



NREL Energy Storage Projects – FY2012 Annual Report

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

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Foreword

The Energy Storage Team within the Center for Transportation Technologies and Systems and the Chemical and Material Science Center at the National Renewable Energy Laboratory (NREL) performed the work detailed in this report under the Energy Storage Research and Development (R&D) activity of the Vehicle Technologies Program, which is managed by David Howell of the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy, in support of the automotive and battery industries. In fiscal year 2012, NREL performed several R&D projects under its Annual Operating Plan submitted to DOE on anode materials, coatings on cathodes, battery modeling, computer-aided engineering of batteries (CAEBAT), battery testing, life trade-off study modeling, techno-economic analysis of battery-powered vehicles, and secondary use of batteries. A summary of each project was prepared and submitted to DOE for inclusion in its Energy Storage FY12 Annual Progress Report. This report is a collection of the individual reports submitted to DOE.

This research and report would not have been possible without the support and guidance of many people. The authors wish to thank Brian Cunningham, Tien Duong, Peter Faguy, and David Howell from the Vehicle Technologies Program of the DOE 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.

Ahmad A. Pesaran
Energy Storage Group Manager
National Renewable Energy Laboratory

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)]*
- *Battery Testing, Analysis and Design*
- *Applied Battery Research (ABR)*
- *Focused Fundamental Research, or Batteries for Advanced Transportation Technologies (BATT)*

In FY12, DOE funded NREL to make technical contributions to all of these R&D activities. This report summarizes NREL's R&D projects in FY12 in support of the USABC; Battery Testing, Analysis and Design; ABR; and BATT program elements. Additionally, we continued the enhancement of NREL's battery testing facilities funded through the American Reinvestment and Recovery Act (ARRA) of 2009. The FY12 projects under NREL's Energy Storage R&D program are briefly described below. Each of these is discussed in depth in this report.

ARRA – Battery Thermal Test Facility: With investment from ARRA, NREL expanded its laboratory space at the Thermal Test Facility by 1,000 ft² to accommodate most of the new equipment purchased using ARRA funds. The expansion included upgrades to the electricity infrastructure and added chilled water capabilities.

Battery Ownership Model: NREL applied the Battery Ownership Model (BOM) developed in FY11 to study the sensitivity of plug-in hybrid electric vehicle (PHEV) and battery electric vehicle (BEV) economics to drive patterns, charge strategies, electric range, and other operational considerations under traditional ownership schemes and published two journal papers thereon. We found that PHEV and BEV economics are highly sensitive to individual drive patterns and that nationally averaged cross-sectional drive patterns inaccurately portray the cost effectiveness of these vehicles for a large fraction of the population. NREL also developed a new service provider evaluation module and employed it to study the economics of a battery swapping approach to BEVs. We found that BEVs operated under a service plan with battery swapping infrastructure may be cost effective relative to traditional BEV ownership when the cost of unachievable travel is high.

PEV Battery Second Use: NREL constructed an analysis framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications. We applied the framework to a lithium-ion (Li-ion) PEV battery second use analysis, which has highlighted the need for efficient repurposing strategies, identified promising markets for repurposed batteries, and began to quantify the potential of second use strategies that may affect the cost of energy storage in both automotive and secondary markets. The subcontract with California Center for Sustainable Energy (CCSE) and partners, in its second year, is on schedule while addressing some challenges in the fields. NREL acquired aged batteries, developed a long-term

test site and strategy, and initiated long-term testing via a subcontract with CCSE to address the major remaining uncertainty of battery life time.

Updating USABC Battery Technology Targets for Battery Electric Vehicles: NREL worked closely with DOE Energy Storage Program Managers and the USABC Technical Advisory Committee to identify the vehicle-level performance required for commercial success of BEVs, and develop a simulation-based approach for calculating the BEV battery technology targets necessary to deliver this level of vehicle performance. NREL implemented the process across a range of inputs and provided results to the USABC and DOE for finalizing inputs and assumptions. NREL provided a preliminary set of battery technical targets for the consideration of the USABC Management Committee. Following their review, NREL will complete this effort – resulting in a finalized set of BEV battery technical targets – in 2013.

Battery Life Trade-Off Studies: NREL quantified the impact of variable thermal scenarios on battery lifetime, together with simplified daily/seasonal temperature profiles suitable for the laboratory test environment; quantified opportunities for life-extending control strategies using previously developed life model for graphite/nickel-cobalt-aluminum (NCA) chemistry; and developed a new life model of graphite/iron-phosphate (FeP) chemistry, incorporating into the model new effects of low temperature degradation, high C-rate charge and discharge, and rapid fade regime at end-of-life.

Low Energy Hybrid Electric Vehicle Requirements Analysis: NREL secured a Ford Fusion hybrid electric vehicle (HEV) and designed modifications to create a lower-energy energy storage system (LEESS) conversion/test platform. NREL executed a Cooperative Research and Development Agreement with Ford to support the conversion, and a Non-Disclosure Agreement and Bailment Agreement with JSR Micro to obtain the initial Li-ion capacitor modules to test (at JSR Micro's expense). NREL developed a detailed understanding of the production battery system and the approach to use components from a salvaged battery along with dSpace equipment to implement the conversion.

Battery Thermal Analysis and Characterization Activities: NREL obtained cells from various USABC battery partners including A123 Systems, Actacell, Cobasys, Johnson Controls Incorporated (JCI), Quallion, LG Chem Power Inc. (LGCPI), K2 Energy Systems, JSR Micro, and SK Innovation. Obtained infrared thermal images of cells provided by USABC battery developers and identified any areas of thermal concern. NREL's unique calorimeters were used to measure heat generation from cells and modules under various charge/discharge profiles. NREL obtained thermal and electrical performance data of cells under HEV, PHEV and electric vehicle (EV) power profiles and evaluated the thermal performance of two PHEV packs (air-cooled JCI and liquid-cooled A123 Systems). The results of cell thermal characterization and pack thermal evaluation were presented at USABC/battery developers review meetings.

Development of an On-Demand Internal Short Circuit: NREL continues to make progress towards the development of an on-demand internal short circuit (ISC) for Li-ion batteries. Our internal short circuit emulator does not affect the performance of the battery under test and can be activated without puncturing or deforming the battery. The NREL ISC emulator was improved and successfully tested in cylindrical 18650 cells and a large-format pouch cell.

Computer-Aided Engineering of Batteries – CAEBAT (NREL): NREL 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. The three subcontractors are on track to deliver software tools to the industry by the end of their period of performance.

Development of CAEBAT Design Tools (GM Subcontract): A Newman Pseudo-2D model and various simplifications, including NTGK and ECM models, have been implemented into the first

cell-level tool, which was delivered in August 2012. A Simplorer-FLUENT co-simulation feature has been developed. Reduced Order Model (ROM) research has been conducted, and successful ROM concepts have demonstrated the feasibility of this approach for pack level simulation. Cell level tests and procedures for collecting test data from production cells to validate the cell design tool have been completed. A CAE capability matrix has been defined for pack-level applications in the automotive industry.

Development of CAEBAT Design Tools (CD-adapco Subcontract): The project has now delivered a simulation method that can describe and resolve the component parts of a spirally wound Li-ion battery cell. This resolution includes the overall shape and topology, cylindrical or prismatic, of the cell as well as the details of the electrode design, coating dimensions, and underlying electrochemistry. The simulation methods allow the cell to be considered in a lumped space in isolation, removing the effect of external packaging and focusing on the electrochemistry solution, or this same representation can be read in to STAR-CCM+ to create a three-dimensional representation that can then be duplicated to create a module or pack representation.

Development of CAEBAT Design Tools (EC Power Subcontract): The second version of EC Power's large-format software tool, "Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model" (ECT3D) was completed. It was updated to include electrochemical-thermal coupled pack simulation capability, parallel computing ability, the ability to model both rolled and stacked electrode designs, and a safety simulator that models nail penetrations/internal shorts, etc. More than 100,000 coin cells have been tested as part of the development of the materials database. The materials relevant to the automotive industry that were tested include, but are not limited to: graphite and LTO (anode); NCM, LFP, and LMO (cathode).

NREL Multi-Scale Multi-Dimensional (MSMD) Framework and Modeling Activities: In FY12, NREL has focused on extending the MSMD model to simulate the response of large-format prismatic wound cells by adding new capabilities. NREL's capability now includes a complete set of cell-domain modeling tools to simulate all major Li-ion battery form factors: stacked pouch, wound cylindrical, and wound prismatic. Development of the MSMD framework was documented in a peer-reviewed article for the Journal of the Electrochemical Society.

Lithium-Ion Abuse Model Development: NREL built a model for gas generation due to decomposition of the electrolyte during overcharge and linked the results from the electrode-level model to the cell level to simulate swelling of prismatic (pouch) Li-ion cells. NREL also conceived a "Fail-Safe-Design" for battery systems and built a mathematical model to demonstrate the concept of fail-safe-design for a large-capacity Li-ion battery system. The study was published in a peer review journal, and a US patent was filed for the resultant fail-safe-design invention.

Development of Industrial Viable Electrode Coatings: Demonstrated improved performance for an atomic layer deposition (ALD) alumina-coated commercial electrode material. ALD alumina coatings were demonstrated on up to 6-in. by 6-in. substrates. Atmospheric pressure ALD deposition was demonstrated on a moving substrate. NREL designed a new in-line ALD system for deposition on porous substrates.

Evaluate Impact of ALD Coating on Li/Mn-Rich Cathodes: NREL collaborated with LGCPI and obtained commercial samples of lithium (Li)/manganese (Mn)-rich cathode materials. NREL collaborated with ALD NanoSolutions, a leading company for coating ALD on battery materials, to scale up ALD coating using alumina on high-capacity Mn-rich cathode material. Initial evaluation of the coated powders shows little to no reduction in cell capacity over 50 cycles. Modification of the reactor to coated electrode sheets was initiated. Initial results indicated that two- to three-cycle ALD coatings with Al₂O₃ could decrease the Li/Mn-rich fade rate.

Stabilization of Amorphous Silicon Anodes with ALD: NREL successfully developed a silicon (Si) thick electrode ($\geq 15 \mu\text{m}$) with a highly reversible capacity of at least $2,000 \text{ mAh g}^{-1}$ at C/20 (175 mA/g) and demonstrated a high-rate capability (at C/3, $\sim 1,200 \text{ mA/g}$) for Si-polyacrylonitrile (PAN) composite electrodes. NREL demonstrated mechanistic information about ALD coatings via in-situ synchrotron X-ray diffraction, and ex-situ X-ray photoelectron spectroscopy and time of flight secondary ion mass spectrometry (TOF-SIMS). The cycling performance of full cells was greatly improved by applying Al_2O_3 ALD coating on electrodes and separators. Density functional theory simulations of lithiation in silica through partial reduction were also conducted.

List of Acronyms and Abbreviations

A123	A123 Systems
AB	acetylene black
ABR	Applied Battery Research
Al ₂ O 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
BEV	battery electric vehicle
BOM	Battery Ownership Model
BTM	battery thermal management
CAE	computer-aided engineering
CAEBAT	Computer Aided Engineering of Automotive Batteries
CCSE	California Center for Sustainable Energy
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
EELS	electron energy loss spectroscopy
EES TT	Electrochemical Energy Storage Technical Team
ESS	energy storage system
EV	electric vehicle
FeP	iron-phosphate
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.
K2	K2 Energy Solutions, Inc.
LCPM	levelized cost per mile
LEESS	lower-energy energy storage system
LGCPi	LG Chem Power, Inc.
Li	lithium
LiCoO ₂	lithium cobalt oxide
Li-ion	lithium-ion
MCMB	mesocarbon microbead
MLD	molecular layer deposition
Mn	manganese
MoO ₃	molybdenum trioxide
MPPC	multiple potential-pair continuum
MSMD	multi-scale, multi- dimensional
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 (John Newman)
PA-HEV	power-assist hybrid electric vehicle
PAN	polyacrylonitrile
PEV	plug-in electric vehicle
PHEV	plug-in hybrid electric vehicle
PVDF	polyvinylidene difluoride
R&D	research & development
RED	rolled electrode design regenerative braking
RFP	request for proposals
ROM	reduced order modeling
SED	stacked electrode design
SEI	solid electrolyte interphase
SEM	scanning electron microscope
Si	silicon
SK	SK Innovation
SOC	state of charge
SPPC	single potential-pair continuum
ST	small tab cell design
TOF-SIMS	time of flight secondary ion mass spectrometry
USABC	United States Advanced Battery Consortium

II.E.5 ARRA-Battery Thermal Test Facility (NREL)

Brian Cunningham (DOE Contact)
Grant Recipient: National Renewable Energy
Laboratory

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Start Date: March 2010
End Date: June 2013

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 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. The objective of this project was to expand and upgrade the NREL Battery Thermal Test Facility. 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) assisting DOE and United States Advanced Battery Consortium (USABC) battery developers in designing cells/modules/packs for improved thermal performance, and (2) benchmarking and validating the thermal performance of cell/module/pack deliverables from DOE/USABC battery developers and suppliers.

Benchmarking cells, modules, and packs being developed has been critical for integration of battery systems in advanced vehicles. NREL's current thermal test facilities identify areas of thermal concern as well as characterizing 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 few

years, 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 the ARRA funding, we are adding capacity and enhanced capability by adding new equipment and additional space in our existing facilities. We have added 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: 99.8% – End of FY12

Progress and Current Status

Thermal Test Facility Laboratory

We completed the expansion of the Energy Storage Thermal Test Facility. NREL expanded its laboratory space by 1,000 ft² in the Thermal Test Facility to accommodate most of the new equipment purchased under the ARRA funds. The expansion included upgrades to the electricity infrastructure and added chilled water capabilities.



The Energy Storage Thermal Test Facility occupies 2,000 ft² in NREL's Thermal Test Facility; Photo credit: Warren Gretz, NREL

Safety and Characterization Laboratory

We also completed development of the battery laboratory in Building 16 of the Denver West Building Complex by installing several thermal characterization pieces of equipment.

Equipment was purchased for two specific purposes: (1) Battery cycling channels and environmental controls, and (2) energy storage material characterization equipment such as a bulk and thin film thermal conductivity meter.

Equipment

Under the ARRA program, NREL expanded the number of low-, medium-, and high-power channels available for battery and other energy storage testing. Table II.E.5-1 outlines the number of testing channels and their respective current and voltage capabilities.

Table II.E.5-1. Low-, Medium-, and High-Power Battery Channels Purchased with ARRA Funds

# Channels	Voltage (Volts)	Current (Amps)
2	8-440	±265
4	0-100	±300
12	0-36	±300
16	0-5	±00
16	0-5	±50
64	-10-10	±0.5
104	-5-10	±2.0

NREL also purchased a number of environmental chambers and isothermal baths in order to perform thermal and cycle life testing of batteries. Table II.E.5-2 outlines the size and temperature range of the various chambers purchased under this task.

Table II.E.5-2. Environmental Chambers and Isothermal Baths Acquired with ARRA Funds

Number of Chambers/Baths	Temperature Range (°C)	Internal Volume (ft ³)
4 – Chambers	-45 to 190	32.5
1 – Chamber	-45 to 190	64
2 – Chambers	-20 to 85	4.1
1 – Chamber	-40 to 150	12.4
2 - Baths	-35 to 80	1.6
3 - Baths	-30 to 200	0.46

Finally, the following special-purpose equipment was purchased or designed/fabricated at NREL to expand our thermal testing capabilities:

- One coin cell calorimeter
- Two cell calorimeters
- One pouch cell calorimeter
- Glove box for destructive physical analysis
- Thin-film thermal conductivity meter
- Bulk material thermal conductivity meter
- Electrochemical impedance spectroscopy unit
- Data acquisition systems
- Thermal management test loop
 - Liquid
 - Air

Cost savings realized after the original statement of work was written allowed NREL to purchase several additional pieces of equipment not originally identified in the Statement of Work. The additional equipment not identified in the original Statement of Work included: the electrochemical impedance spectroscopy unit, the

three small environmental chambers (<15 ft³), the two large isothermal baths, a pouch cell calorimeter, a cell calorimeter, and the 16-channel ±50 amp battery cycler.

Since the completion of the new laboratory, the installed battery cyclers and environmental chambers are being used for USABC activities. In particular, we have been using the equipment to test energy storage systems from A123, ActaCell, Cobasys, JCI, JSR Micro, K2, Quallion, and SK Innovation. We have begun using the thin film and bulk thermal conductivity meters and the coin cell calorimeter purchased with ARRA funds.

