design (SED) cell with a mesocarbon microbead (MCMB) anode and a nickel-cobalt-manganese cathode, using version 1 of ECT3D. Specifically, the figure shows temperature contours for the 15-Ah SED cell under 6C discharge current at (a) t = 100s and (b) t = 300s. Clearly, in this design, the hottest points in the cell are the tabs welded onto the top. Further, the center of the cell is significantly warmer than the edges, which are cooled more effectively.



(a) (b)

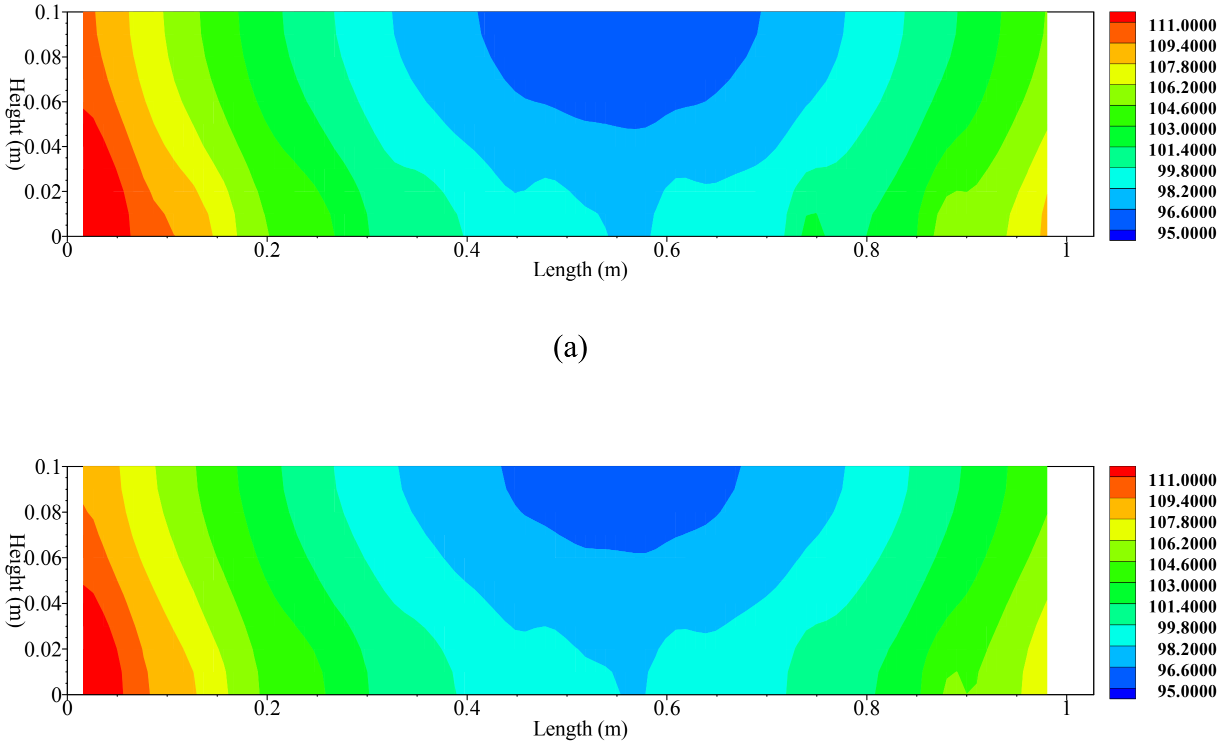
Figure 30: Temperature (K) contours for the 15-Ah SED at 6C discharge rate: (a) t=100s, and (b) t=300s

Figures 31 and 32 show the temperature and current density contours for a 3-Ah prismatic rolled electrode design (RED) cell under 6C discharge current at (a) t = 100s and (b) t = 200s. Once again, the anode is MCMB and the cathode is nickel-cobalt-manganese. The contours given in Figure 31 show the actual wound geometry of the cell, with hot spots clearly in the tabs at both 100s and 200s. Figure 32 illustrates the current density distribution for the *unwound* electrode. The current density is clearly non-uniform over the unwound electrode surface. Note that these results represent only a small snapshot of ECT3D's capabilities.



(a) (b)

Figure 31: Temperature contours (K) for the 3-Ah RED at 6C discharge rate: (a) t=100s, and (b) t=200s



(a)

(b)

Figure 32: Current density (A/m^2) distribution for 3-Ah RED at 6C discharge rate: (a) t=100s, and (b) t=200s

Conclusions and Future Directions

Our team has successfully developed and demonstrated the first version of our large-format Li-ion battery simulation tool, ECT3D. As an integral part of ECT3D, our team has begun developing an extensive materials database to incorporate into our model.

Our next steps will include model validation, both at EC Power and by our industrial team members, Ford and JCI. We are also working on developing more advanced sub-models to incorporate into ECT3D, along with further development of the materials database.

FY 2011 Publications/Presentations

- C.Y. Wang, W. Zhao, C.E. Shaffer, G. Luo and J. Zhu, “Breakthrough in Large-Format Li-ion Battery Safety through Computer Simulation,” Battery Safety 2011, Knowledge Foundation, Nov. 9–10, 2011, Las Vegas, NV.
- G. Luo and C.Y. Wang, “A Multi-dimensional, Electrochemical-Thermal Coupled Li-ion Battery Model,” Chap. 6 in *Lithium-Ion Batteries: Advanced Materials and Technologies,* CRC Press, 2011.

MSMD Framework and Modeling Activities

Objectives

- Perform research and development to support the goal of the CAEBAT program.
- Continue to develop cell- and pack-level models, methods, and code implementation in the context of the MSMD framework.
- Support subcontractors by providing technical guidance and expertise and evaluating project outcomes.

Technical Barriers

- Interdisciplinary multi-scale physics interactions in the intricate geometries of Li-ion batteries.
- Wide spread time and length scales in physico-chemical processes in Li-ion batteries.

Technical Targets

- Provide a flexible and expandable platform.
- Achieve efficient computation.
- Perform validation and verification.
- Identify critical physics, develop models and methods in context of the MSMD framework, and implement them into computer code.
- Perform computational simulation to enhance knowledge of Li-ion battery performance, aging, and safety behavior.

Accomplishments

- Enhanced and further developed the single potential-pair continuum (SPPC) model as an option of cell domain model to resolve cell domain physics, and applied the model to simulating large-format stacked prismatic cell behaviors.
- Developed the wound potential-pair continuum (WPPC) model as an option of the cell domain model to resolve cell domain physics in wound cell formats, and applied the model to simulating large format cylindrical cell behaviors.
- Developed the multiple potential-pair continuum (MPPC) model as an option of the cell domain model to resolve cell domain physics in alternatively stacked cells.
- Developed the finite volume linear superposition methods (FVLSM) as a fast solution method to achieve enhanced computation speed without compromising accuracy.
- Documented development of the MSMD framework in an article published in the *Journal of the Electrochemical Society*.

Introduction

In the last few years, NREL has developed the multi-scale, multi-dimensional (MSMD) model framework, constituent models for describing various physics, new solution methods, and accompanying codes for simulating Li-ion battery behaviors. The hierarchical MSMD framework separates the computational domain where time or length scale segregation occurs, reflecting the intrinsic nature (physics and design) of conventional Li-ion battery systems.

Therefore, NREL's MSMD framework serves as an expandable development platform providing pre-defined protocol, and a generic and modularized flexible architecture, resolving interactions among multiple physics occurring in varied length and time scales with various fidelity and complexity. Figure 33 shows the conceptual diagram of the multi-scale multi-domain approach used in the MSMD model framework. Each domain uses its own independent coordinate system for spatial discretization of the variables solved in that domain.