During FY12, we concentrated on the design and fabrication of our cell and pouch calorimeters. We filed U.S. non-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, NREL finished the design and construction of the air/liquid battery thermal management test loop.

- Construction complete: 100%
- Equipment Installed: 100%
- Jobs: permanent: 1
- Jobs: temporary/construction: 10

Planned Work for FY 2013

The NREL Battery Thermal Test Facility is complete and no additional purchases are planned for FY 2013. We are utilizing the newly acquired equipment for the thermal characterization of energy storage systems developed by the U.S. battery and automotive industry.

Pictorial Overview

Photographs of New NREL Laboratory Space and Equipment Purchased under the ARRA Program



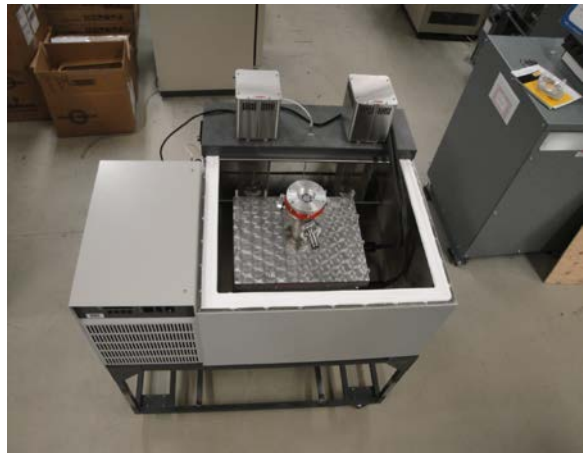
New battery space at the Thermal Test Facility laboratory before construction; Photo credit: Dirk Long, NREL



Thermal Test Facility laboratory after construction and equipment installation; Photo credit: Ahmad Pesaran, NREL



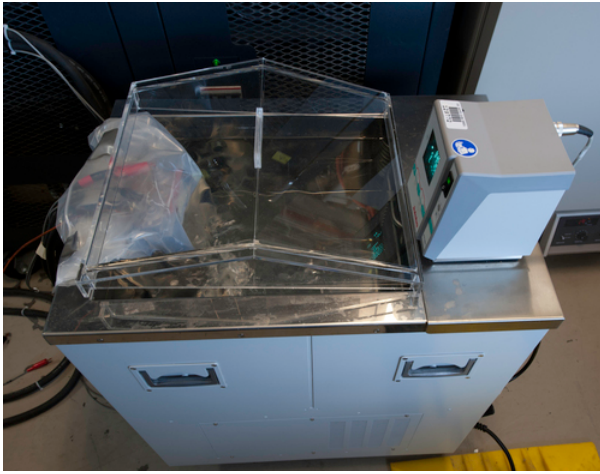
High- and medium-power battery cyclers; Photo credit: Ahmad Pesaran, NREL



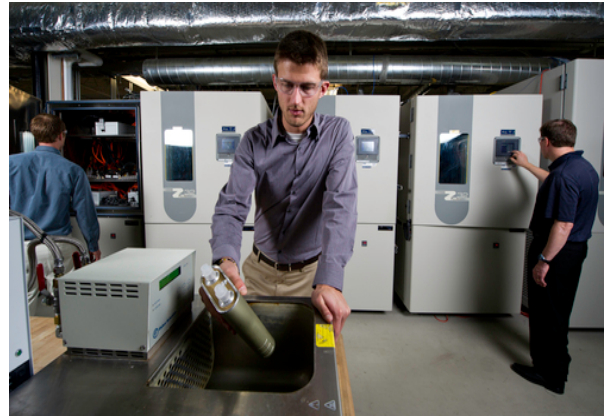
NREL designed/fabricated cell calorimeter in fluke isothermal bath; Photo credit: Dirk Long, NREL



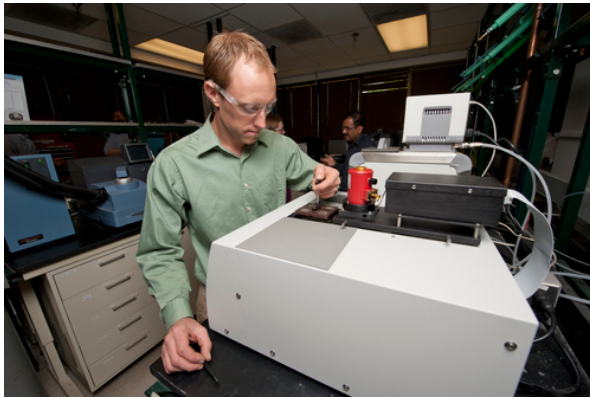
Liquid-handling thermal management in-the-loop; Photo credit: Dirk Long, NREL



Isothermal bath with battery under test; Photo credit: Dennis Schroeder, NREL



Environmental chambers/isothermal bath for battery cell and pack testing; Photo credit: Dennis Schroeder, NREL



Laser flash thermal conductivity meter for thin battery electrodes; Photo credit: Dennis Schroeder, NREL



Life cycle testing of batteries for secondary-use applications; Photo credit: Dennis Schroeder, NREL

III.C.1.2 Battery Ownership Model: A Tool for Evaluating the Economics of Electrified Vehicles and Related Infrastructure

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NREL

Start Date: FY2009
Projected End Date: FY2014

Objectives

- Identify cost-optimal electric vehicle (EV) use strategies capable of achieving national oil displacement goals.
- Use the NREL-developed Battery Ownership Model (BOM) to evaluate various business models and impact of other factors such as driving patterns, geography, battery wear, and charge profiles.

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 gasoline-powered vehicles (CVs).

Accomplishments

- Applied the BOM developed in FY11 to study the sensitivity of plug-in hybrid electric vehicle (PHEV) and battery electric vehicle (BEV) economics to drive patterns, charge strategies, electric range, and other operational considerations under traditional ownership schemes. Two journal papers were published thereon.
- Found that PHEV and BEV economics are highly sensitive to individual drive patterns and that nationally averaged cross-sectional drive patterns inaccurately portray the cost-effectiveness of these vehicles for a large fraction of the population.
- Developed a new service provider evaluation module and employed it to study the economics of a battery swapping approach to BEVs.
- Found that BEVs operated under a service plan with battery swapping infrastructure may be cost-effective relative to traditional BEV ownership when the cost of unachievable travel is high.

Introduction

Wide-scale consumer acceptance of alternatives to CVs such as hybrid electric vehicles (HEVs), PHEVs, and BEVs will depend at least in part on their cost effectiveness and their functionality, including driving range and ease of refueling. The present state of technology presents challenges in each of these areas

when traditional ownership and usage models are employed. However, a number of advanced technical and business strategies have been proposed to enable the transition to these alternative powertrain technologies, including: the electric utility utilization of the vehicle batteries as a distributed resource; battery leasing by a service provider who takes on the risk and upfront cost of battery ownership; public infrastructure development to recharge EVs while they are parked; fast-charge and/or battery swap stations that effectively extend BEV range; and alternative car ownership models that allow users to own a BEV but rent other vehicles for long-distance excursions. Each strategy has unique implications to the vehicle design, operating characteristics, and battery life. Accordingly, it can be challenging to compare different system options on a consistent basis to assess their ability to support the consumer adoption of such advanced vehicles.

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

Approach

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

In FY11, the BOM received two major upgrades. The first enabled the analysis of real-world daily driving distance distributions, using 398 vehicle-specific discrete probability distribution functions of daily vehicle miles travelled (DVMT) compiled from the Puget Sound Regional Council's Traffic Choices Study. The second enabled the BOM to better capture the sensitivity of battery degradation to variances in usage and vehicle design, via the integration of NREL's high fidelity battery degradation model that calculates capacity loss and resistance gain based on depth of discharge, temperature, and state of charge (SOC) histories. An additional upgrade of note is the inclusion of two accounting methods to address the cost of a BEV's limited range, which we denote as the cost of unachievable vehicle miles traveled (VMT). A low-cost method assumes a multi-vehicle household with a CV available for long travel days, while a high cost method assumes a rental car is acquired for long travel days.

In FY12, work focused on leveraging these upgrades to study the sensitivity of PHEV and BEV

economics to drive patterns, charge strategies, electric range, and other operational considerations under traditional ownership schemes. We also developed a new service provider evaluation module this year, which we employed to study the economics of a battery swapping approach to BEVs. The results of each of these studies are discussed below.

Results

A major finding of this year's work was that the total cost of ownership of PHEVs and BEVs is a strong function of the driver's distribution of DVMT. For illustrative purposes, the DVMT distributions we employed are shown in Figure III.C.1.2-1. Note that the longitudinal data sources from the Traffic Choices Study show immense variability between drivers, as well as a tendency for individual drivers to have fairly consistent DVMTs day to day (indicated by high, narrow peaks in a probability distribution function). Applied to BEV economics, we find that this variation of DVMT distributions within the Traffic Choices Study data set can affect the relative cost effectiveness of a BEV by a factor of 3.5:1.

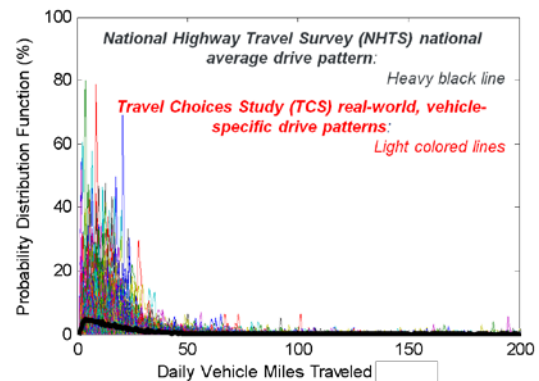


Figure III.C.1.2-1: Probability distribution function of daily vehicle miles travelled

We have also found that the cost of unachievable VMT also has a strong effect on BEV economics. Figure III.C.1.2-2 shows the total cost of a BEV relative to a CV for both the high and low cost of unachievable VMT accounting methods, three ranges (50 to 100 miles), and all Traffic Choices Study drive patterns (min, 25th percentile, 50th percentile, 75th percentile, and max indicated by the box plots). We find that switching from the low to the high cost accounting method increases the total cost of ownership and the sensitivity to drive pattern, while significantly altering the effect of vehicle range.

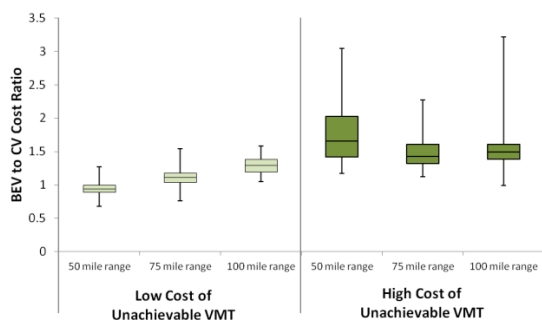


Figure III.C.1.2-2: Distribution of BEV to CV cost ratios for various vehicle ranges, cost of unachievable VMT, and drive patterns

By considering the vehicle’s changing range over time (as calculated by our newly integrated battery degradation model) alongside a forecast for future battery prices, we have been able to develop a cost-optimal battery replacement algorithm. This algorithm effectively determines when a battery should be replaced to minimize the total cost of ownership. Interestingly, we find it to be highly unlikely that rational BEV and PHEV owners would replace their batteries within a vehicle’s normal life expectancy without unusually high levels of degradation. This is due primarily to the fact that the cost to the driver of reduced vehicle range is generally low, whereas the cost of a replacement battery is high even under exceedingly optimistic circumstances.

We further built upon these results with a thorough study of battery swapping to extend BEV range. Our approach consisted of four main steps: (1) identifying drive patterns well suited to a battery swapping service plan, (2) calculating average service usage statistics for the selected drive patterns, (3) making a bottom-up calculation of service plan fees based on the identified service usage statistics and a rigorous economic model of the service provider’s business, and (4) studying individual driver economics under both the service plan and traditional ownership options.

Ultimately we found that a battery swapping service plan could be more cost-effective than traditional BEV ownership for many drivers when the cost of unachievable VMT is high. Under a low cost / low service infrastructure network scenario, we found that more than 80% of our down-selected drive patterns could benefit financially from this approach. If a high cost / high service infrastructure network (which seeks to mimic the convenience of today’s gasoline infrastructure) is necessary for consumer adoption, this percentage is reduced but still significant (>40%). However, under all scenarios, it is unlikely that a battery swapping service plan offers enough financial benefit to make the BEV more cost effective than a CV for the high-cost-of-unachievable-VMT drivers. Nor is it likely that a battery swapping service plan BEV will

be more cost effective than direct ownership of a BEV where the low cost of unachievable VMT is low.

Conclusions and Future Directions

In FY12, we made significant advances on using the BOM to the study of drive patterns, charging strategies, vehicle range, and other factors with respect to the total cost of EV ownership. This was made possible by the unique capabilities added to the BOM in FY11, particularly the integration of a high-fidelity battery degradation model and high-quality longitudinal drive pattern data. Notably, this has enabled the quantification of the impact of both DVMT distributions and BEV range limits on EV economics. It has been demonstrated that improper consideration of each of these factors can heavily bias high-level analysis results, and thus must be addressed carefully and thoroughly to provide accurate comparisons of different technologies.

In future work, we plan to expand our consideration of driver habits—incorporating elements of individual trips, destination locations, and variability of driver aggression—and battery thermal response. We intend to apply this more powerful capability to higher resolution studies of climate, battery thermal management strategies, and a variety of range extension techniques (opportunity charging, fast charging, etc.). The results of these studies will place us closer to identifying cost-optimal EV strategies for reducing national gasoline consumption.

FY2012 Publications/Presentations

1. Neubauer, Jeremy, Aaron Brooker, Eric Wood, “Sensitivity of plug-in hybrid electric vehicle economics to drive patterns, electric range, energy management, and charge strategies,” *Journal of Power Sources*, In Press.
2. Neubauer, Jeremy, Aaron Brooker, Eric Wood, “Sensitivity of battery electric vehicle economics to drive patterns, vehicle range, and charge strategies,” *Journal of Power Sources*, Volume 209, 1 July 2012, Pages 269-277.
3. Neubauer, Jeremy, Kandler Smith, Matthew Earleywine, Eric Wood, Ahmad Pesaran, “The Impact of Thermal Management, Geography, and Driving Habits on Plug-In Hybrid Electric Vehicle Battery Life and Economics,” April 2012.
4. Neubauer, Jeremy, Kandler Smith, Matthew Earleywine, Eric Wood, Ahmad Pesaran, “Comparison of Plug-In Hybrid Electric Vehicle Battery Life across Geographies and Drive Cycles,” SAE 2012 World Congress, April 2012.
5. Neubauer, Jeremy, “Applying the Battery Ownership Model in Pursuit of Optimal Battery

- Use Strategies,” DOE Vehicle Technologies Program Annual Merit Review, May 2012.
6. Neubauer, Jeremy, “Addressing Challenges in EV Economic Analyses with the Battery Ownership Model,” Plug-in 2012, July 2012.
 7. Neubauer, Jeremy, “Building the Complete Picture of Electric Vehicle Ownership Costs: Impacts of Driver Behavior, Range Limitations, and Battery Replacement,” EV Battery Tech USA, Sept. 2012.

III.C.1.3 PEV Battery Second Use (NREL)

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A. Pesaran, NREL

Start Date: February 2009

Projected End Date: September 2014

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.
- Collaborate with industry through cost-share projects to evaluate the potential of battery second use in real applications.

Technical Barriers

- PEV costs are high. *Re-using PEV batteries in secondary applications and delaying recycling can reduce the total cost of ownership.*
- The processes and costs of repurposing PEV batteries are yet to be identified, and could have a major impact on the viability of second use strategies.
- Quantifying post-automotive applications for PEV batteries is challenged by uncertain electrical demands, complex and difficult to assess revenue streams, and prohibitive regulatory structures.

- Battery degradation in both automotive and post-automotive use is notoriously difficult to ascertain, yet has a strong impact on the potential profitability of secondary use strategies.

Technical Targets

- Identify 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

- Constructed an analysis framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications.
- Applied the framework to a Li-ion PEV battery second-use analysis which has highlighted the need for efficient repurposing strategies, identified promising markets for repurposed batteries, and begun to quantify the potential of second-use strategies to affect the cost of energy storage to both automotive and secondary markets.
- The subcontract with California Center for Sustainable Energy (CCSE) and partners, in its second year, is going on schedule while addressing some challenges in the fields.
- Acquired aged batteries, developed a long term test site and strategy, and initiated long term testing via subcontract with CCSE to address the major remaining uncertainty of battery life time.

Introduction

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

One means of reducing battery costs 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 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 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 be, in part, 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. In order to facilitate and accelerate these efforts, we identified interested second use partners by issuing a request for proposals (RFP) for a collaborative project. A team consisting of AeroVironment, University of California, Davis, University of California, Berkeley, University of California, San Diego, and San Diego Gas & Electric led by the California Center for Sustainable Energy (CCSE) was selected in FY10 for collaboration. The CCSE team started work in FY11. Since then, the NREL / CCSE team has been working collaboratively to perform techno-economic analyses, acquire aged

batteries, and set-up an in-field experiment to evaluate the performance and longevity of 2nd use batteries as discussed below.

Results

Repurposed Battery Sale Price

Assuming that suitable applications of sufficient value are present in the future, it is reasonable to assume that the selling price of repurposed automotive batteries will be set not by the value of the application, but by the price of competing technology. Further, assuming the competition for used Li-ion batteries to be new Li-ion batteries, repurposed battery prices become a strong function of future battery prices. Accounting for the anticipated future decline in new battery prices, degraded battery health at automotive retirement, and a repurposed product discount factor, we can then forecast anticipated repurposed battery sale prices (Figure III.C.1.3-1) The possible variations in the aforementioned inputs – particularly forecasts for future battery prices – lead to significant uncertainty in the results, but in all cases the expected cost of repurposed batteries to grid or other applications is low.

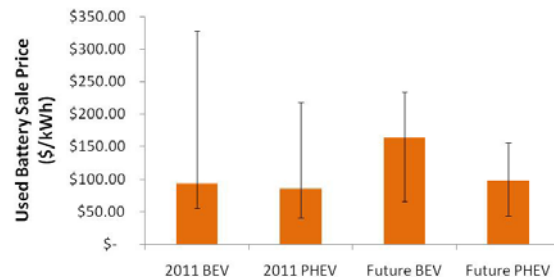


Figure III.C.1.3-1: Projected second use battery sale price

Used Battery Repurposing Costs

Next, we apply knowledge of the repurposed-battery selling price to the calculation of the costs involved in the processes between retiring a battery from automotive service and selling it to a secondary market (collection, testing, repackaging, warranty, etc.), herein referred to as repurposing costs. Using a bottom-up approach that considers all labor, capital equipment, facility needs, required rate of return by the operating entity, and many other factors, we calculate these costs as a function of the size of the module being repurposed and the frequency of occurrence of irreparable cells (cell fault rate).

Our results imply that the costs of capital and technician labor are the most significant cost elements of repurposing activities. These sensitivities have two considerable implications: the prior makes repurposing costs a strong function of the price at which a repurposing facility buys used batteries, while the latter

rules out the possibility of labor intensive repurposing operations (such as addressing individual instances of faulty cells). Our results, a subset thereof shown in Figure III.C.1.3-2 below, reveal large variations in repurposing costs resulting from the interplay of module size and cell fault rate: efficiencies of scale encourage repurposing larger modules, but larger modules also mean more waste when a faulty cell is identified.

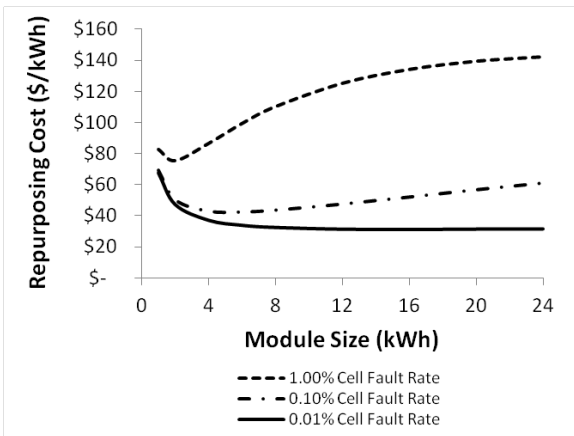


Figure III.C.1.3-2: Projected second use battery repurposing cost for a repurposed battery selling price of \$132/kWh

Stationary Applications: Preliminary Analysis

All of the preceding estimates are contingent on the existence of demand for repurposed batteries. Stationary applications are often indicated as a likely source of such demand, given the potential scale of the market and present trends in variable and distributed generation and intelligent systems. Accordingly, we assessed the value and market potential of possible grid-based secondary use applications. Accounting for the value of service, the expected limitations of repurposed automotive batteries, and the costs of the balance of system necessary to provide said service, our findings suggest that area regulation, electric service power quality and reliability, and transmission and distribution upgrade deferral offer considerable value, as seen in Figure III.C.1.3-3. However, we also see considerable uncertainty in both value and market potential that warrants closer study.

Stationary Applications: Area Regulation

Area regulation is a service intended to balance the supply and demand for energy on a relatively fast time scale (~15 minutes and less). As such it is typically characterized by frequent variations in demanded power. Batteries are thought to be a well suited resource for providing area regulation, due to the notion that regulations signals are energy neutral (at least in

principle) and can respond much faster than traditional generation resources.

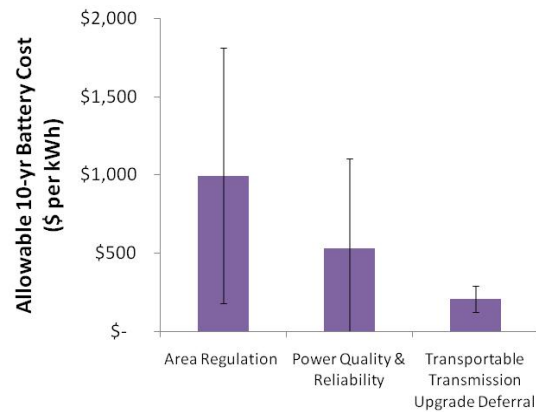


Figure III.C.1.3-3: Preliminary Application Analysis Results

However, the value of regulation services is highly uncertain. Regulation prices are often set in the free market and are highly variable. The data underlying our preliminary analysis came from a period of high regulation prices circa 2006; had our analysis been based on 2010 data, a much less optimistic estimate would have been made. Further, the size of the regulation market is extremely small compared to that of the automotive market. Our estimates suggest that the next ten years of market demand could be saturated by repurposed batteries from fewer than 40,000 BEVs.

The state of the market today, though, may not be relevant to the state of the market when repurposed automotive batteries become widely available. The increased penetration of renewables on the grid, as well as changing consumer load profiles, could vastly increase the market for regulation. The open market price for regulation could be vastly higher as well, and batteries and other fast response resources could be paid a considerable premium relative to conventional generation for its superior performance.

Stationary Applications: End-User

Power quality and reliability is a high value market that is well established today (e.g. uninterruptible power supplies). Sold at a price of \$132/kWh, it is quite likely that repurposed automotive batteries could compete with the incumbent technology – lead acid. Repurposed automotive batteries would enable systems integrators to reduce the footprint of their products, while potentially extending product lifetime and reducing maintenance costs. Therefore, as repurposed automotive batteries become accepted as a reliable resource, we believe this will become a common application.

Going one step further, it is reasonable to think that the use of Li-ion technology, with its superior cycle life, may also enable the use of backup power systems for

time-of-use energy and demand charge management to reduce electricity bills. After considerable study, we find several barriers to such a strategy, particularly the possibility of sequential demand charge and reliability events that impede the sharing of battery capacity between the two applications.

Stationary Applications: Transmission Upgrade Deferral

This application entails use of an energy storage system to reduce peak loads on transmission assets with projected overloads, enabling the upgrade or replacement of such assets to be deferred. The value comes from the elimination of carrying charges that would have been incurred over the deferral period had the transmission upgrade investment been made. It is generally accepted that the required duty cycle is fairly benign, only requiring a few discharges per year at low rate. This offers the additional opportunity to serve other high value applications (e.g. regulation) and generate complimentary revenue streams.

Battery Acquisition and Testing

We acquired numerous aged automotive battery packs spanning multiple Li-ion chemistries, including iron phosphate, nickel manganese cobalt, and manganese oxide cathodes, and graphite, hard carbon, and lithium titanate anodes. Acceptance 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 site on the University of California – San Diego microgrid also has been completed, as seen in Figure III.C.1.3-4. The down-selected battery packs were installed and long term grid connected testing has been initiated. Duty cycles for regulation, power reliability, demand charge management, and transmission upgrade deferral have been employed, which were generated from our application analysis discussed previously. Figure III.C.1.3-5 shows a representative response of one pack being tested to the regulation duty cycle.



Figure III.C.1.3-4: Second Use Battery Field Test Installation at University of California, San Diego; Photo credits: Jeremy Neubauer, NREL

The challenges with this application are as follows: (1) value is highly sensitive to the specifics of each possible installation, (2) value per unit of battery capacity installed decays rapidly as load continues to grow on the transmission asset, (3) market size is questionable (but likely to grow with increased deployment of solar and wind generation), and (4) conventional generators may offer a better value case when applicable. We note, though, that when conventional generators are not an option, Li-ion batteries offer a competitive solution relative to other energy storage mechanisms thanks to their high specific energy, high energy density, and good mechanical robustness. This makes them easily transportable, which is important to overcome challenge (2) above in making a profitable business case.

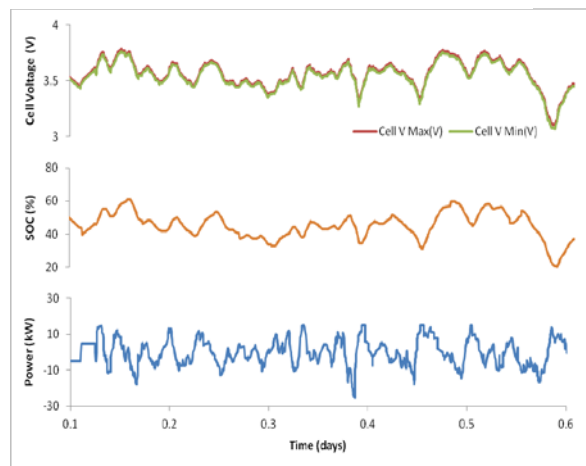


Figure III.C.1.3-5: Measured battery response to regulation testing

Conclusions and Future Directions

NREL has created a detailed framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications. The applications of this framework to Li-Ion PEV batteries has highlighted the need for efficient repurposing strategies, identified promising markets for repurposed batteries, and begun to quantify the potential of second use strategies to affect the cost of energy storage to both automotive and secondary markets.

The major uncertainty that remains is the longevity of repurposed batteries in post-automotive applications. To address this matter, NREL has acquired aged batteries, developed a long term test site and strategy, and initiated long term testing via subcontract with CCSE. NREL has also acquired additional aged batteries for on-site laboratory testing. These efforts will be the focus of continued project work in FY13. In addition in FY13 we will be working with Southern California Edison to evaluate the potential of second use batteries in Community Energy Storage applications.

FY 2012 Publications/Presentations

1. Neubauer, Jeremy, and Ahmad Pesaran, "Initial Test Results of the NREL PEV Battery Second-Use Project," 2012 DOE Milestone Report.
2. Neubauer, Jeremy and Ahmad Pesaran, "NREL/CCSE PEV Battery Second Use Project," EESAT, October 2011.
3. Neubauer, Jeremy and Ahmad Pesaran, "Three Angles on PEV Battery Second Use," The Battery Show, October 2011.
4. Neubauer, Jeremy, "Developing and Assessing Battery Second Use Strategies," IEEE Transportation Electrification Conference," June 2012.
5. Neubauer, Jeremy, Ahmad Pesaran, Brett Williams, Mike Ferry, and Jim Eyer, "A Techno-Economic Analysis of PEV Battery Second Use: Repurposed-Battery Selling Price and Commercial and Industrial End-User Value," SAE World Congress & Exhibition, April 2012.
6. Neubauer, Jeremy, et al., "A Techno-Economic Analysis of PEV Battery Second Use: Repurposed-Battery Selling Price and Commercial and Industrial End-User Value," SAE Technical Paper 2012-01-0349, 2012, doi:10.4271/2012-01-0349.

III.C.1.4 Updating USABC Battery Technology Targets for Battery Electric Vehicles

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Start Date: FY2012

Projected End Date: FY2013

Objective

Identify battery available energy, mass, volume, cost, discharge power, and charge power requirements that will enable broad commercial success of BEVs

Technical Barriers

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

Accomplishments

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

Introduction

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

Improvements in battery technology have the capacity to resolve all of these issues. Accordingly, the United States Advanced Battery Consortium (USABC), the Department of Energy (DOE), and others are directing significant resources towards the development of batteries for BEVs. Historically, these developments have been focused towards a set of USABC BEV battery targets developed more than 20 years ago. Documentation providing insight into the development of these targets is exceptionally scarce, thus the justification for these values is unclear. For this reason, and on the basis that the necessary vehicle performance for market success has changed since the creation of the original targets, there is motivation to develop an updated set of BEV battery technology targets.

In 2012, the USABC and DOE began the process of creating a new set of battery technology targets for BEVs. It was desired that the targets be designed to deliver a BEV capable of broad market success if achieved. To this end, the resources of the National Renewable Energy Laboratory (NREL) were leveraged to supply detailed technical analysis, guided by the insight of the USABC's vehicle OEM members on consumer requirements and future technology trends.

Approach

The objective of this analysis is to identify battery available energy, mass, volume, cost, discharge power, and charge power requirements that will enable broad commercial success of BEVs once achieved. Working closely with USABC and DOE, NREL has developed a simulation-based approach to achieving this objective. It begins by first specifying the relevant vehicular level performance requirements necessary for commercial

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

Results

In addition to defining the high level approach discussed previously with our USABC and DOE partners, we have made significant progress in implementing it. Vehicle acceleration and range have been defined, based upon both OEM input of market needs and analysis of large amounts of real-world driving data. A baseline vehicle platform and vehicle technology forecasts have also been selected, leveraging a recent US DRIVE analysis to ensure broader industry agreement on the assumptions of our analysis. We have achieved agreement within the group on all necessary simulation inputs, including how to use standard (e.g. US06, UDDS, etc.) and real-world drive cycles for the specification of vehicle range, efficiency, discharge power characteristics, etc.; what assumptions to apply to financial comparisons; and other necessary input values.

We have also prepared the necessary simulation tools to perform our specified calculations and explored a broad spectrum of the design space to study the interplay of assumptions and resultant target values. The results of this study are currently being employed by USABC and DOE to select the final remaining process assumptions.

Conclusions and Future Directions

Moving forward, we will be implementing the finalized simulation assumptions and parameters based on USABC and DOE feedback of our design space exploration. Once this is done, we will complete our analysis and define a new set of USABC BEV battery technology targets. The results and process will be described in detail in a journal article targeted for publication in 2013.

III.C.2.4 Low Energy HEV Requirements Analysis (NREL)

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Collaborators:
Ford Motor Company
JSR Micro
USABC

Start Date: April 2007
Projected End Date: December 2013

Objectives

- Support development of a cost-effective hybrid electric vehicle (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 using a lower-energy ESS (LEESS) would lead to larger aggregate petroleum savings.
- Evaluate LEESS operation by engaging with industry partners to design a “full” or power-assist HEV (PA-HEV) test platform for in-vehicle LEESS demonstration.

Technical Barriers

Market penetration of the power-assist HEVs has been limited due to the cost of high power batteries. It is anticipated that a power-assist HEV with LEESS can be of lower cost. However, 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 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 which has not been achieved due to requirement of 300 Wh available energy)

Accomplishments

- Secured a Ford Fusion HEV and designed modifications to create a LEESS conversion/test platform.
- Executed a Cooperative Research and Development Agreement (CRADA) with Ford to support the conversion, and a Non-Disclosure Agreement and Bailment Agreement with JSR Micro to obtain the initial lithium-ion capacitor (LIC) modules to test (at JSR Micro’s expense).
- Developed detailed understanding of the production battery system, and approach to use components from a salvaged battery along with dSpace equipment to implement the conversion.

Introduction

Automakers have been mass producing HEVs for well over a decade, and the technology has proven to be very effective at reducing per-vehicle fuel use. However, the incremental cost of HEVs such as the Toyota Prius or Ford Fusion Hybrid remains several thousand dollars higher than the cost of comparable conventional vehicles, which has limited HEV market penetration. The battery energy storage device is typically the component with the greatest contribution toward this cost increment, so significant cost

reductions and/or performance improvements to the energy storage system (ESS) can correspondingly improve the vehicle-level cost vs. benefit relationship. Such an improvement would, in turn, lead to larger HEV market penetration and greater aggregate fuel savings.