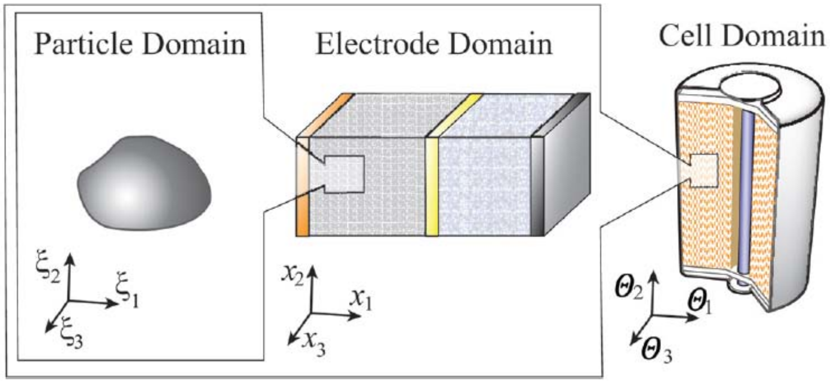


Figure 33: Separation of model domains corresponding to the length scales of physics resolved

Approach

NREL's MSMD framework introduces multiple computational domains for corresponding length scale physics, and decouples geometries between submodel domains while coupling physics bi-directionally using predefined inter-domain information exchange. Thanks to its modularized hierarchical architecture, the MSMD framework allows independent and parallel development of submodels for physics captured at each domain, as illustrated in Figure 34.

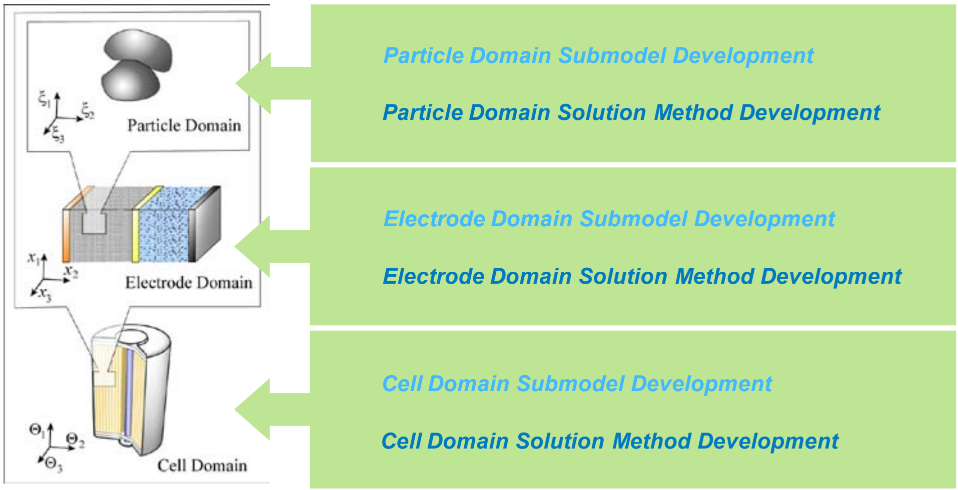


Figure 34: Parallel and independent development of submodels in the MSMD framework

NREL has developed several variations of orthotropic continuum modeling of cell composites to resolve cell domain physics. Table 3 summarizes the cell domain model options for various cell formats.

Table 3: NREL-Developed Cell Domain Model Options

Model Name	Applicable Cell Format
Single Potential Pair Continuum (SPPC) model	stack prismatic cells, tab-less wound cylindrical/ (prismatic) cells
Wound Potential Pair Continuum (WPPC) model	wound cylindrical/(prismatic) cells
Multiple Potential Pair Continuum (MPPC) model	alternating stack prismatic cells
Lumped Potential model	small cells

In FY11, we published a paper introducing the development of the MSMD framework, and demonstrated model analysis that evaluates large-format, stacked prismatic cell designs using the SPPC model as a cell domain model. Large cylindrical cell behavior investigation was also conducted using the WPPC cell domain model.

Results

Macroscopic cell design features regarding thermal and electrical configurations, such as the number of unit stacks of the electrode pair, area of the unit electrode stack layer, thickness of the current collector foils, size and location of current tabs, electric bus geometries, and external heat transfer conditions, are known to greatly impact the microscopic electrochemical processes and degradation mechanisms, and, in consequence, the overall cell performance and life, especially in large battery systems. Therefore, for wide acceptance of Li-ion batteries in large-capacity applications such as hybrid electric and full electric vehicles, the need to enhance knowledge of heat and electric current transport in a Li-ion battery system and the impact on performance, aging, and safety behavior is critical. The MSMD framework is employed to perform thermal and electrical design evaluations for a large-format stacked prismatic cell. Microscopic cell design parameters, including material composition, electrode loading thickness, and porosity, are held constant. Rather, the impact of large-format cell design features such as the location and size of the electrical tabs and the electrode area of the unit stack layer is varied. The schematic in Figure 35 summarizes the four different cell designs investigated. Figure 36 presents the choice of constituent models used in this study.

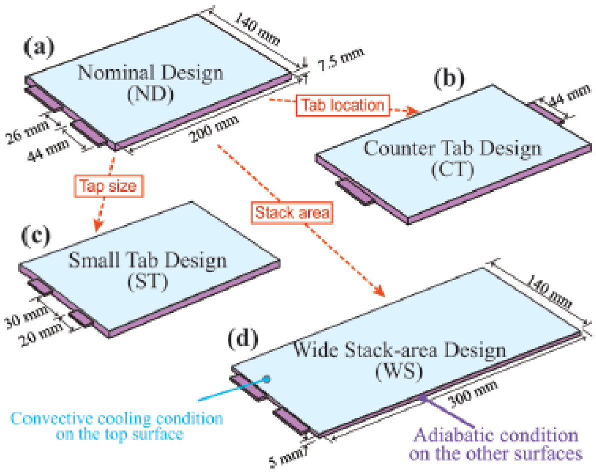


Figure 35: Schematic description of the 20-Ah stacked prismatic cell designs investigated

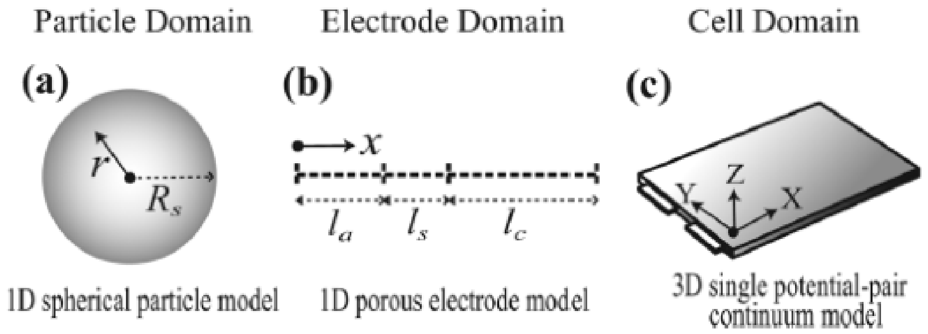


Figure 36: Choices of models at each model domain

In Figure 37, temperature contours at nine cross section surfaces of each cell are presented to show details of the spatial temperature imbalance at the end of 5C discharge. Due to preferential kinetics and electric current convergence, a higher temperature is observed near the tabs in all cell designs. Unlike other designs, the tabs of the counter tab (CT) cell are not co-located on the same end of the cell. So, the CT cell, as shown in Figure 37b, has the most uniform temperature distribution among the compared designs. Its main temperature gradient exists in the normal direction to the stack plate with the lowest temperature at the top surface, which is cooled by ambient coolant. The spatial temperature profile of the small tab (ST) cell, shown in Figure 37c, appears similar to that of the nominal design (ND) cell in Figure 37a because of a similar distribution of kinetics over the electrode plates. The peak temperature, however, is higher near the smaller sized tabs. Thanks to the larger surface area for cooling, the average temperature at the end of discharge of the wide stack-area (WS) cell, shown in Figure 37d, is lower by a few degrees Celsius than those of the other designs; however, the difference in the internal temperature in the WS cell is still high among the cells compared.

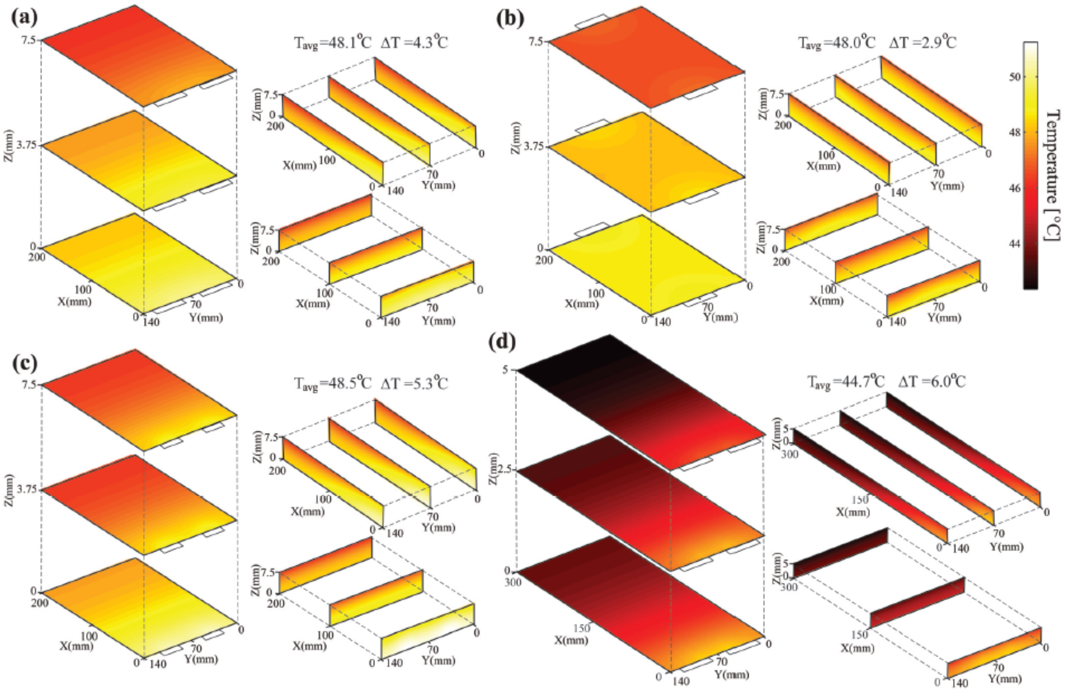


Figure 37: Contours of temperature at nine cross section surfaces in cell composite volume at the end of 5C constant current discharge

Standard cell characterization tests such as the constant current discharge test and the hybrid pulse power characterization test provide useful information about the cell's electrical-thermal performance characteristics. The design of a cell, however, must be evaluated with application-specific use scenarios as well because the response of a battery system is largely affected by the attributes of the application and the operation strategies. The cell designs investigated here are examined for use in a battery system for a mid-size PHEV10 sedan. Vehicle simulation was conducted over a repetition of an aggressive vehicle speed profile known as the US06 cycle to determine the power demand for the vehicle's battery. The simulated PHEV10 vehicle consumes battery energy during CD mode for the initial 16 km (10 miles) of driving, and subsequent cycling occurs in the charge-sustaining (CS) hybrid drive mode maintaining a steady battery charge level. Figure 38 shows the contours of the electrode plate area-specific ampere-hour throughput in the simulated cells. The absolute value of charging and discharging electrode plate current density is integrated over time during the 15-min PHEV10 drive, revealing spatial variation of the cumulative electrochemical cycling over the cell composite volume. In general, cell composites near the tabs are preferentially cycled in all designs, but the unevenness of electrode cycling is also greatly affected by the cells' electrical-thermal configurations. The average values of ampere-hour throughput per electrode plate area are similar across the four cell designs are 13.12, 13.11, 13.15, and 13.20 Ah/m^2 for the ND, CT, ST, and WS cells, respectively. However, the relative magnitudes of their internal variation compared to the average throughputs are significantly different. Ampere-hour throughput imbalances are 6.0%, 2.5%, 6.9%, and 12.7% for the ND, CT, ST, and WS cells, respectively. Non-uniform cycling of a cell is expected to bring subsequent effects in long-term performance degradation of a Li-ion battery system. Therefore, the impact of the electrical and thermal design of a battery should be adequately considered in predicting the life of large battery systems.

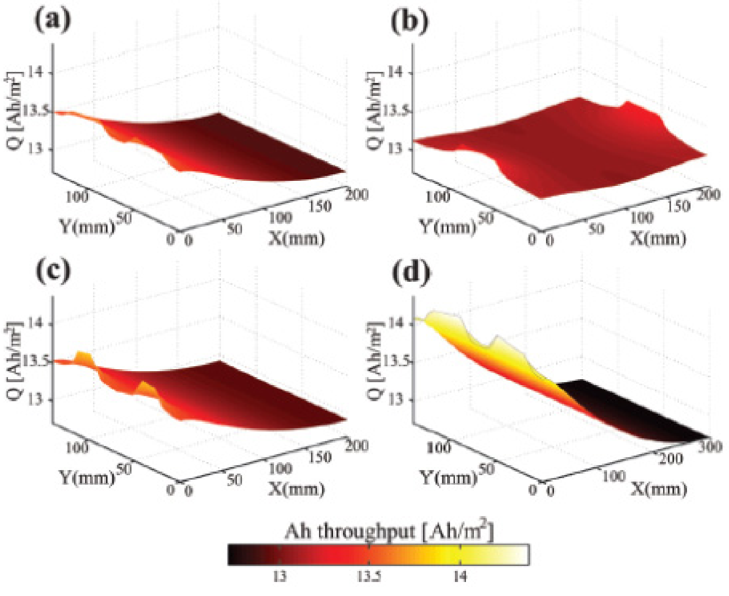


Figure 38: Contour of electrode plate ampere-hour throughput at the cell composite volume near bottom plane of the cells during 15-min PHEV10 drive with the US06 cycle

Wound cylindrical-format cells widely used in batteries for laptops and consumer electronics have problems in direct scale-up to vehicle batteries suffering from thermal and stress issues.

The WPPC model has been developed to resolve complex electrical configurations in a wound cell with discrete electrical tabs causing significant electrical current carried along the spiral structures of its current collectors. A jelly roll of a typical wound cell consists of long and wide double-sided electrodes coated on a pair of metal current collector foils. Complex electrical pairing in a wound cell jelly roll, illustrated in Figure 39, has been captured with the WPPC model. Figure 40 presents simulation results for the multi-physics response of a 10-Ah cylindrical cell with 5 discrete tabs at 5 minutes after 5C constant current discharge. Contour lines of electric potentials in current collector sheets appear almost perpendicular to the winding direction except for the region close to the location of the tabs. This implies that electric current in the current collector foils mainly flows along spiral paths of the wound jelly roll in this cell. The contours of the electrode plate current density reveal the non-uniform kinetics across the wound electrode pairs. More kinetic energy is observed near the tabs due to the larger potential offset and higher temperature of current convergence. Uneven kinetics causes cell-internal SOC imbalance during discharge.

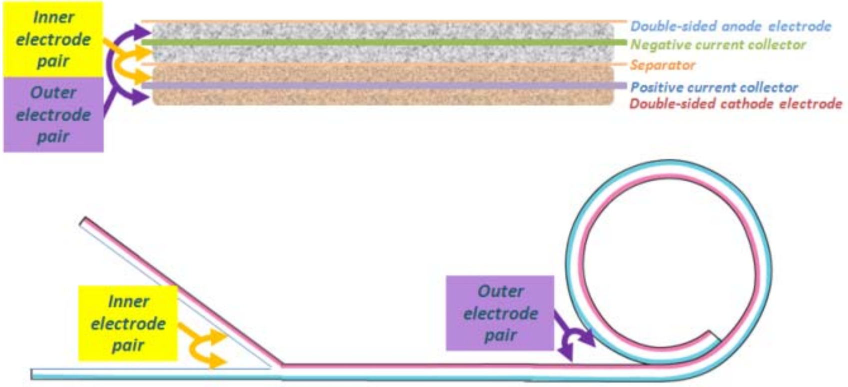


Figure 39: Schematics of a wound cell jelly roll having two sets of electrode pairs on a single pair of current collector sheets