In recognition of these potential benefits, the United States Advanced Battery Consortium (USABC) asked NREL to collaborate with its Workgroup and analyze the trade-offs between vehicle fuel economy and reducing the decade-old minimum energy requirement for power-assist HEVs. NREL's analysis showed that significant fuel savings could still be delivered from an ESS with much lower energy storage than the previous targets, which prompted USABC to issue the new set of LEESS targets and issue a request for proposals to support their development. In order to validate the fuel savings and performance of an HEV using such a LEESS device, this jointly-funded activity has designed a test platform in which alternate energy storage devices can be installed and evaluated in an operating vehicle.

Approach

In fiscal years 2009–2010 (FY09–10) General Motors (GM) supported NREL through a funds-in Cooperative Research and Development Agreement (CRADA) to convert a Saturn Vue belt alternator starter mild HEV to operate on ultracapacitor modules instead of the production 42 V nickel-metal hydride (NiMH) batteries. That effort demonstrated that the mild HEV was able to achieve just as high fuel economy using the ultracapacitors as using the production batteries. For this effort, NREL sought to establish a similar automaker collaboration in order to facilitate a robust conversion of a “full” or power-assist HEV (with a larger motor and battery than a mild HEV) to operate on alternative LEESS devices.

NREL also engaged with device developers to confirm their ability and interest to provide LEESS modules for evaluation in the converted vehicle. The automaker and device developer interactions began in FY11, and came to fruition during FY12 in the form of several contractual agreements.

Results

The first agreement to be completed was a CRADA with Ford, which was executed in April, 2012. NREL and Ford agreed upon the model year 2012 Fusion Hybrid as a good platform for the project, and the acquired research vehicle is shown in the photo, below.



Ford Fusion Hybrid test platform at NREL; Photo credit: Jeff Gonder, NREL

Designing the conversion required first understanding the construction of the production High Voltage Traction Battery (HVTB) and its integration with the rest of the vehicle. Important components of the HVTB include the high-voltage Bussed Electrical Center (BEC), the Battery Pack Sensor Module (BPSM) and the Battery Energy Control Module (BECM). The BEC acts as an interface between the high-voltage output of the HVTB and the vehicle's electric motor, air conditioning compressor, and DC/DC converter. The BPSM measures the voltage and temperature of the NiMH cells and communicates with the BECM, which manages the charging/discharging of the battery and also communicates with the other vehicle control modules over the High Speed Controller Area Network (HS-CAN) bus. Figure III.C.2.4-1 shows a schematic of the HVTB including these components, and a photo of the HVTB in the vehicle, which mounts between the rear seat and the trunk area.

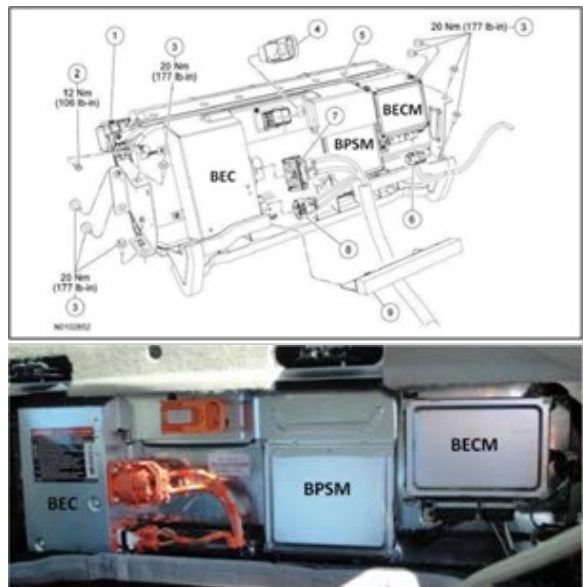


Figure III.C.2.4-1: Schematic and photo of Fusion hybrid's high-voltage traction battery (HVTB); Photo credit: Ahmad Pesaran, NREL

NREL elected to implement the conversion with the production HVTB still installed and the option of operating the vehicle either with the original battery or with the alternative LEESS under test. This arrangement helps retain driveability even if something is not working properly with the replacement system, and allows direct A-to-B comparisons with the vehicle alternately operated using each ESS. In order to implement this configuration, NREL acquired a second HVTB and disconnected the BEC, BPSM, BECM, cell sense leads, and various wiring harnesses so that they could be used with the alternative LEESS under test.

Figure III.C.2.4-2 shows a picture of these disconnected components, and Figure III.C.2.4-3 shows a schematic of their connections within the replacement system and to the vehicle. The dSpace component represented in the schematic is a dSpace MicroAutoBox (MABx), which is used to intercept certain CAN signals pertaining to the BECM's calculations for the production NiMH battery (state of charge, power capability, etc.) and to replace them with corresponding calculations for the alternate LEESS under test. The MABx will also record data during the testing.



Figure III.C.2.4-2: Replacement interface components for use with the alternate LEESS; Photo credit: Ahmad Pesaran, NREL

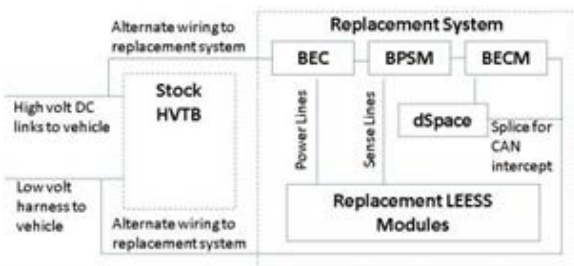


Figure III.C.2.4-3: Schematic of connections between replacement components and the vehicle

Additional project results obtained during FY12 include execution of an agreement with JSR Micro, Inc. to provide (at their expense) lithium-ion capacitor (LIC) modules as the first LEESS device to evaluate in the vehicle, along with proprietary information about the modules to support their integration and testing. The LICs are asymmetric electrochemical energy storage devices possessing one electrode with battery-type

characteristics (lithiated graphite) and one with ultracapacitor-type characteristics (carbon).

The photo below is a picture of the JSR Micro LIC modules that arrived at NREL at the end of FY12. These modules will initially be cycled in a laboratory environmental chamber to verify their performance and to obtain calibration data for the state estimator model in the MABx. By providing this model continuous current and voltage measurements from the LIC pack, it can keep track of variables such as the instantaneous state of charge and power capability of the pack, which need to be reported to the overall vehicle controller over the HS-CAN.



JSR Micro LIC modules; Photo credit: Ahmad Pesaran, NREL

Conclusions and Future Directions

Alternate lower-energy energy storage systems (LEESS) for HEVs such as the lithium-ion capacitor (LIC) technology has the potential for improved life, superior cold temperature performance, and reduced cost relative to traditional battery storage systems. If such LEESS devices can also be shown to maintain high HEV fuel savings, then future HEVs designed with these devices could have an increased value proposition relative to conventional vehicles, thus resulting in greater HEV market penetration and aggregate fuel savings. The vehicle test platform developed through this project will help to validate the in-vehicle performance capability of alternate LEESS devices and to identify unforeseen issues.

This report describes the collaboration agreements established and the test vehicle design completed in FY12. During the continuation of this project in FY13, NREL will evaluate the test vehicle's operation using the LEESS devices from JSR Micro and other developers. Nesscap Energy, Inc. intends to provide the second system to test and has begun the process to execute a CRADA with NREL for this purpose. The Nesscap system will consist of ultracapacitor modules that are believed to satisfy the design requirements of a replacement for the Fusion Hybrid battery. The test vehicle will thus provide a reusable platform for evaluating alternate HEV ESS options, including those under development by the USABC LEESS contract awardees (such as Maxwell), when they become available.

Testing on the various LEESS options is expected to be completed in FY13 or perhaps FY14, pending device availability. Other possible future work on this topic could include evaluating the potential offered by LEESS devices with more extensive vehicle modification, such as by increasing the motor size to leverage a higher-power capability ESS.

FY12 Publications/Presentations

1. Gonder, J., Wang, L., and Pesaran, A., “Evaluating a Hybrid Electric Vehicle (HEV) Lower-Energy Energy Storage System.” Presentation to DOE, October 2011, Washington, DC.
2. Gonder, J., Wang, L., and Pesaran, A., “Evaluating a Hybrid Electric Vehicle (HEV) Lower-Energy Energy Storage System.” Presentation to the U.S. DRIVE Vehicle Systems Analysis Technical Team (VSATT) March 2012, Southfield, MI.
3. Gonder, J., Ireland, J., and Pesaran, A., “Development and Operation of a Test Platform to Evaluate Lower-Energy Energy Storage Alternatives for Full-Hybrid Vehicles.” Submitted to the SAE Hybrid and Electric Vehicles Technology Symposium, February 2013, Anaheim, CA.

III.C.2.2 Battery Life Trade-Off Studies (NREL)

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Start Date: FY08

End Date: FY15

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 electric-drive-vehicle batteries.

Technical Barriers

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

Technical Targets

- 10- to 15-year calendar life for batteries used in electric drive vehicles such as HEVs, PHEVs, and EVs.
- Develop strategies to enable 10-15 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

- Quantified the impact of variable thermal scenarios on battery lifetime, together with simplified daily/seasonal temperature profiles suitable for laboratory test environment
- Quantified opportunities for life-extending control strategies using previously developed life model for graphite/nickel-cobalt-aluminum (NCA) chemistry
- Developed new life model of graphite/iron-phosphate (FeP) chemistry, incorporating into the model new effects of low temperature degradation, high C-rate charge and discharge, and rapid fade regime at end-of-life

Introduction

Electric-drive vehicles (EDVs) offer 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 what 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. It is important to understand degradation impacts for a range of possible duty-cycles to identify worst cases and design appropriate applications, systems and controls that best utilize battery life.

Approach

Significant stressors to a lithium-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 lithium-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. The computationally compact model is well suited for systems engineering, techno-economic analysis and control strategy development.

In FY12, NREL applied the NCA life model in thermal and control analyses and also implemented the model NREL Battery Ownership Model and 2nd Use studies, described elsewhere in this Annual Report.

In FY12, NREL also developed a new life model for the FeP Li-ion chemistry. In support of the FeP life model development, NREL compiled data from the open literature and from partner laboratories for the A123 26650 M1 cell with graphite anode and iron-phosphate cathode. The composite dataset leveraged an estimated \$2M of aging tests conducted by others. The dataset includes more than 50 different test conditions with test temperatures ranging from -20°C to 60°C, C-rates ranging from 0.5C to 9C and depths-of-discharge (DOD) ranging from storage (0%) to 100%.

Results

Thermal and Control Tradeoff Analyses

To better understand the impact of variable temperature on battery lifetime, NREL conducted an analysis of simplified thermal scenarios appropriate to represent variable environmental temperature of different geographic climates. Objectives are to reduce (1) the test burden for automotive battery life testing and (2) the computational burden for large simulation-based analyses of climates and system designs.

Shown in Figure III.C.2.2-1, it is insufficient to only consider variable ambient temperature when simulating battery life. Solar radiation must also be taken into account. Solar loading on the vehicle can raise the average lifetime temperature of the battery by several degrees and, for lifetime analysis, can be treated as a steady-state effect. With solar loading accounted for, the daily and seasonal peaks in ambient temperature have small effect on battery life under storage conditions. When not considering drive-cycle impacts, seasonal temperature variation can be simplified to use one average battery temperature for each season (dotted green line in Figure 1, corresponding to case “D” in Figure 2). When considering drive-cycle heat generation/thermal management interactions, hourly temperature variation must be considered. For large design-space searches where it is not possible to consider all 8760 hours of the year, a reasonable approach is to use one simplified 24-hour profile to represent each season (case “F” in Figure III.C.2.2-2).

Also in FY12, NREL conducted an analysis of opportunities for vehicle battery health management [2] using the NCA life model. Findings included:

- In hot climates, aggressive thermal management systems with the capability to cool below the ambient temperature can extend calendar life by 25-45%. It is also beneficial to maintain cool temperatures while the vehicle is parked (either passively or actively).
- For the NCA chemistry, high temperature fade is most rapid when the battery is also at high SOC. Due to these SOC/T calendar-life interactions, it is advantageous to vary maximum end-of-charge (EOC) SOC with seasonal/geographic temperatures:
 - Using a low EOC SOC in summer/hot climates provides extended calendar life with minimal impact on electric-range due to good performance inherent for warm temperature operation
 - Using a high EOC SOC in winter/cold climates improves cold temperature electric-range with minimal impact on calendar life
- Small PHEV10 batteries will be cycle-life-limited more often than large PHEV40 (or BEV) batteries. This is because 86% of US drivers drive more than 10 miles/day while only 34% drive more than 40 miles/day. Frequent charging behavior represents the worst-case cycle-life condition faced by PHEV10 batteries, however frequent charging also provides the greatest petroleum displacement benefit.
- It may be possible to adaptively reduce useable energy and power limits (DOD and C-rate) to extend battery lifetime, however this limits the utility of the battery with uncertain regulatory implications.
- Intelligent charge control (variable C-rate, scheduling EOC SOC vs. temperature; just-in-time or time-delayed charging schemes) can modestly extend battery lifetime with no such regulatory concerns.
- Improving onboard prognostic life prediction and educating the driver on life/driving/charging behavior tradeoffs is an important path for maximizing battery life cycle value. Prognostics might reduce the cost of ownership by enabling drivers to make their own tradeoff decisions and also improving battery/vehicle residual value.

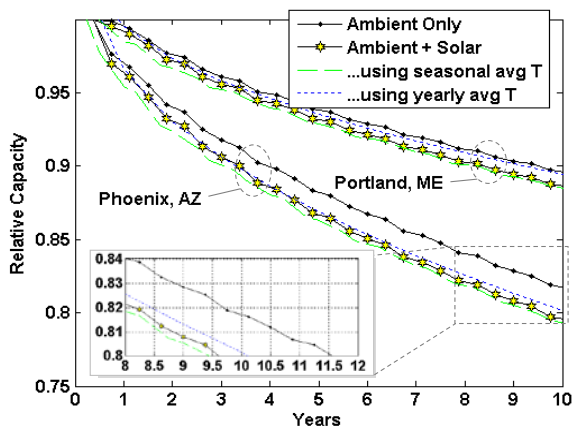


Figure III.C.2.2-1: Capacity fade under storage at 90% SOC for two geographic locations with and without impact of solar loading on the parked vehicle. Blue and green curves consider various simplifications of the full hour-by-hour temperature data and should be compared to the ambient + solar case.

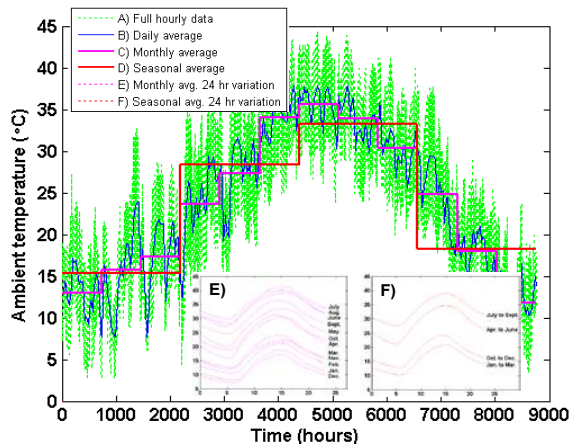


Figure III.C.2.2-2: Typical meteorological year temperature data for Phoenix, AZ. For a resource-constrained test environment, the seasonal average 24 hour temperature variation, case "F", best approximates the impact of daily and seasonal peak temperatures on vehicle battery life.

Life Modeling of Iron Phosphate Chemistry

To promote deeper understanding of battery life dependence on thermal environment and cycling conditions including fast charge, NREL compiled aging data from partner laboratories and the open literature for the A123 26650 M1 cell. The extensive dataset includes more than 50 different test conditions with test temperatures ranging from -20°C to 60°C , C-rates ranging from 0.5C to 9C and depths-of-discharge (DOD) ranging from storage (0%) to 100%.

To capture the full range of capacity fade conditions evident in the FeP chemistry data, NREL's previous life model regression framework was extended to

1. Include separate mechanisms describing capacity loss during both high and low temperature

cycling. Possible explanations for these separate mechanisms are binder failure at high temperature and diffusion-induced intercalation stress at low temperature.

2. Capture the coupled impact of DOD and C-rate (or pulse time), based on test data with C-rates ranging from 0.5C to 9C and 10% to 100% DOD.
3. Capture the nonlinear, mildly accelerating capacity loss behavior observed as a mildly degraded cell is cycled over constant duty-cycle.
4. Capture the nonlinear, rapidly accelerating capacity loss behavior observed as a severely degraded cell is continually cycled beyond $\sim 35\%$ capacity loss.

Conclusions and Future Directions

In FY12, a new life-predictive model for the Li-ion FeP chemistry was developed. NREL's model framework was extended to capture the impact of high C-rate cycling and low temperature cycling. The FeP life model will be applied in future fast charge analysis studies to assess suitability of fast charge for increasing the utility of BEVs. The life model was also extended to capture the rapid fade regime when electrode stoichiometry windows become out-of-balance near end-of-life. The FeP life model is being incorporated into NREL second-use studies to quantify the impact of second-use scenarios on life-cycle value. Upcoming publications will more fully detail the FeP life model as well as the statistical regression methods used to fit the model. That regression toolset is flexible and extensible so that physics based degradation models may be incorporated in the future.

Tradeoff analyses conducted in FY12 using the NCA life model predict that peak daily temperatures have less impact on battery life than the overall average temperature seen by the battery during its lifetime. So while one objective for thermal management systems is to suppress peak temperatures during driving and charging, for long battery life it is perhaps more important that thermal management systems lower the overall average lifetime temperature seen by the battery. In climates with high ambient temperature, this requires that a refrigeration system or chilled fluid cooling loop be used. Another important aspect of thermal management is to maintain temperature uniformity across the pack. Future work will couple the life model within a cell-to-cell thermal / electrical network model to capture differential aging of individual cells within a multi-cell pack.

FY2012 Publications/Presentations

1. K. Smith, M. Earleywine, E. Wood, J. Neubauer, A. Pesaran, "Comparison of Plug-In Hybrid Electric Vehicle Battery Life Across Geographies and Drive Cycles," SAE World Congress, Detroit, April 24-26, 2012.
2. K. Smith, M. Earleywine, E. Wood, A. Pesaran, "Battery wear from disparate duty-cycles: Opportunities for electric-drive vehicle battery health management," American Control Conference, Montreal, Canada, June 27-29, 2012.

III.D.6 Battery Thermal Analysis and Characterization Activities (NREL)

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Collaborators:
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GM, Ford, Chrysler, USABC

A123 Systems, Johnson Controls Inc., LG Chem Power, Inc. (LGCPI), Quallion, ActaCell, SK Innovation, Cobasys

Start Date: October 1, 2009
Projected End Date: September 2013

Objectives

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

Technical Barriers

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

Technical Targets

- Battery operating temperature from -30°C to 52°C.
- Develop a high-power battery technology exceeding 300,000 cycles.
- 15-year calendar life at 30°C.

Accomplishments

- Obtained cells from various USABC battery partners including A123 Systems, Actacell, Cobasys, Johnson Controls Incorporated (JCI), Quallion, LGCPI, K2 Energy Systems, JSR Micro, and SK Innovation.
- Obtained infrared thermal images of cells provided by USABC battery developers and identified any areas of thermal concern.
- Used NREL’s unique calorimeters to measure heat generation from cells and modules under various charge/discharge profiles.
- Obtained thermal and electrical performance data of cells under HEV, PHEV, and EV power profiles.
- Evaluated thermal performance of two PHEV packs (air cooled JCI and liquid cooled A123Systems).
- Presented results of cell thermal characterization and pack thermal evaluation at USABC/battery developers review meetings.

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 and evaluate thermal performance of battery packs (air or liquid cooled). We also use our electro-thermal finite element models to analyze the thermal performance of battery systems in order to aid battery developers with improved thermal designs.

Approach

Using NREL's unique calorimeters and infrared thermal imaging equipment, we obtain thermal characteristics (heat generation, heat capacity, and thermal images) of batteries and ultracapacitors developed by USABC battery developers and other industry partners. NREL supports the Energy Storage Technical Team by participating in various work groups such as the Actacell, Cobasys, JCI, LG CPI, Quallion, CPI, A123Systems, K2, and SK Innovations Work Groups. The following picture shows some of the equipment in the NREL Energy Storage Laboratory in the Thermal Test Facility.



NREL's Energy Storage Laboratory; Photo credit: Ahmad Pesaran, NREL

Results

Calorimeter Testing

NREL's calorimeters provide critical heat generation and efficiency data for the battery under test. Figure III.D.6-1 shows the efficiency of cells tested in FY12 at NREL. The lithium-ion cells were fully discharged from 100% SOC to 0% SOC under a C/2, C/1, and 2C currents. It should be noted that the cells in the figure are for both power and energy cells and have been developed for the HEV, PHEV, EV, or the Low-Energy Energy Storage System (LEESS) programs with USABC. The figure shows that most of the lithium-ion cells, A-G, are very efficient over this cycling regime – typically greater than 94%. Looking more closely at the cells A-G shows most of the cells decline in efficiency at a similar rate except for Cell G. Cell G's efficiency decreases at a slower rate than the other cells in this group (A-G). Finally, Cell H shows a fairly low efficiency as compared to many of the other cells tested in FY12. NREL's calorimeter can identify these outliers but can also help determine if the inefficiency is due to chemistry or cell design.

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 state of charge (SOC). The limitation of this technique is that you can't determine the discharge and charge efficiency 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.

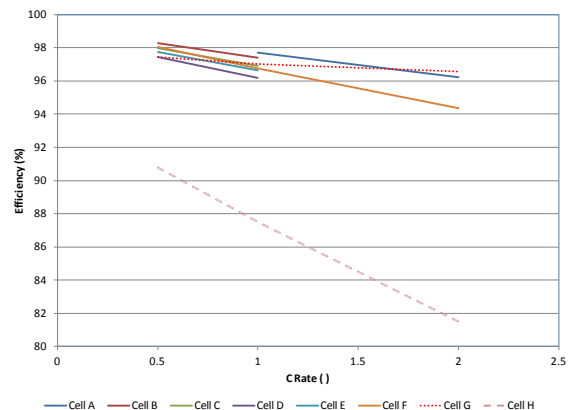


Figure III.D.6-1: Efficiency of cells tested at 30°C in NREL's calorimeter during FY12

Figure III.D.6-2 shows the efficiency of cells A, F, and G under a constant current discharge at 30°C and 0°C. The dotted lines denote the cells tested at 30°C and the solid lines denote the cells tested at 0°C. Figure III.D.6.2 shows that the efficiency of cell A and Cell F changes approximately 3% to 4% as the temperature is decreased from 30°C to 0°C. In contrast, the efficiency of Cell F decreases approximately 8% over the same temperature range. NREL's calorimeter can help understand how a battery's impedance (efficiency) changes as a function of temperature. Furthermore, it can help to determine how low temperature additives affect the performance of the cell.

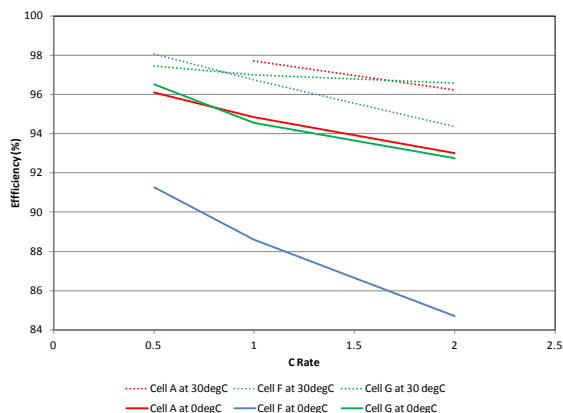


Figure III.D.6-2: Efficiency of selected cells tested in FY12 at 0°C and 30°C in NREL's calorimeters

Figure III.D.6-3 shows the normalized heat generation of cells as a function of C-rate. The heat generation data is critical to the development of thermal management systems for batteries. The data can be used to identify the type of cooling mechanism (air, liquid, and/or active) needed for the battery application — HEV, PHEV, EV, or LEES. The data are used to keep the batteries temperature at an appropriate level which, in turn, affects the battery's cycle life performance and safety.

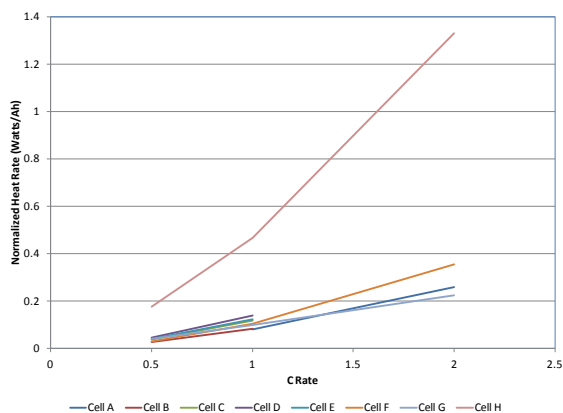


Figure III.D.6-3: Normalized heat rate of cells tested at 30°C in NREL's calorimeter during FY12

NREL's calorimeters are designed to be accurate enough to measure the electrochemical response from batteries under test. As car manufacturers progress from HEVs to PHEVs and EVs, the design of the battery pack will also change. For instance, an HEV battery pack is cycled within a very narrow band—typically within a window encompassing 10% of the overall energy window of the pack. In contrast, a PHEV and EV battery is typically cycled over a much wider range — typically, 80-90% of the battery's capacity. Figure III.D.6-4 shows the normalized heat rates of three different cells tested during FY12. 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 endothermic and exothermic heat generation over the cycling range. The figure also shows how the battery chemistry affects the entropic signature of the battery. Cell 1 is endothermic at the beginning of the discharge as compared to cells 2 and 3 which are exothermic. The figure also shows where a cell is most inefficient—typically, below 85% DOD for this example. The data from this graph helps manufacturers and OEMs to understand where to cycle their battery and which areas to avoid thereby increasing the cycle life of the battery. Observing the phase transition requires an extremely accurate calorimeter with a very stable baseline that only NREL's calorimeters can provide for these large format cells.

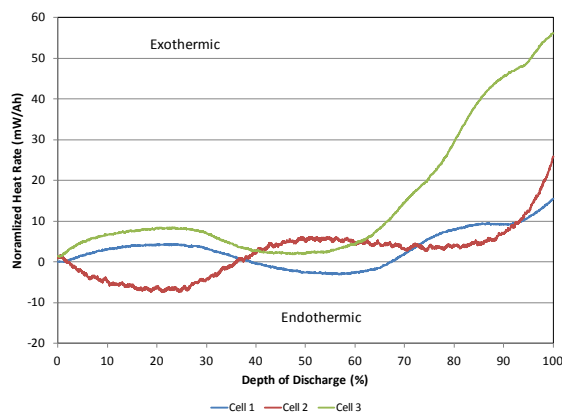


Figure III.D.6-4: Normalized heat rate at 30°C for cells discharged from 100% to 0% SOC in FY12

Infrared Imaging

NREL performs infrared (IR) imaging of battery manufacturer's cells to determine areas of thermal concern. NREL combines the IR imaging equipment with a battery cyler to place the cells under various drive cycles, such as a US06 charge depleting 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 III.D.6-5 shows the thermal images of three cells connected in series at the end of constant current discharge. As can be seen from the image, one terminal of the cell preferentially heats more as compared to the other cell terminal.

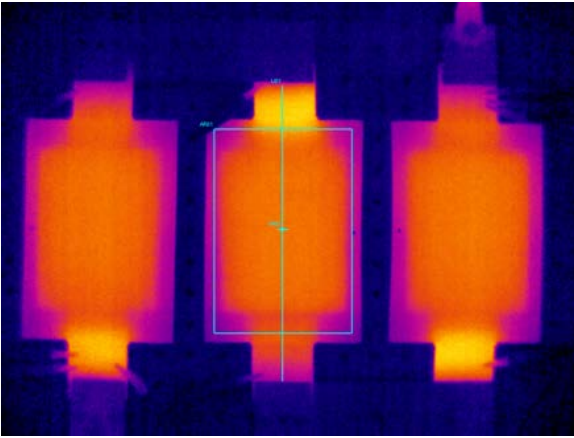


Figure III.D.6-5: Infrared image of cells under constant current discharge

Pack Thermal Studies

In FY12, NREL evaluated air, liquid, and vapor compression cooled packs for USABC battery developers. 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% to 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 and can cause imbalances with the pack and warranty issues could be a result.

Figure III.D.6- 6 shows the temperature spread of various cells in a pack for a charge depleting and then a charge sustaining US06 drive cycle. The lower part of the figure shows the temperatures of various cells in the pack – notice the dip in temperature for thermocouples 15 and 20. The slight temperature dips are due to the interconnects in the pack and therefore affect the cell-to-cell temperature difference within the pack.

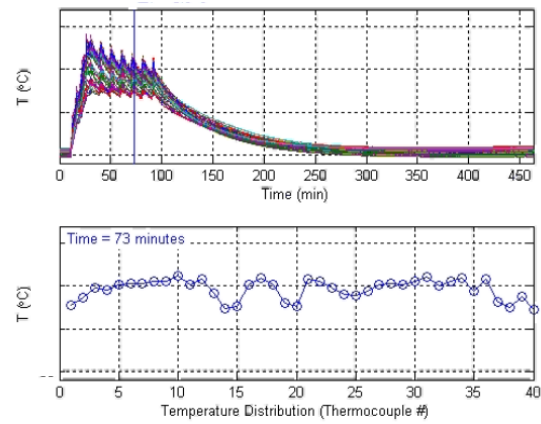


Figure III.D.6-6: Thermal management system performance during US06 cycling

Conclusions and Future Directions

NREL has thermally tested cells, modules, and/or packs from A123Systems, Actacell, LGCPI, Johnson Controls, JSR Micro, Quallion, K2, and SK Innovation. We’ve provided critical data to the battery manufacturers and OEMs that can be used to improve the design of the cell, module, pack and their respective thermal management systems. The data included heat generation of cells under typical profiles for HEV, PHEV, and EV applications. We found that the majority of the cells tested had a thermal efficiency greater than 94% when cycled under a 2C constant current discharge. The heat generation of these cells was between 0.1 to 0.4 W/Ah for currents between a C/2 and 2C rate at 30°C . During the thermal imaging of the cells, we identified areas of thermal concern and helped the battery manufacturers with the electrical design of their cells. Finally, we evaluated multiple packs during FY12 and determined that all aspects of the design need to be evaluated for the best thermal performance of the pack and the longest life.

In FY13, NREL will continue to thermally characterize cells, modules, packs for USABC, DOE, and USDRIVE.

FY 2012 Publications/Presentations

1. Thermal data was shared with the Energy Storage Tech Team and each of the individual battery manufacturer’s work groups.
2. March 2012 DOE Milestone Report, “Thermal Analysis and Characterization of Advanced Lithium-Ion Batteries.”
3. September 2012 DOE Milestone Report, “Thermal Analysis and Characterization of Advanced Lithium-Ion Batteries and Packs.”

III.D.8 Development of an On-Demand Internal Short Circuit (NREL)

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Collaborators:
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E. Darcy, NASA

Dow Kokam

E-One Moli

Start Date: October 2009
Projected End Date: September 2013

Objectives

- The objective of this effort is to establish an improved internal short circuit (ISC) cell-level test method that replicates a catastrophic field failure due to latent flaws that are introduced during manufacturing
- Is capable of triggering all 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 lithium-ion batteries in advanced vehicles. The existing electrode/electrolyte in lithium-ion cells is prone to catastrophic thermal runaway under some rare internal short circuit conditions. To make the occupants of advanced vehicles safe from an internal short, the cost and size of lithium-ion battery systems could increase.

Technical Targets

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

Accomplishments

- NREL continues to make progress towards the development of an on-demand internal short circuit for lithium-ion batteries.
- Our internal short circuit emulator does not affect the performance of the battery under test and can be activated without puncturing or deforming the battery.
- The NREL ISC emulator was improved and successfully tested in cylindrical 18650 cells and a large format pouch cell.

Introduction

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

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

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

Due to the dormant nature of this flaw, battery manufacturers have found it difficult to precisely identify and study. NREL's device introduces a latent flaw into a battery that may be activated to produce an internal short circuit. NREL uses the internal short-

circuit device to better understand the failure modes of Li-ion cells and to validate NREL's abuse models.

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

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

Approach

NREL conceptualized and initiated laboratory testing of an internal short that has an insulating wax layer which 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 are shown in Figure III.D.8-1.