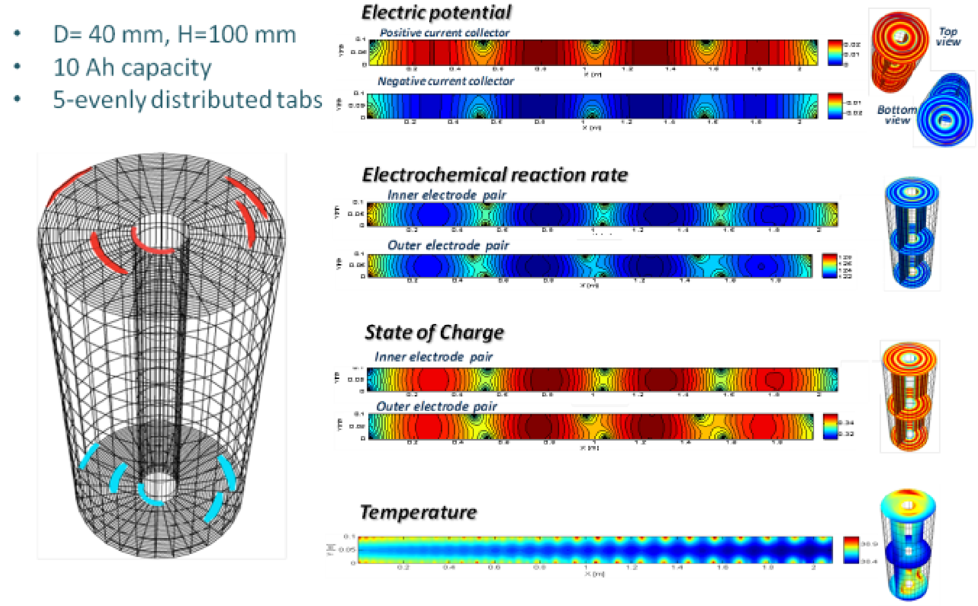


Figure 40: Schematics of a wound cell jelly roll having two sets of electrode pairs on a single pair of current collector sheets

Future Directions

NREL will continue to develop constituent models for the MSMD framework to address interdisciplinary multi-scale physics interactions in intricate geometries of Li-ion batteries while resolving widespread time and length scales in physico-chemical processes in Li-ion batteries. In FY12 and upcoming years, we will finalize documentation for the WPPC, the MPPC, and the FVLSM models/methods in peer-reviewed journal papers to transfer knowledge. We will establish a prismatic wound cell simulation model using the WPPC model through collaboration with EV industry partners to help them improve their prismatic wound cell designs. Experimental studies will be continued to validate the predictions made using the MSMD framework for the prismatic stacked Li-ion cell model. Various model-level order reduction methods will be further developed and investigated to use in upper hierarchy simulations. Multi-cell (pack) simulation will be demonstrated by applying newly developed fast computation methods for cell-level simulation. Extension of the MSMD approach from cell- to pack-level will be investigated.

FY 2011 Publications/Presentations

- Gi-Heon Kim, Kandler Smith, Kyu-Jin Lee, Shriram Santhanagopalan, Ahmad Pesaran, "Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales," *Journal of The Electrochemical Society*, 2011, Vol. 158, No. 8, pp. A955–A969
- Gi-Heon Kim, Kandler Smith, Kyu-Jin Lee, Shriram Santhanagopalan, Ahmad Pesaran, "Integrated Lithium-Ion Battery Model Encompassing Multi-Physics in Varied Scales," presented at the 11th International Advanced Automotive Battery Conference, Pasadena, CA, January 24–28, 2011.
- Ahmad Pesaran, Gi-Heon Kim, Kandler Smith, "Accelerating Design of Batteries Using Computer-Aided Engineering Tools," presented at 25th Electric Vehicle Symposium, Shenzhen, China, November 5–9, 2010.
- Kyu-Jin Lee, Gi-Heon Kim, Kandler Smith, "3D Thermal and Electrochemical Model for Spirally Wound Large Format Lithium-ion Batteries," presented at the 218th ECS Meeting, Las Vegas, NV, October 14, 2010.

Lithium-Ion Abuse Model Development

Objectives

- Build theoretical tools to:
  - Assess the safety of large format Li-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

- Safety concerns over Li-ion batteries in EDVs are one of the major barriers to widespread adoption of EDVs.
- There are numerous design parameters for Li-ion batteries, and the interaction among them is complicated; it is not feasible to experimentally identify the weakest link by conducting tests on a case-by-case basis.
- Test results for battery packs built with the same material by different manufacturers are very different, especially when it comes to safety evaluations. The cost associated with building and safety testing large-format cells, modules, and packs is quite high. Whenever such data are collected, it is treated as proprietary, thus preventing information sharing with other battery developers.
- Predicting material properties is currently done at the level of a few layers of atoms or molecules. This often does not incorporate the engineering challenges faced by the industry and does not scale well to battery size.

Technical Targets

- Build theoretical tools to investigate localized abuse events within Li-ion cells.
- Leverage NREL's understanding of thermal and electrochemical reactions that take place within a cell under abuse conditions to build a model for overcharge.
- Understand the impact of various components on the overcharge response of a Li-ion cell and suggest design changes to mitigate the limiting factors for operating the cell at low temperatures.

Accomplishments

- Developed software to generate meshable geometries from scanning electron microscope (SEM) images with a lever to control surface morphologies.
- Built an overcharge model that incorporates a mechanism for dendrite growth and relates the detailed electrolyte composition to the size, shape of the dendrites, and the growth rate of the surface film.
- Used the model to compare factors that limit cell performance over a wide range of temperatures and identified material modifications that will increase the operating range of the cell.

Introduction

During FY08–10, NREL built a multi-scale multi-physics simulation tool for three-dimensional modeling of internal short circuits within Li-ion cells by combining electrochemical, electrothermal, and abuse kinetics reaction models. This tool was used to characterize abuse response under a variety of cases and was received well by the industry. Following that effort, this year we initiated a mechanistic study on the growth of dendrites under various operating conditions (charge rates, operating temperature, electrolyte composition, etc.) when a cell is overcharged.

Approach

Most abuse reactions are strong functions of local geometry. Reactions such as lithium plating or particle fracture take place at specific weak points. In such instances, a volume averaging approach and the porous-electrode framework provide limited insight. Efforts to address these issues in the industry usually involve choosing different quality electrodes (parameterized by the particle size D50, the calendaring level, smoothness of the particle surface, and the like) and/or by adjusting the electrolyte composition. Mathematical models often do not include such design parameters explicitly; often an "average" value for the parameter in question is used. Incorporating details like surface energies of the particle/electrolyte interface, the shape of the particles, or detailed composition of the electrolyte (e.g., impact of a given additive on the plating potential for lithium) provides the missing link between practical problems faced by the cell manufacturer and the mathematical tools available today.

The first step in simulating abuse reactions in real geometries is to build the geometry from experimental observations (e.g., SEM images). NREL researchers have developed a tool to automate this process. The challenges involved include recognition of the particles, creating the particle-electrolyte boundaries, generating the mesh, refining the boundaries to capture the localized phenomena adequately, and defining the relevant physics in the different domains. Our automated process (summarized in Figure 41) enables one to specify various threshold levels for the geometry refinement and couple it with a multi-physics model (as shown in Figure 42).