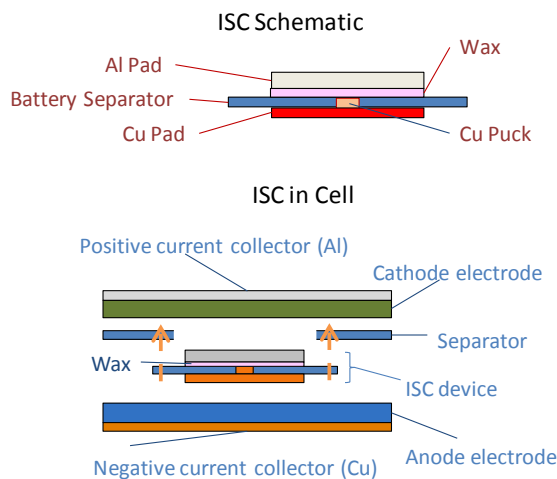


Figure III.D.8-1: ISC schematic (top picture) and ISC placed in a cell (bottom picture) – not to scale

A unique feature of NREL's internal short device is that it has the ability to simulate all four types of shorts within a battery: 1) cathode active material to anode active material, 2) cathode active material to anode current collector, 3) cathode current collector to anode active material, and 4) cathode current collector material to anode current collector. Furthermore, the

resistance of the short can be tuned to simulate a hard (more energetic) or soft (less energetic) short. Once the short is activated, the positive and negative components of the battery are internally connected within the cell and internal short circuit begins.

Results

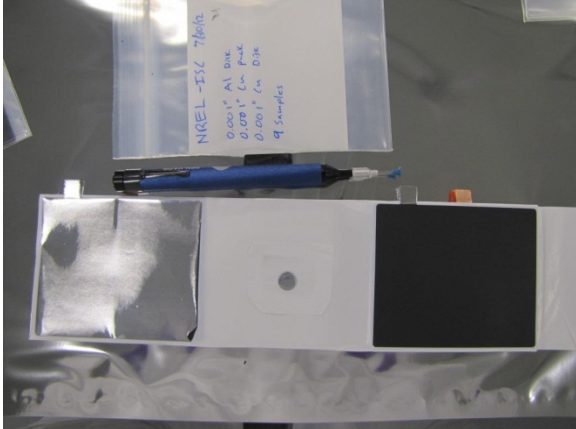
In FY11, NREL incorporated the wax ISC in pouch cells from Dow Kokam (DK). NREL found that the wax ISC was flexible enough to survive bend radiuses less than 0.050 inches without damage to the ISC or to its initial inactivated impedance. Furthermore, the implanted ISC did not affect the performance of the DK cell– the capacity and discharge/charge voltage curves of the cells with the ISC matched the control DK cells. During testing of the wax ISC in the DK cells, it was determined that:

- The amount of wax needs to be controlled/limited
- In order 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 thickness needs 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 in FY11.

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

During the second half of FY12, we incorporated all four types of shorts in the E-One Moli (cylindrical) 18650 2.4 Ah cell and in an 8-Ah Dow Kokam cell (prismatic stacked pouch). The following photos show the device implanted in both of these cells.



ISC in E-One Moli 18650 cell (top picture) and ISC placed in a Dow Kokam 8-Ah cell (bottom picture). Note that the actual size of the short (Cu puck) is 0.125" in diameter; Photo credits: Dirk Long, NREL

Figure III.D.8-2 shows the voltage response to three of the four types of activated ISCs within the E-One Moli cell at 0% SOC. NREL's previous modeling indicated that different types of shorts should exhibit different voltage and temperature responses within the cell. In particular, the cathode and anode materials for most lithium cells have high impedances as compared to the aluminum or copper electrode/collector material. Thus, when the active material is part of the ISC circuit, then the voltage should decay slowly or act as a "soft" short. When there is an aluminum collector to copper collector internal short, then the voltage should precipitously drop or act as a "hard" short. Figure III.D.8.3 confirms the NREL modeling data showing that the collector to collector short is the most severe. The thermal response during this round of testing was minimal since the cells were at 0% SOC. The largest thermal response, a temperature rise of 12°C upon activation, was measured with the collector to collector internal short circuit.

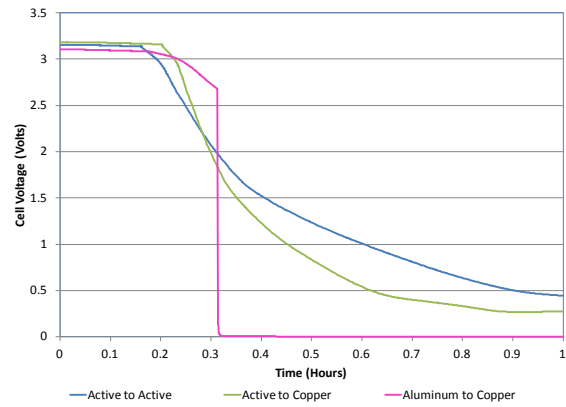


Figure III.D.8-2: Voltage response to various ISC activations in E-One Moli 18650 cell at 0% SOC

The second round of testing in the E-One Moli 18650 cell was at 100% SOC. Figure 4 shows the voltage and temperature response to this activation. The melting point of the wax for this ISC was chosen to be 57°C – the melting point was engineered by choosing a mixture of waxes for their hardness to avoid an accidental ISC activation and ductility so that the ISC could be wound in an 18650 cell. As the cell temperature is slowly increased, the wax melts and the metal components of the ISC come in contact with each other creating an electrical circuit between the aluminum and copper current collectors. As can be seen from the following graph, the ISC activates at around 0.197 hours and the cell temperature increases to 117°C. Furthermore, the voltage of the cell drops to zero volts and then recovers to around 2.5 volts after activation. This result was unexpected for two reasons: (1) performing a basic energy analysis of the cell yields a cell temperature in excess of 300°C if all the energy is dissipated and (2) the cell voltage should not recover but remain at zero volts. A destructive physical analysis (DPA) of the cell yielded the answer to these two anomalies.

The DPA revealed that the shut-down separator in the cell activated and prevented all the energy in the cell from being dissipated. The photo shows the copper charged electrode after the DPA – the slight bright coppery patina on the anode indicates unused lithium. The DPA also revealed that the current interrupt device activated due to pressure build up in the cell. The CID activation prevented the accurate measurement of the cell voltage– thus, the apparent recovery in cell voltage.

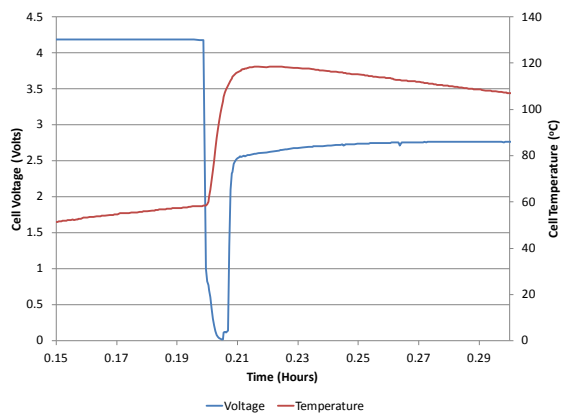


Figure III.D.8-3: Voltage response to a collector to collector ISC activation in the E-One Moli 18650 cell at 100% SOC



E-One Moli 18650 cathode and anode assemblies unrolled after ISC activation; Photo credit: Dirk Long, NREL

Test results from the ISC activation in the Dow Kokam 8 Ah cells are preliminary but show that a slight pressure (< 2 psi) needs to be applied to the ISC/cell to encourage the wax to flow from between the various metal components in the ISC. The pressure is probably needed in the pouch cell since the pouch material is flexible and will allow for the wax expansion/contraction. It is hypothesized that the pressure is not needed in the cylindrical cells due to the plastic (hard) casing. Thus, the melted wax is forced away from the ISC due to the relatively constrained housing and the expansion of the wax after melting.

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 phase change material (wax) melting temperature
- Can handle currents in excess of 200 amps– 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 than connecting the aluminum and copper current collectors. The end goal is not to send the cell into thermal runaway when activating the ISC but to accurately simulate an emergent short.

The internal short device can be used to determine how changes to the battery affect the safety of the battery – 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 FY13, NREL will optimize the design for both pouch and cylindrical cell designs. NREL observed a large percentage of cylindrical cell formation failures during initial testing and will need to address how the metal parts in the cell are fabricated to prevent edge burrs.

FY 2012 Publications/Presentations

1. 2012 NASA Aerospace Battery Workshop, Alabama.
2. 83rd 85th Li Battery Technical/Safety Group Meeting, San Diego, CA, September 2012.
3. 2012 DOE Milestone Report, “Evaluate NREL Improved Version of Internal Short-Circuit Instigator in Large Cells.” NREL, September 2012.
4. Internal Short Circuit Device Helps Improve Lithium-Ion Battery Design (Fact Sheet). Research & Development Highlights, National Renewable Energy Laboratory (2012). NREL Report No. FS-5400-52865.

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

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GM, ANSYS, ESim

EC Power, Ford, JCI, PSU

CD-adapco, Battery Design, JCI, A123Systems

Start Date: April 2010

Projected End Date: September 2015

Objectives

- Coordinate the activities of the DOE/NREL Computer Aided Engineering of automotive Batteries (CAEBAT).
- 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 electric drive vehicles.
- Collaborate with other National Labs to support 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.

- Disseminate the results to public and promote collaboration on modeling and software tools among the automotive battery community.

Technical Barriers

- Cost, life (calendar and cycle), high performance at all temperatures, and safety are barriers for widespread adoption of lithium-ion batteries in electric drive vehicles (EDV).
- Large investment and long lead time in cell and pack research, design, prototyping, and testing cycle—and then repeating the design-build-test-break cycle many times with changes—increase production costs.
- Lack of advanced computer-aided engineering tools to quickly design and simulate battery packs for electric drive vehicles impede optimizing cost-effective solutions.

Technical Targets

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

Accomplishments

In mid FY11, after a complete procurement process, NREL entered into subcontract agreements with three industry-led teams to develop CAEBAT tools with 50-50 cost sharing.

The three subcontract teams which started the technical work in July 2011 are:

CD-adapco (teamed with Battery Design LLC, Johnson Controls-Saft and A123 Systems); technical monitor: Kandler Smith

EC Power (teamed with Pennsylvania State University, Johnson Controls Inc., and Ford Motor Company); NREL technical monitor: Shriram Santhanagopalan

General Motors (teamed with ANSYS and ESim); NREL technical monitor: Gi-Heon Kim

In FY12, NREL continued to monitor the technical performance of the three subcontract teams through monthly progress conference calls, quarterly review meetings, and annual reporting with DOE/HQ.

The three subcontractors are on track to deliver software tools to the industry by the end of their period of performance. (Specific progress for each subcontract is provided in Section III.E. of this report).

The following are major accomplishments from each team in FY12:

CD-adapco developed a model for spirally wound cell and released it in a software tool in Star-CCM+ platform for public evaluation; initial simulations results compared well to experimental data from A123Systems and JCI.

EC Power developed and released a user-friendly, electrochemical-thermal coupled software in ANSYS platform for large-format cell simulations for internal team evaluation and comparison with PSU, JCI and Ford data

GM has prototyped and implemented particle and electrode sub level models into the first cell level software tool in ANSYS platform and delivered it for team evaluation.

NREL had close collaborations with ORNL with evaluation of elements of the OAS such as Battery Input and Battery State. (Specific progress for ORNL work is provided in Section III.E.5 of this report)

NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT. (This activity is further discussed in Section III.E.6 of this report)

Introduction

In April 2010, DOE announced a new program activity called Computer-Aided Engineering of Electric Drive Vehicle Batteries (CAEBAT) to develop software tools for battery design, R&D, and manufacturing. The objective of CAEBAT is to incorporate existing and new models into battery design suites/tools with the goal of shortening design cycles and optimizing batteries (cells and packs) for improved performance, safety, long life, and low cost. The objective was to address the existing practices that battery and pack developers operate: tediously experiment 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 cost of the battery. There have been extensive modeling efforts going on in national laboratories, Universities, private companies and other institutions to capture the electrochemical performance, life, thermal profiles and cost of batteries. NREL has been developing an electrochemical-thermal model of lithium-ion cells with 3-dimensional geometries. However, these tools were not integrated into a 3-D computer aided engineering approach, the 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. The CAEBAT project is broken down into four elements, as shown in Figure III.E.1-1.

- Material and component level models (mostly developed under the BATT and ABR program elements of the DOE Energy Storage R&D),
- Cell level models,
- Pack level models, and
- Open architecture software for interfacing and linking all models particularly the ones from National Labs.

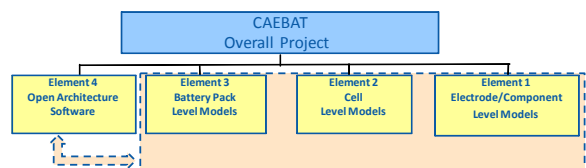


Figure III.E.1-1: Four elements of the Computer-Aided Engineering for Batteries (CAEBAT) activity.

The goal of the CAEBAT activity is to “develop suites of software tools that enable automobile manufactures, 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.” So 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 suit(s) for design of batteries.

Approach

To oversee the successful execution of the CAEBAT program, DOE has designated NREL as the Overall Project Coordinator. The *Cell Level Modeling* and *Pack Level Modeling* will be performed by industry, national laboratories, and academia coordinated through NREL. The *Open Architecture Software* element will be performed by the national laboratories to be coordinated by ORNL. The *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 ANL, LBNL, and other national labs to incorporate and interface with models developed under BATT and ABR.

To engage serious involvement of industry, NREL, with guidance with DOE, issued a Request for Proposals (RFP) in FY10 to seek proposals for development of the cell and pack battery design tools for a period of 3 years with 50%-50% cost sharing. CD-adapco, GM, and EC Power teams were awarded in middle of 2011. The three subcontract teams started the technical work in July 2011 and have made steady progress and on track with their proposed work schedule.

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

Results

Subcontracts with Industry

In FY12, NREL continued to monitor the technical performance of the three subcontract teams through monthly progress conference calls, quarterly review meetings, and annual reporting with DOE/HQ. Quarterly review meetings took place at the subcontractor sites, NREL, or near DOE/HQ.

Significant progress has been reported by each subcontractor according to the agreed upon timetable. More details about GM subcontract progress could be found in Section III.E.3 of this report. Progress on CD-adapco subcontract is described in Section III.E.4 of this report. Finally Section III.E.5 of this report provides details on the progress by EC Power. Summary of the major progress for each subcontractor is provided below.

CD-adapco

- A computational spiral cell model was created which contains considerable fidelity making the projects developments applicable to cell designers as well as module/pack designer

- The spiral cell representation operates with a number of numerical models to represent the electrochemistry
- Released the first version of developed spiral cell model as a software tool in Star-CCM+ to the public

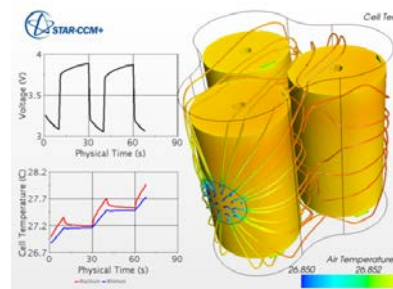


Figure III.E.1-2: Typical result from CD-adapco coupled flow, thermal and electrochemical model of pack with cylindrical cells

EC Power

- Initial development of materials database completed
- Developed user-friendly, electrochemical-thermal coupled software for automotive large-format cell and pack simulations in ANSYS
- Performed large-format cell safety simulations (e.g. internal short, partial and full nail penetration) and (simultaneous prediction of electrochemical and thermal performance)
- 3D spatio-temporal data being generated for large-format cell validation
- Industrial partners (Ford & Johnson Controls) using software internally

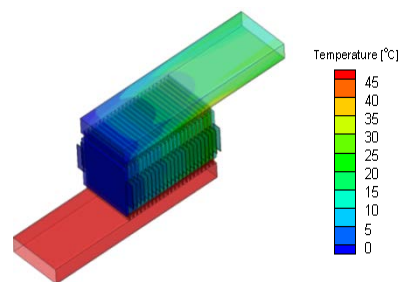


Figure III.E.1-3: Typical result from EC Power thermal and electrochemical model of pack with prismatic cells

GM

- Scale coupling between particle, electrode, and cell levels has been tested based on NREL's MSMD approach
- All three cell-level sub-models have been prototyped and implemented into the first cell level software tool in ANSYS and delivered it in August 2012
- Simplorer-FLUENT co-simulation feature has been prototyped

- Reduced Order Model (ROM) research has been conducted is on-going for pack level simulation; a few successful ROM concepts demonstrated the feasibility of this approach
- A test plan and procedure for collecting test data from production cells to validate the cell design tool has been completed
- CAE capability matrix has been defined for pack level applications in automotive industry

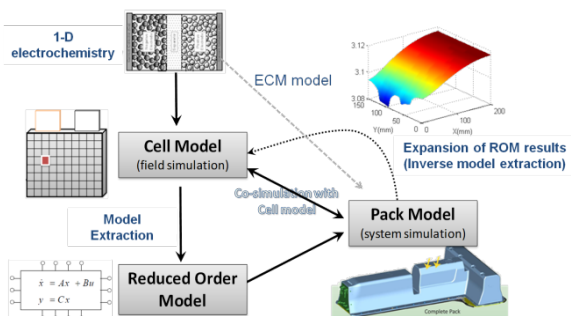


Figure III.E.1-4: Pack level simulation vision by GM/ANSYS/ESim team

Collaboration with ORNL on Open Architecture Software

NREL and ORNL held monthly meetings to discuss the best approach and strategy for OAS. This included collaboration on the Battery Input and Battery State. NREL provided its electrochemistry model to ORNL and demonstrated the ability of the OAS framework to seamlessly integrate different submodels. CAEBAT subcontractors were engaged with ORNL for understanding the standard battery input. Further details about ORNL progress could be found in Section III.E.2 of this report.

Development of Multi-Physics Battery Models at NREL

NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT. GM team is working with NREL to incorporate the MSMD lithium-ion battery modeling framework for their CAEBAT tools. (This activity is further discussed in Section III.E.6 of this report).

Conclusions and Future Directions

The three CAEBAT subcontract teams GM (with ANSYS and ESim), CD-adapco (with Battery Design, JCI, and A123 Systems) and EC Power (with Pennsylvania State University, JCI and Ford) continued their progress toward the objectives of their respective programs. Monthly technical meetings and quarterly program review meetings were held to monitor technical progress. Experimental data are being collected by each team to validate the models. First version of cell software tools by each company has been released for partner and NREL evaluations.

NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT. We also collaborated with ORNL on their development of the Open Architecture Software (OAS) to link the developed and existing models.

In FY13, we will continue to monitor the technical progress of each team by monthly and quarterly meeting to assure success. We anticipate that models to be further developed or internal evaluation by each subcontractor. We expect each subcontractor to continue collection validation data for the next generation of each CAEBAT tool. We will also continue collaborating with ORNL on development of the OAS and performing example problems. We plan to coordinate an operational meeting on the computer aided engineering of batteries with the battery community and the US Drive Electrochemical Energy Storage Team.

FY 2012 Publications/Presentations

1. A. A. Pesaran, G.-H. Kim, K.A. Smith, S. Santhanagopalan, "Annual Progress Report on CAEBAT Subcontracts," NREL Milestone Report, September 2012.
2. A.A. Pesaran, G.-H. Kim, K. Smith, S. Santhanagopalan, and K.-J. Lee, "Overview of Computer-Aided Engineering of Batteries and Introduction to Multi-Scale, Multi-Dimensional Modeling of Li-Ion Batteries," presented at Vehicle Technologies Program (VTP) Annual Merit Review (AMR), May 14-18, 2012, Washington, DC.
3. A.A. Pesaran, G-H. Kim, K. Smith, K.-J. Lee, S. Santhanagopalan, "Computer-Aided Engineering of Batteries for Designing Better Li-Ion Batteries," presented at Advanced Automotive Battery Conference, Battery Modeling Software and Applications Workshop, Orlando, FL; Feb. 6, 2012.

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

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Collaborators:
L. Collins, ANSYS Inc.
R.E. White, ESim LLC

Start Date: June 2011
Projected End Date: January 2015

- Various cell physics sub-models exist, but they have not been integrated in a single framework in commercial code
- Current engineering workstations do not have the computational power required to simulate pack-level thermal response coupled with electrochemistry; system-level analysis typically requires Reduced Order Modeling (ROM) be employed to simulate integrated pack-level physics; however, ROM approaches for battery packs are not well understood
- In the past, collaboration among software developers, automakers, and battery developers has been difficult because all parties want to guard intellectual property

Objectives

- Establish Computer-Aided Engineering for Automotive Batteries (CAEBAT)
- Develop battery cell/pack design tools and system level software tools to shorten the product development cycle for electric drive vehicles (EDVs) and to reduce the cost associated with the current hardware build and test design iterations
- Validate battery cell/pack/system models using GM's six-step math model verification and validation approach in conjunction with production cell and pack experimental data
- Participate in the Open Architecture Software program led by Oak Ridge National Lab to develop a flexible and scalable computational framework to integrate multiple battery physics sub-models produced by different teams

Technical Barriers

- Battery cost and associated packaging of cells into a battery system; *design tools are needed and are being addressed by CAEBAT project*
- Existing design tools are not practical for realistic battery pack design and optimization

Technical Targets

Reducing the design time for a battery managements system from thermal, electrical, and structural perspective must be reduce to days rather weeks and months. Requirements are summarized schematically in Figure III.E.3-1. For a given current or power profile and ambient/coolant conditions, the battery design tool needs to predict terminal voltage, power, temperature distribution within the cell, total heat generation, lithium concentration profiles, current density profiles, electrical potential profiles, battery life, and safety attributes. The battery user interface will support prismatic can, pouch cells, and also cylindrical cells. Key geometric features need to be parameterized for cell sizing. For each internal component, analysts need access to design-specific parameters, cost, thermal properties, electrochemical/ thermodynamic and transport properties – temperature or concentration dependent where appropriate. Ability to post-process results at particle, electrode and cell level domains is another key requirement. To enable a design breakthrough, GM has established a technical target of less than 12 processor-hours per run for a transient pack-level simulation, with this complete scope of multi-scale physics, parameterization, and visualization.

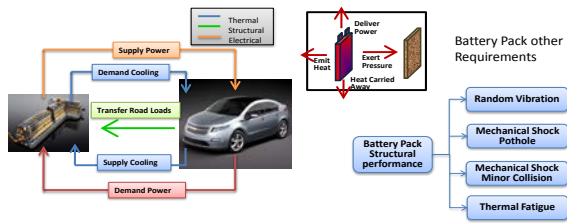


Fig III.E.3-1: Battery design tool user requirements

Accomplishments

- End user needs have been defined; these include: comprehensive set of model inputs and outputs, geometry requirements, meshing requirements, GUI requirements, and performance requirements, CPU time and turnaround time. Standard input parameters were shared with the OAS Work Group.
- A Newman Pseudo-2D model (P2D) and various simplifications including NTGK and ECM models have been implemented into the first cell-level tool which was delivered in August 2012.
- Simplorer-FLUENT co-simulation feature has been developed.
- Reduced Order Model (ROM) research has been conducted and successful ROM concepts have demonstrated the feasibility of this approach for pack level simulation.
- Cell level test and procedure for collecting test data from production cells to validate the cell design tool has been completed.
- CAE capability matrix has been defined for pack-level applications in the automotive industry.

Introduction

Existing tools are not practical for realistic battery pack design and optimization. While various cell physics sub-models exist, they have not been integrated in a single framework in commercial code. Further, current engineering workstations do not have the computational power required to simulate pack-level thermal response coupled with electrochemistry. System-level analysis therefore typically requires Reduced Order Modeling (ROM) be employed to simulate integrated pack-level physics. However, ROM approaches for battery packs are not well understood. Finally, collaboration of necessary parties to develop battery pack design and optimization tools has been

limited by the proprietary nature of software developers' commercial code, automakers' electrification strategies, and battery developers' cell designs and chemistry.

Accordingly, the primary objective of this project is to develop battery cell/pack design tools and system level models that shorten the product development cycle for electric drive vehicles (EDVs) and reduce the cost associated with the current hardware build and test design iterations. Additionally, we seek to validate these battery cell/pack/system models both mathematically and in conjunction with production cell and pack experimental data.

Approach

The project has two main tasks, namely cell- and pack-level model developments. GM has assembled a CAEBAT Project Team composed of GM researchers and engineers, ANSYS software developers, and Prof. White of the University of South Carolina and his ESIM staff. GM provided end-user requirements, physical validation of the models, and a leadership with the OEM's vision for vehicle electrification. Prof. White and his team provided coupled thermal-electrochemical modeling expertise, along with cell aging models. ANSYS provided a state-of-the-art framework for multi-physics simulation and the platform for process automation in commercial software.

The principal objective of the GM team is to produce an efficient and flexible simulation tool for prediction of multi-physics battery response. In partnership with DOE/NREL, the Project Team will interact with the CAEBAT working groups to integrate and enhance existing sub-models, develop cell- and pack-level design tools, and perform experimental testing to validate the tools. The GM team will also create interfaces to enable these new tools to interact and interface with current and future battery models developed by others. NREL has been providing the technical consultations and monitored the overall progress. ORNL has provided the standard for OAS.

Results

For the Li-ion cell, the most commonly used electrochemical model is the pseudo-2D (P2D) model developed by Doyle et al. This model has the capability to accurately predict cell behaviors over a wide range of C-rates. The Newman-Tiedemann-Gu-Kim (NTGK) model and the equivalent circuit model (ECM) are also commonly used empirical models describing the electrical and thermal behavior of Li-ion cells. In the NTGK model, the Li-ion cell conductance is a fitting expression of depth-of-discharge (DOD). In the ECM,

the Li-ion cell is regarded as an equivalent circuit with several components connected in a mixed series/parallel configuration; each circuit component is dependent on DOD. These empirical models require significantly less computational time compared to the P2D model.

The physics-based P2D model includes several nonlinear partial differential equations in two mesoscopic dimensions; and due to the large number of discretized state-variables, it takes much longer to call the P2D model than other simplified models. Therefore, in the multi-scale modeling, calling the P2D model iteratively at all the nodes is extremely time-consuming. In order to reduce the computational time, the following approaches are under consideration.

Approach 1: Reduce simulation time by replacing the P2D model with simplified electrochemical models (NTGK or ECM). In each iteration, the simplified electrochemical models are called at every node/element with shorter time than that of the P2D model for each call.

Approach 2: Reduce the simulation time by the linear approximation method. In each iteration, the P2D model is called only once with the domain-average inputs. The current source is regarded as uniform through the domain. This approach reduces the computation time significantly while maintaining accuracy.

As shown in the Table III.E.3-1, the linear model is the fastest among all the simplified models. Also, the linear model has excellent accuracy in the prediction of the cell electrical and thermal behaviors. (Figure III.E.3-2 and Figure III.E.3- 3)

Table III.E.3-1: Cell level simulation time for various simplifications compared to the full P2D model

	Number of states	Simulation Time (s)		
		1C Discharge	3C Discharge	5C Discharge
Full distribution model	7576	6635	5806	5616
Linear model	361	6.37	4.2	5.31
NTGK model	632	58.6	20.96	20.71
EC model	856	140.47	45.41	44.5

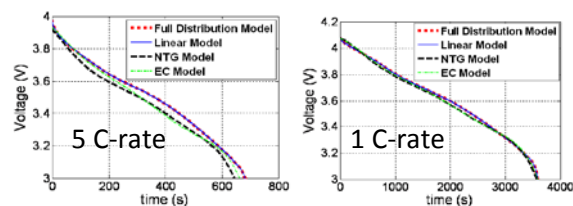


Figure III.E.3-2: Comparison of the discharge voltages for various simplifications compared to the full P2D model

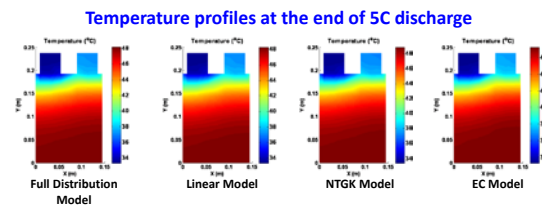


Figure III.E.3-3: Comparison of the cell temperatures for various simplifications compared to the full P2D model

ANSYS has implemented battery modeling capabilities that account for the multi-physics involved in battery cell operation. The commercial CFD software product ANSYS FLUENT is now capable of solving for electrical potential, fluid flow and thermal fields, electrochemistry, and electrical and thermal contact resistance. The multi-scale multi-dimensional (MSMD) modeling framework has been implemented into ANSYS FLUENT (Figure III.E.3-4). The MSMD model approach achieves computational efficiency for resolving multi-physics interactions occurring over a wide range of length scales by introducing separate solution domains for electrode-scale physics and cell-scale physics.

Under MSMD, the CFD model solves two additional scalar equations for the positive and negative potentials, using non-isotropic conductivities, and stores the solid-phase and electrolyte lithium concentrations. These values, together with the temperature, are passed to the electrode scale sub-model, called at each computational cell, which in return calculates current density, heat generation, and the new concentrations. Three electrochemical sub-models, NTGK, ECM, and P2D, are included in the code. The implementation offers a robust numerical procedure (stability, speed), parallel computing capabilities, graphical user interface, and detailed post-processing capabilities (Figure III.E.3-5).

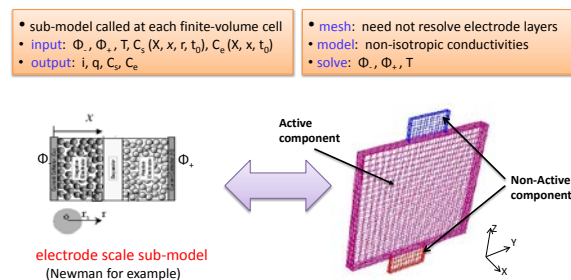


Figure III.E.3-4: MSMD approach for the cell level

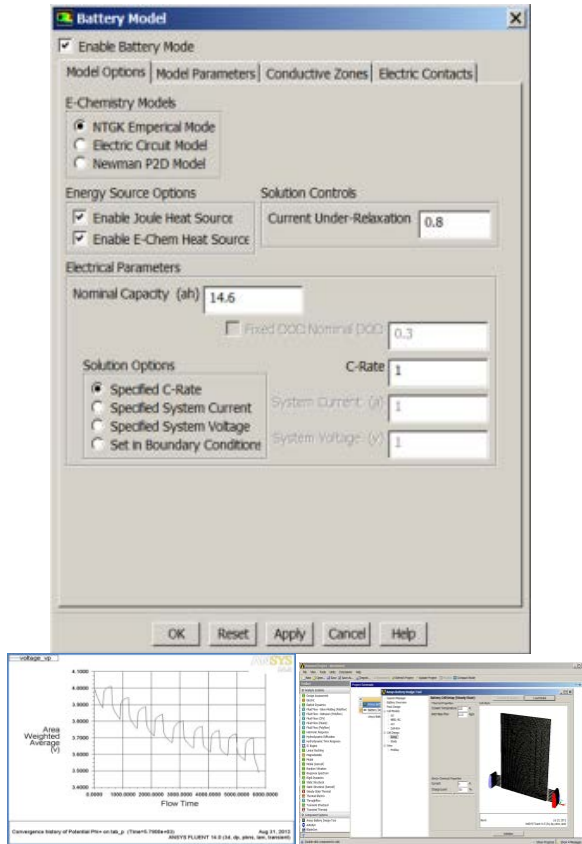


Figure III.E.3-5: First version of cell level tool from ANSYS

The GM team has developed a complete cell-level test facility for lithium-ion batteries. The test facility consists of a battery cell charge/discharge system, a custom designed environmental chamber with temperature and air flow control, an infrared thermal imager, a data acquisition (DAQ) system, as well as test, control, and data-analysis software. Testing has been performed in the following areas: battery thermal characterization test, including static capacity test, HPPC test, thermal imaging, and battery thermistor validation test (Figure III.E.3-6). The accuracy and usefulness of the proposed cell-level tool will be demonstrated through rigorous verification and validation processes.

In the context of system-level modeling of the battery pack, we are also considering the coupling of electrochemical behavioral effects via an electrical circuit model (ECM) which will generate heat from load current as input with a linear parameter varying (LPV) model that mimics the thermal cooling behavior of the battery under varying mass flow rates. Then, the temperature calculations of the cell are fed back into the ECM because the open-circuit voltage of the ECM is a function of not only state of charge (SOC) but also temperature. The battery-voltage calculations are also captured from the ECM in the ANSYS Simplorer system simulation software tool. The nonlinear

elements of the ECM can be calibrated against measurements.