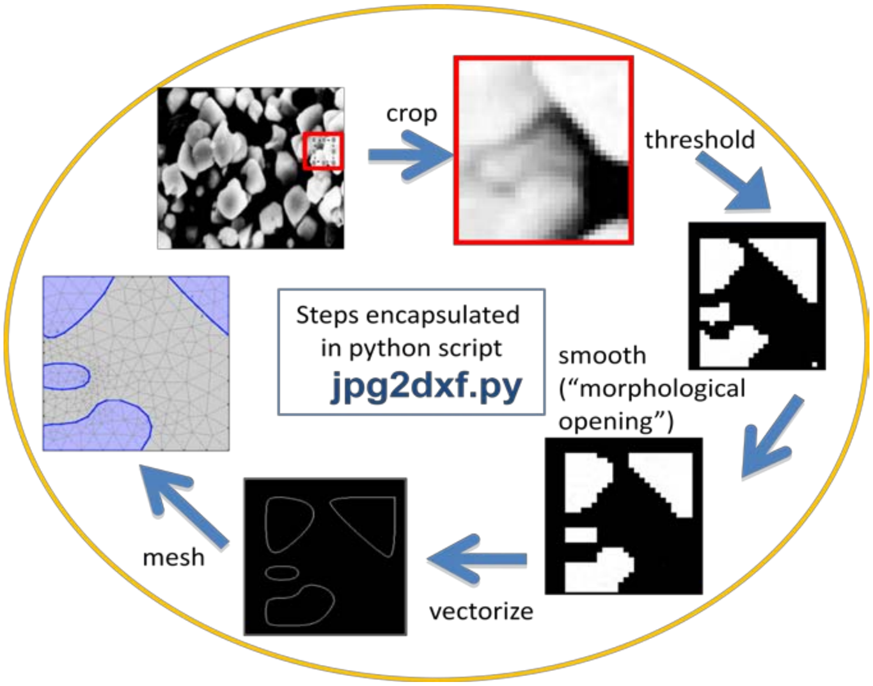


Figure 41: Steps to convert an SEM image to a computational mesh

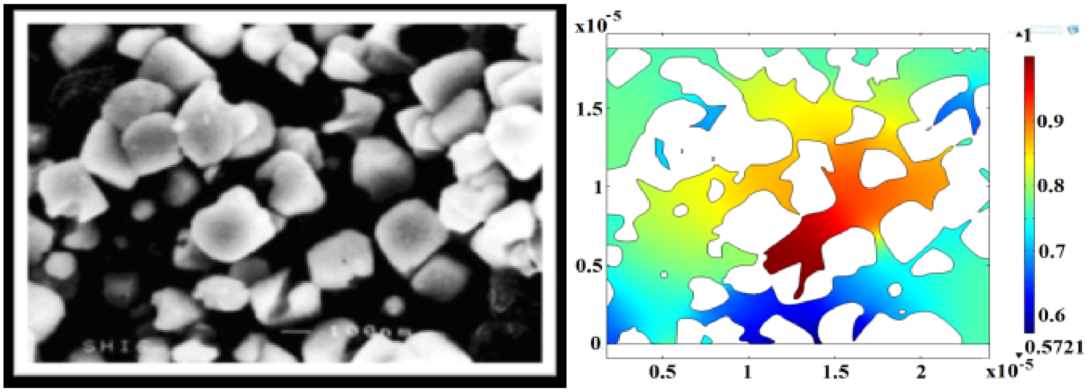


Figure 42: Sample results from NREL's simulations in actual electrode geometries. This model was built using an SEM image of an MCMB anode shown on the left; electrolyte distribution within a slice of the anode during overcharge is shown on the right.

Results

Using the tool described above, a mechanistic model for dendrite growth was built. The size of the dendrites is governed by the velocity of the interface and the shape of the dendrite is governed by the bulk properties of the electrolyte, the distribution of the reaction current (which in turn depends on the shape of the particles), balance of the surface forces versus the mechanical properties of the deposit, and external forces on the electrode (e.g., winding tension on a jellyroll), as shown in Figure 43.

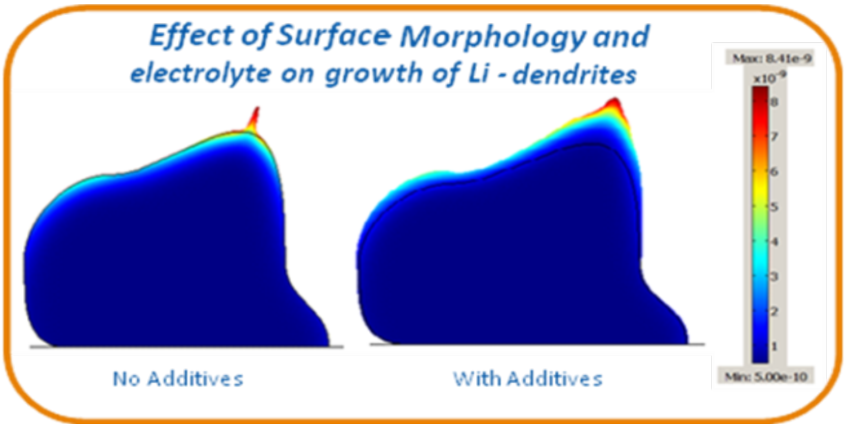


Figure 43: Comparison of the dendrite shape and size over an irregular particle. The image on the left is for 1.2 M $LiPF_6$ electrolyte in EC/EMC; the image on the right is for the same electrolyte in the presence of a hypothetical leveling agent.

Effect of the Particle Morphology

The normalized plating currents are plotted for various particle morphologies in Figure 44. The surface roughness is captured in the model by varying the threshold parameter described in Figure 41—the surface area for the case of hypothetical spherical particles is scaled by the area of the reacting surface for the different cases in the figure below. Thus, the ratio of 1 represents a smooth spherical particle, and lower values for the ratio indicate increasing surface roughness values.

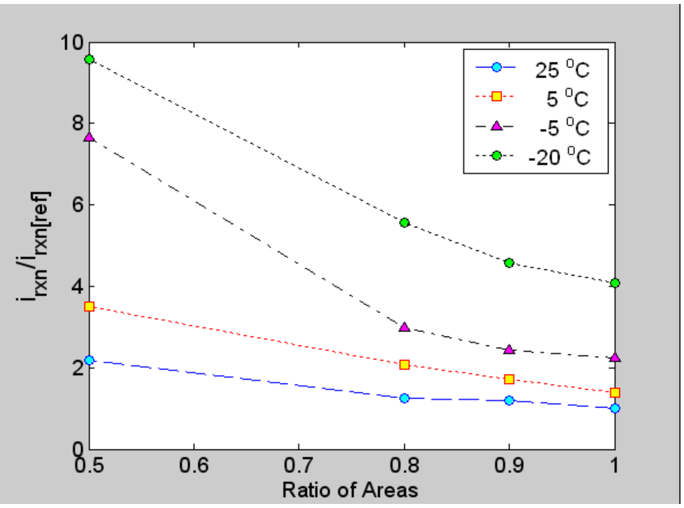


Figure 44: Comparison of overcharge reaction rates for different particle morphologies under 2C rate charge to 200%.

As expected, the dendrite growth progressively worsens with increases in the reacting surface area. The plating reaction is accelerated by a factor of almost 10, for the worst case presented, at -20°C. Reaction rates for a given ratio of the areas increasingly become larger with temperature, implying that the limitations from the electrolyte are more significant than the surface effects at low temperatures (especially below -5°C). For the worst case, when the area of the reacting surface is double that of the reference case, the reaction rate tapers off between -5°C and -20°C despite the high over-potential; for this case, bulk limitations result in non-availability of lithium at the surface.

Effect of Transport Properties

Electrolyte-based limitations such as poor conductivity, high viscosity and/or low diffusivity, have a strong influence on lithium plating—particularly when the temperature is lowered. The model captures widely reported trends—viscosity of the electrolyte increases with salt concentration and lowers diffusivity of ions, and resistance within the electrode increases leading to faster growth of dendrites. For the two molar (highly viscous) cases, the rate of growth of dendrites is comparable in the temperature range -5°C to 5°C, after which there is a steep increase. Localized heating effects result in better transport properties at the interface compared to bulk properties reported in the literature for this temperature range (see Figure 45). However, for temperatures below -5°C, the heat generated due to the resistance buildup is not sufficient to alleviate poor transport.

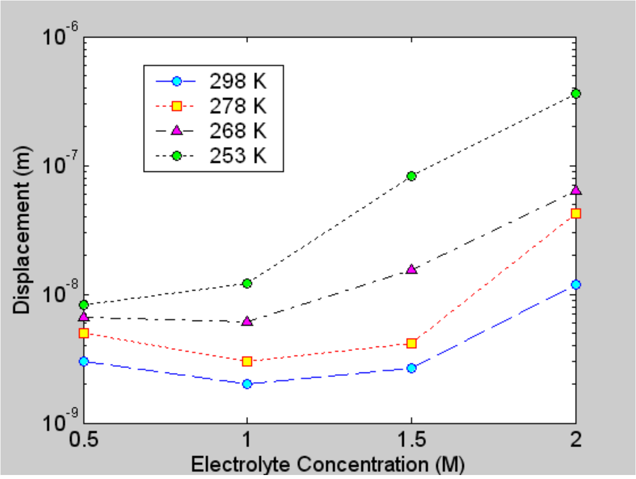


Figure 45: Effect of bulk properties of the electrolyte on the size of lithium dendrites during overcharge.

Surface Effects

Besides the size/shape of the particles and the transport properties of the charge carriers in the electrolyte, interfacial effects like wetting often play a key role in determining the rate of growth of the dendrites. In practice, such issues are overcome by employing suitable wetting agents. In this study, a higher surface tension value was used to simulate poor wetting. The results are shown in Figure 46 together with the baseline results from Figure 44. For the same electrolyte and particle morphology, significant resistance buildup at the interface results in aggravated lithium plating. The effects of poor wetting are more pronounced at lower temperatures; at room temperature, there is a slight increase in the deposition rate (for the set of parameters used in this study). This result is commonly reported in experiments as premature failure of the cells during the first few cycles. Another interesting observation is that the effects of the particle morphology supersede those of the surface properties. In other words, the limitation seen at -20°C is mainly because the lithium ions are not available at the surface rather than their inability to cross the interface. As a result, irrespective of the electrode wetting condition, the reaction rates at this very low temperature is about the same.

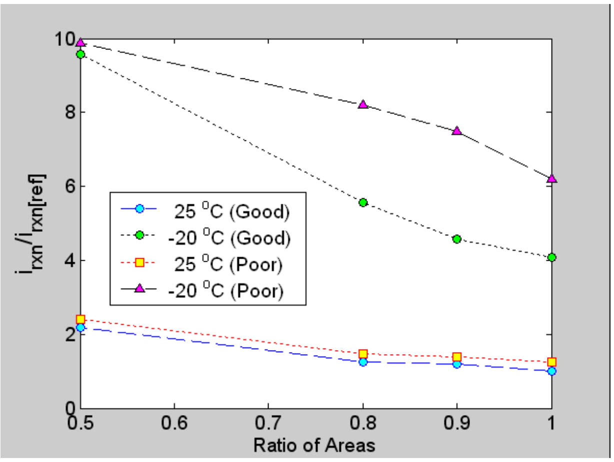


Figure 46: Effect of poor wetting of the particle surface on the lithium plating current during overcharge.

Conclusions and Future Directions

Modeling of abuse reactions in realistic geometries using NREL's in-house code to import SEM images provides a good insight into mitigation strategies appropriate to prevent localized overcharge in Li-ion cells. For example, for the system studied here, experimental efforts to improve safe operation of the cell at temperatures as low as -5°C should focus on improving the particle morphology and/or surface energies; however, bulk properties of the electrolyte are still the dominant factors at very low temperatures (-20°C). For such instances, unless the cell designer improves the transport properties in the electrolyte, surface modifications on the electrode particles will have limited impact. Future work will include incorporating the nature of the film formed in determining the safety of the cell during overcharge under various scenarios.

FY 2011 Publications/Presentations

- Shriram Santhanagopalan, Kandler Smith, Kyu-Jin Lee and Gi-Heon Kim, "Model for Lithium-Ion Batteries at Low Temperatures," 2010 MRS Fall Meeting, Boston, MA, November 29–December 3, 2010.
- Shriram Santhanagopalan, Kandler Smith, Kyu-Jin Lee and Gi-Heon Kim, "Simulating Overcharge Reactions in a Lithium-ion Cell," *J. Electrochemical Society*, Under Review, August 2011.
- Shriram Santhanagopalan, Gi-Heon Kim, Kyu-Jin Lee, Kandler Smith and Ahmad Pesaran, "Simulating Overcharge Reactions in a Lithium-ion Cell," 220th ECS Meeting, Boston, MA, October 11th 2011.

Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes (NREL, University of Colorado)

Objectives

- Use inexpensive and scalable deposition techniques for the production of either amorphous silicon (a-Si) or nano-Si powders and/or doped a-Si or nano-Si.
- Develop novel atomic layer deposition (ALD) coatings that will enable durable cycling to be achieved for the high volume expansion Si materials (~ 400 %).
- Explore the importance and mechanism of various coatings via the new BATT Coating Group.
- Collaborate within the BATT program with the aim of developing high-rate plug-in hybrid electric compatible electrodes (both anodes and cathodes).

Technical Barriers

- Major barriers addressed include:
    - Cost: Inexpensive processing techniques are employed to fabricate conventional thick electrodes.
    - High Capacity: Silicon is predominantly being explored as a high capacity anode material. There is also a collaborative emphasis to enable high capacity cathode materials.
    - High Rate: Both ALD coatings and nanostructured materials are being developed such that high-rate capability is demonstrated for emerging materials.
    - Safety: The ALD coatings are targeted to improve safety for a variety of electrode materials.

Technical Targets

- Demonstrate that ALD coatings can enable durable cycling for high-volume expansion Si anodes with a capacity ≥ 1,000 mAh/g.
- Demonstrate ALD coatings and nanostructured or amorphous materials for prolonged high rate cycling.
- Demonstrate that ALD coatings may serve as an artificial solid electrolyte interphase and, more importantly, will help minimize degradation upon volume expansion.
- Explore ALD coatings to minimize the first cycle capacity loss in Si anode materials.

Accomplishments

- This is a new award and NREL/University of Colorado – Boulder (CU) have met all of the Year One milestones as outlined briefly below:
    - Demonstrate scale-up of hot wire chemical vapor deposition (HWCVD) for a-Si or nano-Si powder.
    - Optimize HWCVD-produced a-Si or nano-Si in conventional coin cells.
    - Demonstrate an ALD coating for improved performance of Si anodes.

  - Optimize coated electrode and demonstrate durable cycling.
- A new Coatings Group has been formed to better understand the importance of coatings in next-generation material.
- Explored internally a variety of systems, including full cells to achieve better coating understanding.
- Established collaborations with external BATT partners, including Stan Whittingham, Clare Grey, Arugumum Mantharam and Gao Liu, to better understand coatings via the Coatings Group.
- Assisted in employing NREL techniques to enable high-capacity cathodes via collaboration within BATT.
- NREL established collaboration with Marca Deoff for spray deposition of spinel structures.
- In collaboration with Stan Whittingham, NREL has helped to show that $LiNi_yMn_yCo_{1-2y}O_2$ have inherent high rate capabilities.

Introduction

Significant advances in both energy density and rate capability for Li-ion batteries will be necessary for implementation in next-generation EVs. In our previous BATT award, NREL/CU demonstrated that thick (~15 µm) molybdenum trioxide (MoO_3) could be stabilized with a thin ALD coating of aluminum oxide (Al_2O_3) despite the relatively extreme volume expansion of greater than 100%. In the proposed efforts, both inexpensive routes for the synthesis of Si as well as the Al_2O_3 ALD coating and other new coatings to enable Si anodes will be employed.

Both high rate, durable cycling of Si will be achieved by employing the Al_2O_3 ALD coating and/or by developing new molecular layer deposition techniques to develop elastic (polymer-like) coatings and also coatings with low elastic moduli that are similar to polysiloxanes. Extensive collaboration is emphasized to employ both the ALD coatings and demonstrated nano-structured materials expertise to enable development of both high-capacity anodes and cathodes within the BATT program that exhibit durable high-rate capability.

Approach

The utilization of silicon as a Li-ion anode material is very desirable because of its high theoretical capacity of 4,200 mAh/g. Unfortunately, crystalline Si exhibits a rapid capacity degradation resulting from large volume expansion that produces fracturing, loss of electrical conductivity and mechanical degradation. a-Si and nano-Si have been demonstrated to exhibit improved cycling performance but have not achieved the durability and rate capability needed for application in PHEVs and EVs. In addition, Si has only been demonstrated for thin films (significantly less than 1 µm) and in nanostructured electrodes that are not suitable for large-scale vehicular applications. Here, inexpensive and commercial techniques for the formation of thick Si electrodes are employed.

In the first year, inexpensive Si production techniques were demonstrated. ALD coatings have also been employed to demonstrate reversible high capacity Si for thick electrodes. Finally, a mechanistic understanding of the new coatings is being obtained via both internal and collaborative work (Coatings Focus Group). Through collaborative efforts, various technologies are being employed to assist in the development of high-capacity cathode materials.

Results

Material

Scale-up of the inexpensive HWCVD process to achieve phase pure a-Si has been achieved. For the HWCVD depositions of a-Si powders, the substrate temperature (T_S) was at room temperature. In theory, this should completely remove the possibility of growing any crystalline silicon species. However, local hot spots depending on the proximity of the filament to the substrate and duration of the run/film thickness resulted in the nucleation of crystalline silicon particles. Figure 47a displays an *in situ* microscope image taken of an unutilized a-Si powder. The magnification is 100 times, and the green spots represent the μ-Raman spot size. In Figure 47a the large particles are ~ 30 μm in diameter and in general had a Raman line consistent with crystalline silicon, as represented by the blue curve in Figure 47b. Other portions of the initial samples appeared completely amorphous, shown as the red curve in Figure 47b, and a mixed phase was also observed, depicted by the orange curve in Figure 47b. By optimizing the synthesis conditions, it was possible to produce pure amorphous powder as shown in the micrograph of Figure 47c and the Raman spectrum of Figure 47d. X-ray diffraction of the a-Si powders also did not exhibit any crystalline peaks.

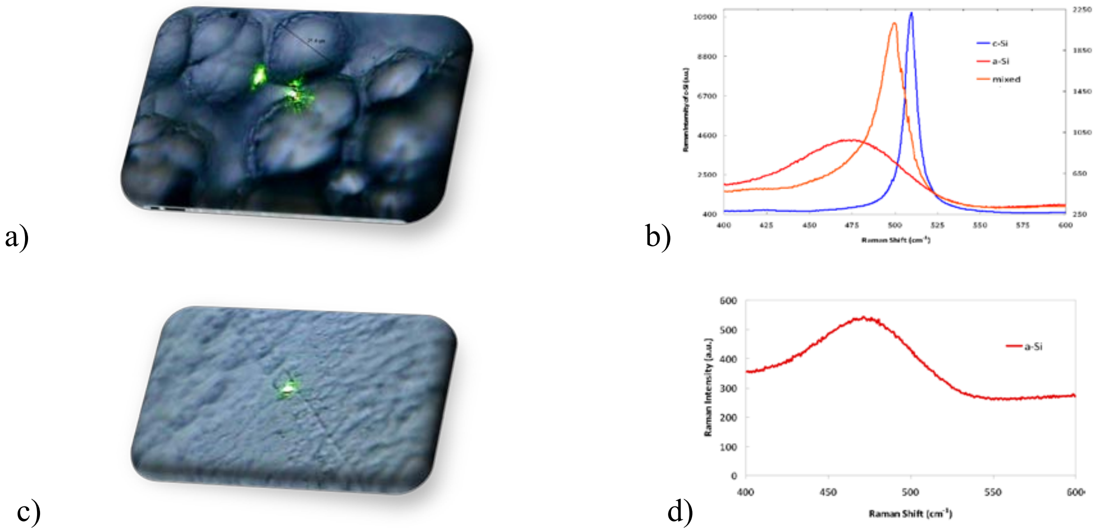


Figure 47: a) Image of mixed phase HWCVD Si, and b) corresponding Raman spectra compared with c) image of optimized a-Si and d) corresponding Raman spectrum.

Coin Cell Testing of HWCVD Materials

Initially, the a-Si was tested in a conventional coin cell electrode that was ~15 μm thick. Unfortunately, in this conventional electrode containing 60:20:20 silicon (Si):acetylene black (AB):polyvinylidene difluoride (PVDF), the first cycle irreversible capacity loss was ~30%, and stable cycling was not observed. Thus, a unique technique employing copper as both the binder and conductive additive was employed. Figure 48 displays the cycling performance of both the initial attempt (60:20:20 Si:AB:PVDF) as well as that of the new electrode fabrication technique. The new technique enables the creation of an electrode that is ~30 – 40 μm thick. The electrode has an initial first cycle irreversible capacity loss of only ~13% and a total reversible capacity of ~2,500 mAh/g. After the first cycle capacity loss, the electrode has a Coulombic efficiency of ~95 %. This represents a very significant improvement over the conventional electrode with AB and PVDF (Figure 48).

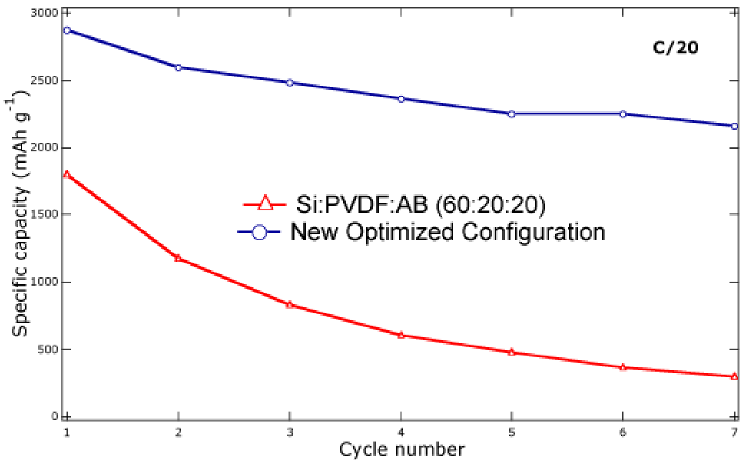


Figure 48: Cycling performance of a 15-μm-thick electrode containing 60:20:20 Si:AB:PVDF compared to our new 30- to 40-μm-thick electrodes fabricated with a novel technique.

ALD Coatings for Improved Si Durability

Thick coin cells with only copper as a conductive additive were employed for both a-Si and various sizes of crystalline nanoparticles (including commercial particles). In general, initial capacities of approximately 2,500 mAh/g and a Coulombic efficiency of ~95% are observed for all of the different materials.

As part of the coating focus group presentation in August 2011, it was shown that by applying an ALD Al_2O_3 coating to these materials the initial capacity is reduced to ~1,200 mAh/g, but the Coulombic efficiency is increased to greater than 99%. Coating thicknesses from 0.5–2.5 nm were explored, and it was found that 1 nm is the optimal ALD Al_2O_3 coating thickness. Figure 49a shows that a 1-nm Al_2O_3 ALD-coated electrode, containing commercial crystalline nano-Si particles, has a capacity of over 1,000 mAh/g for 160 cycles. Furthermore, there is no fade in the Coulombic efficiency. The ALD coating may limit the lithium insertion and simultaneously improve durability.

Figure 49b shows the voltage discharge and charge curves for a bare electrode and the coated electrode at cycle 50 using the novel configuration. Note that the capacity of the bare electrode has faded to ~1,200 mAh/g (from ~2,500 mAh/g) and is now roughly the same as the coated electrode. Importantly, after only two cycles (not shown), the discharge curves look significantly more similar than those shown in Figure 49b. Specifically, the Li^+ insertion voltage drops over time for the bare electrode but not for the coated electrode. This indicates that the structure of the ALD-coated Si is not altered as much with cycling as that of the bare electrode. Thus, it is possible that limiting the number of Li^+ ions that are inserted allows more structural integrity to be maintained and extends the durable cycling.

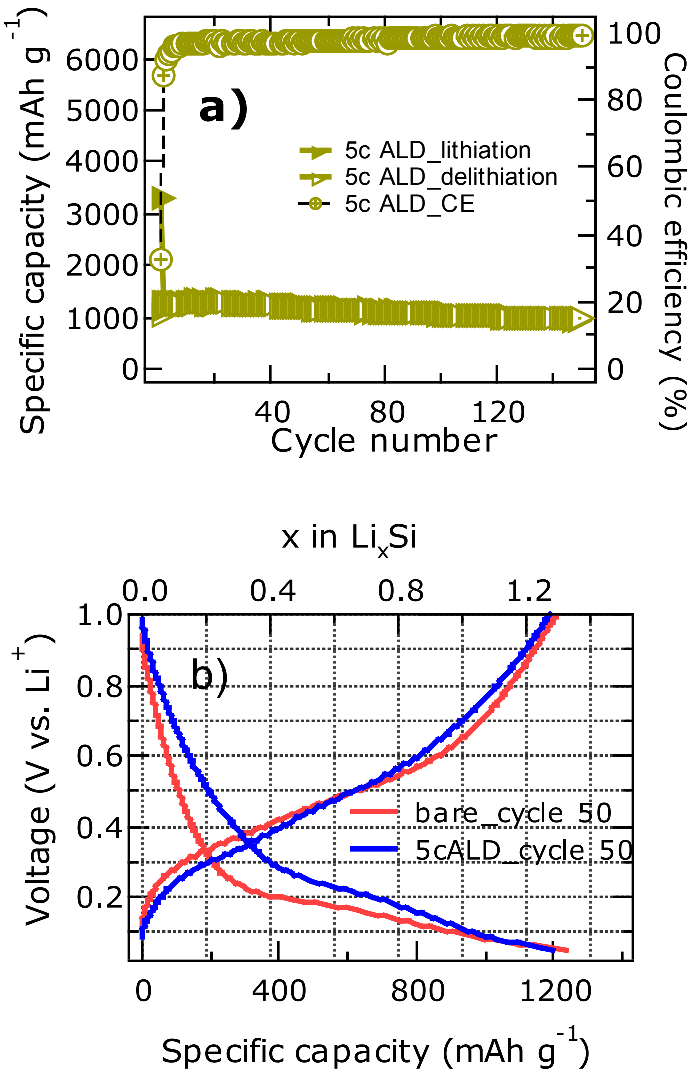


Figure 49: a) Durable cycling performance and Coulombic efficiency of an ALD-coated nano-Si electrode employing the novel matrix with copper employed as both the conductive additive and binder; b) Voltage discharge and charge profiles of both bare and coated electrodes at cycle 50.

Mechanistic Studies of ALD Coatings

Coating a variety of materials such as nano-lithium cobalt oxide ($LiCoO_2$) will enable mechanistic studies of Al_2O_3. NREL/CU has also fabricated full cells of natural graphite (NG) and $LiCoO_2$ where both electrodes, one or the other electrode, as well as neither electrode were coated. In creating these full cells, some surprising results that led to greater understanding of the ALD coatings were observed. Figure 50 shows the cycling behavior of the various electrodes that were cycled to 4.45 V vs. Li/Li$^+$, representing a very high voltage window for $LiCoO_2$. The uncoated electrodes are represented in the figure by (c) and the bare electrodes by (b). Note that improved cycling was observed, as expected, when both electrodes were coated as well as when the cathode was coated. Surprisingly, when only the anode was coated, improved cycling was also observed. Extensive characterization studies including impedance analysis, x-ray photoelectron spectroscopy, and time of flight secondary ion mass spectrometry were employed to analyze this effect. It was found that the surface species of the anode and cathode interact. Thus, coating only the anode dramatically affects the cathode.

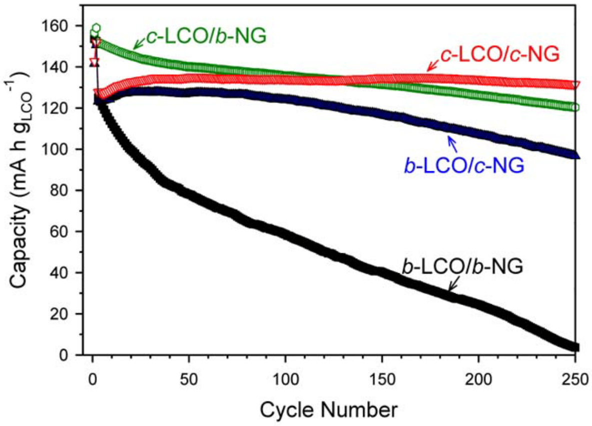


Figure 50: Cycling performance of NG and $LiCoO_2$ full cells where various electrodes are coated with Al_2O_3.

Noteworthy First-Year Collaborations

NREL worked with Stan Whittingham's group at the State University of New York – Binghamton to show that $LiNi_yMn_yCo_{1-2y}O_2$ can cycle stably for 500 cycles at both 5C and 10C with capacities of approximately 130 and 110 mAh/g, respectively. The cathode was enabled by using carbon single-walled nanotubes as both the conductive additive and binder with an active material loading of 95 wt.%. Anodes containing Si and a conductive binder developed by Gao Liu at Lawrence Berkeley National Laboratory (LBNL) were also coated with Al_2O_3, and preliminary results indicate that the performance of thicker electrodes is improved.

Conclusions and Future Directions

It has been demonstrated that ALD coatings of Al_2O_3 improve the durable cycling of thick Si-electrodes containing various forms of Si. A Coatings Group has been formed to better understand the mechanism of various coatings on new electrodes. In future work, the mechanisms of Al_2O_3 and other coatings will also be explored. In FY12, exploration of the mechanism as well as enabling a durable high rate capability for thick Si electrodes will be emphasized.

FY 2011 Publications/Presentations

- Jung, Y.S., *et al.*, "Unraveling the Unexpected Improved Performance of ALD Coated $LiCoO_2$/Graphite Li-ion Batteries," *JACS* (Submitted).
- Kang, E., *et al.*, "Magnetite Nanoparticles Confined in Mesocellular Carbon Foam for High Performance Anode Materials of Lithium-Ion Batteries," *Adv. Funct. Mater.*, **21**, 2430 (2011).
- Dillon, A.C., *et al.,* "HWCVD MoO_3 Nanoparticles and a-Si for Next Generation Li-Ion Anodes," *Thin Solid Films* **519**, 4495 (2011).
- Ban, C., *et al.* "Extremely Durable High-Rate Capability of an $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ Cathode Enabled with Single-Wall Carbon Nanotube," *Advanced Energy Materials* **1**, 58 (2011).

- Riley, L.A., *et al.,* “Improved mechanical integrity of ALD-coated composite electrodes for Li-ion Batteries,” *Electrochemical and Solid State Letters* **14**, A29 (2011).
- Riley, L.A., *et al.* “Electrochemical Effects of ALD Surface Modification on Combustion Synthesized $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ as a Layered-Cathode Material,” *Journal of Power Sources* **196**, 3317 (2011).
- Scott, I.D., *et al.* “Ultrathin Coatings on Nano-$LiCoO_2$ for Li-Ion Vehicular Applications,” *Nano Lett.* **11**, 414 (2011).
- Dillon, A.C., “Carbon Nanotubes for Photoconversion and Electrical Energy Storage,” *Chem. Rev.* **110**, 6856 (2010).
- Dillon, A.C., “ALD of Al_2O_3 for Highly Improved Performance in Li-ion Battery Electrodes,” *invited*, ALD2011, Boston, MA, July 2011.
- Ban, C., “Binder-free High Rate Capability Li-ion Electrodes” *invited,* Materials Research Society Spring Meeting, San Francisco, CA, April 2011.
- Dillon, A.C., *invited,* International Battery Association Meeting, Cape Town, South Africa, April, 2011. (Presented by M.S. Whittingham).
- Dillon, A.C., “Methods to Achieve Durable High Rate with High Capacity for Li-ion Batteries,” *key note,* Special ACS Symposium in Honor of Debra R. Rolison, Anaheim, CA, March 2011.
- Dillon, A.C., “High Rate and High Capacity Metal Oxide Anodes,” *invited,* American Vacuum Society Fall Meeting, Albuquerque, NM, October 2010.

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