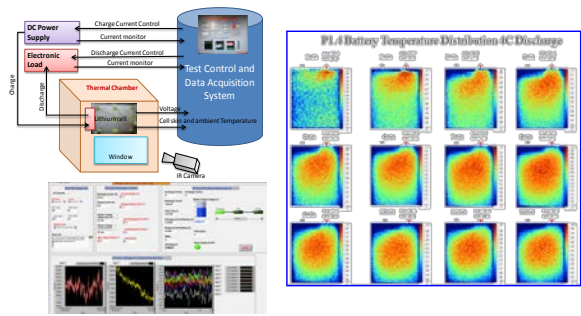


Figure III.E.3-6: Cell level validation test setup and test data

Once the battery electrical circuit model and the reduced order thermal model are generated, they can be coupled to form a complete battery pack model (Figure III.E.3-7). The circuit on the left represents the battery electrical circuit model, and the box on the right represents the battery thermal model. The two models are coupled with each other. The electrical model needs temperature as input since the resistance and capacitance of the model are temperature-dependent. The electrical circuit model predicts heat generation. The thermal model, on the other hand, needs heat generation as input and supplies the temperature that the electrical circuit model needs.

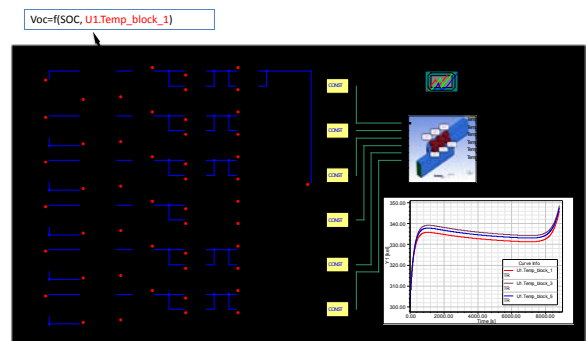


Figure III.E.3-7: System level modeling for pack level simulations

Conclusions and Future Directions

We recognized that a successful solution would require several technology threads and options. System simulation based on ROM generation offers a computationally inexpensive approach. As battery power densities increase and thermal management becomes more complex, a simple ECM simulation is not sufficiently reliable and cannot provide the resolution necessary to guide pack design. Applying advances in co-simulation and ROM technologies, the Project Team is developing and validating a flexible pack-level toolbox that overcomes these challenges.

Overall the project is on-track to meet all objectives and Year 1 technical progress is consistent with the project plan. Moving forward we plan to address the following items:

- Verify and validate of the first version of cell-level tool
- Develop model order reduction methods for the pack level
- Extend cell-level models for aging and abuse effects
- Define pack-level validation requirements to meet the future capability matrix for pack-level CAE
- Identify suitable existing pack level tests in progress or from previous tests (liquid or air cooling) performed in GM battery group
- Build up the pack level simulation model including meshing, physical boundary conditions, and operating conditions
- Improve battery-specific graphical user interface for workflow automation
- Build a standard data-exchange interface based on specifications from the OAS Workgroup

FY 2012 Publications/Presentations

1. Taeyoung Han, Gi-Heon Kim, Lewis Collins, "Multiphysics simulation tools power the modeling of thermal management in advanced lithium-ion battery systems," *ANSYS Quarterly magazine "Advantage,"* 2012.
2. Taeyoung Han, Gi-Heon Kim, Lewis Collins, "Development of Computer-Aided Design Tools for Automotive Batteries-CAEBAT," *Automotive Simulation World Congress (ASWC),* Detroit, October 2012.
3. Xiao Hu, Scott Stanton, Long Cai, Ralph E. White, "A linear time-invariant model for solid-phase diffusion in physics-based lithium-ion cell models," *Journal of Power Sources* 214 (2012) 40-50.
4. Xiao Hu, Scott Stanton, Long Cai, Ralph E. White, "Model order reduction for solid-phase diffusion in physics-based lithium ion cell models," *Journal of Power Sources* 218 (2012) 212-220.
5. Meng Guo, Ralph E. White, "A distributed thermal model for a Li-ion electrode plate pair," *Journal of Power Sources* 221 (2013) 334-344.

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

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K. Obasih, Johnson Controls, Inc.

K. Gering, Idaho National Laboratory

Start Date: July 2011
Projected End Date: July 2014

Objectives

- As one of the subcontract teams, support the DOE/NREL Computer Aided Engineering for Batteries (CAEBAT) activity.
- Provide simulation tools that expand the inclusion of advanced lithium-ion battery systems into ground transportation.
- Specifically develop a numerical simulation model which can resolve the appropriate phenomena required to create a coupled thermal and electrochemical response of lithium-ion spirally wound cells.
- Apply advanced numerical techniques to expedite the solution of the governing fundamental equations within lithium-ion battery cells to enable advanced electrochemical models to be used in module and pack simulations.
- Validate the models and design tools with experimental data.

Technical Barriers

- Lack of advanced computer-aided engineering tools to quickly design and simulate battery packs for electric drive vehicles impede optimizing cost-effective solutions. A major challenge for this project is to include the important aspects of the rapidly maturing lithium-ion battery simulation field in to an easy to use, widely accepted computer aided engineering tool. This implementation should be flexible and extensible to ensure the methods can move forward as the level of understanding in the fundamental physics evolves. Also ensuring this technology is available in an easy to use form will ensure that mass acceptance is achieved.
- Another significant challenge is the creation of a modeling concept for cylindrical cells and their underlying architecture. Spiral cells can be grouped in to several categories and hence flexible templates were created, the user then provides appropriate data to populate such templates creating a complete cell model. This would include the specification of the 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 overall method is a significant part of this project.

Technical Targets

- Create a spiral cell analysis framework which includes the positive and negative electrodes, which are wound together to create the spiral jellyroll. This method should resolve the planar electrical 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 data provided by sub-contractors including both cylindrical and prismatic forms of spiral cells with both power and energy optimized designs.
- Use the validated methods within a larger framework to create simulations of battery modules which include such cells. Module models should include electrical and thermally conducting components which interface cells together and the appropriate physics within these components.

- Finally, validate the results of these simulations with relevant module-level test work from the sub-contractors.

Accomplishments

- The project has now delivered a simulation method which can describe and resolve the component parts of a spirally wound lithium-ion battery cell. This resolution includes the overall shape and topology, cylindrical or prismatic, of the cell as well as the details of the electrode design, coating dimensions and underlying electrochemistry.
- The simulation methods allow the cell to be considered in a lumped space in isolation, removing the effect of external packaging and focusing on the electrochemistry solution, or this same representation can be read in to STAR-CCM+ to create a 3 dimensional representation which can then be duplicated to create a module or pack representation. Within STAR-CCM+ this complex 3 dimensional model computes a complete cooling system flow, thermal and electrochemical analysis.
- This analysis enables the user to understand the coupled effects of electrical load and thermal management system on the performance of a battery pack. Figure III.E.4-1 shows an example of previous work conducted using the existing lithium-ion pouch cell methods showing the level of complexity of design that can be simulated.
- Electrochemical input information has been generated to represent three of the four wound cells to be validated within the project. These have been created after the provision of cell specific data from Johnson Controls Inc. and then regression from specific test work was carried out to arrive at the remaining electrochemical properties. These models have now been refined to provide a good fit across the whole range of three tested temperatures for constant discharge and high pulse power characterization tests.
- The enhancements to the electrochemistry model include an extension to the model to allow for the concentration dependence of the solid phase diffusion coefficient for increased accuracy. The model based on the work of Newman et al is also extended to include multiple active materials as often found in contemporary lithium-ion cell design.

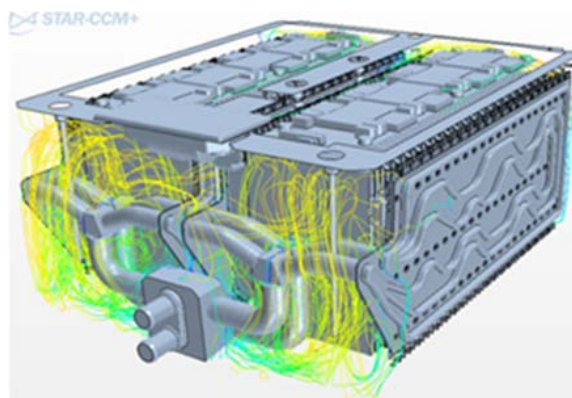


Figure III.E.4-1: Previous work using flow, thermal, and electrochemistry models, courtesy of Automotive Simulation Centre Stuttgart (ASCS) project, Germany (Daimler, GM Opel, Porsche)

- The above listed electrochemistry model has also been re-implemented in to STAR-CCM+. The reimplementation allows the use of parallel computations within the electrochemistry level and therefore users can expedite results using massive parallel machines. This development addresses one of the major draw backs often repeated regarding Newman type models which is the runtime of the calculation. By addressing this issue simulations will become more able to effect designs rather than companies relying on test work. This is a key feature with regard to enabling the usage of this technology.
- An approach to simulating aging within lithium-ion cells has been formulated which considers SEI layer growth. This model is based on the work of H. Ploehn. This model is now implemented in beta code and will be available early 2013 for users as part of this project. This will allow users to understand the major effect of calendar aging on a predefined cell and cast forward a simulation to understand how the cell will perform in either a number of months or years' time.

Introduction

DOE established the Computer Aided Engineering for Electric Drive Vehicle Batteries (CAEBAT) activity to develop multi-physic design tools. CD-adapco has extended its class leading computational aided engineering code, STAR-CCM+, to analyze the flow, thermal and electrochemistry occurring within spirally wound lithium-ion battery modules and packs. CD-adapco was one of the teams awarded, after a competitive procurement, to develop CAEBAT design tools. This project created additional coding and methods which focus on the electrochemistry analysis

of the spirally wound electrodes. This coding has been developed in collaboration with Battery Design LLC, a subcontractor to CD-adapco with considerable experience in the field of electrochemistry modeling.

The work has created a new piece of analysis code which embodies a method to produce electrochemistry and thermal understanding using state of the art electrochemistry models based on the work of Newman. The methods will use a matrix of electrochemistry unit cell models, representing the cell sandwich, which communicate through the metallic current collectors, shown in Figure III.E.4-2. Current enters and leaves the spiral electrodes via the tabs, which although not shown are also integral to the problem and resolved in the simulation. The surrounding terminals and packaging components are also included in the analysis as they act as heat paths into and out of the jelly roll.

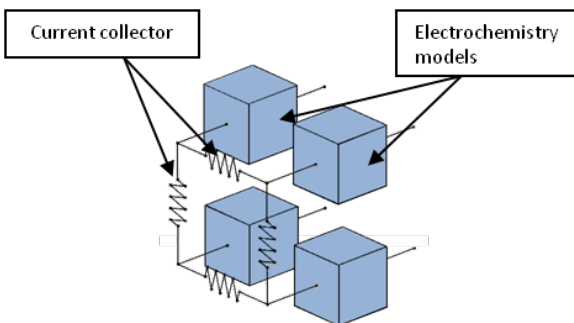


Figure III.E.4-2: Schematic of the underlying modeling abstraction

Work has begun on creating electrochemistry datasets which represent the wound cells listed in Table III.E.4-1. Detailed test work has been defined through discussion with the cell manufacturer and these have been carried out at different temperatures. The electrochemistry models were created cover a wide range of temperature and also charge/discharge rate as appropriate for the design of cell.

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

Table III.E.4-1: Automotive Li-ion cell formats used for validation of electrochemical thermal models

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

Approach

Detailed design information was obtained from the cell supplier to describe the dimensions of the electrode, the details of the can and finally details of the electrodes chemistry used in each of the designs. This information was entered in to the newly created performance model which accounts for both the effect of the cell sandwich response and also the distribution of potential along the lengths of the electrodes. This second phenomena can have a significant effect on long electrodes similar to those found in wound cells. Figure III.E.4-3 shows some of the parameters required to fully define the inputs to the model.

Once the initial dataset is created then its performance is compared with specific test work to fine tune modeling parameters such as electrode tortuosity and porosity. Several researchers have suggested computational methods to compute tortuosity which is still in the research phase therefore, for this work, the more practical approach of tuning parameters compared to test work was used. This is done using both constant current test work and also high pulse power characterization tests as defined by the USABC organization. Each test allows specific parameters to be optimized within the model.

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+.

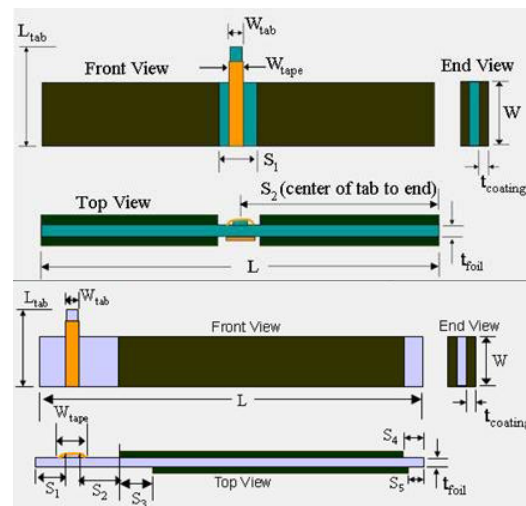


Figure III.E.4-3: Parameters used to describe the positive and negative electrodes in the host BDS code

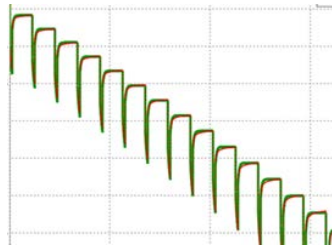


Figure III.E.4-4: Voltage against time, simulation (green) plotted against test data (red) for a given set of discharge pulses. Note, this is example data not related to the clients confidential results

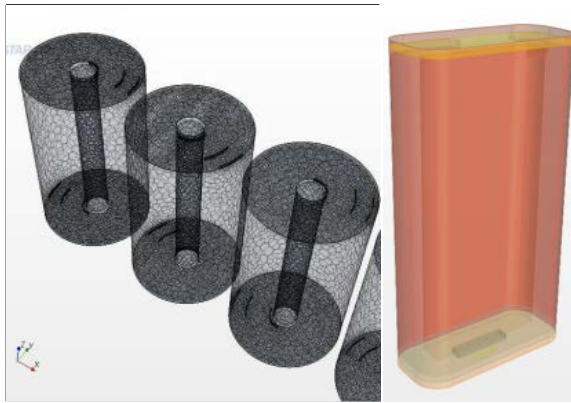


Figure III.E.4-5: Screen shots of spiral cell examples within STAR-CCM+ showing the resolved current carrying tabs

The concept resolves the spiral electrodes, commonly known as the jelly roll, as a homogeneous material with anisotropic quantities and also the tabs, tab collection mechanisms, outer can and end caps as separate bodies. Figure III.E.4-6 shows the effect of the anisotropic properties on a typical thermal distribution on an active jelly roll. 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.

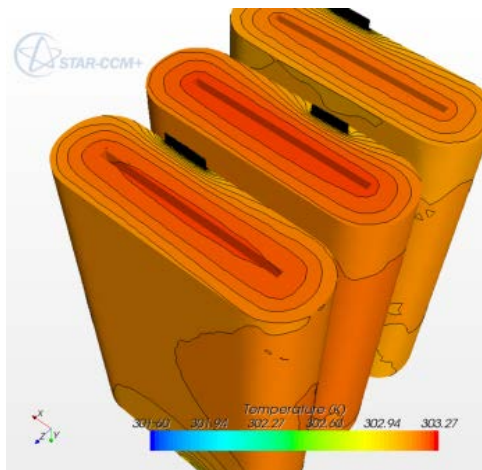


Figure III.E.4-6: Prediction of temperature on the jelly roll of 3 cells in series

Results

Cell Development

At present the created electrochemical performance model has been used in the spiral cell configuration for three of the four spiral cells to be investigated within this project. This input information has been created to produce a viable model from -10° Celsius up to 40° Celsius and operating from gentle constant currents up to high pulse currents. The comparison of model performance and test work cannot be shown due to confidentiality. At present, final validation tests are taking place which will cycle the cell through a drive cycle. This same drive cycle will be used to validate the numerical model created before this is transferred to the module or pack level.

Module and Pack Development

Module and pack level development has been limited to test cases currently, an example of which is shown below. This is a 3S2P configuration using a generic prismatic spirally wound cell. The six battery cells are then encased and air is slowly blown through the case to provide some form of cooling.

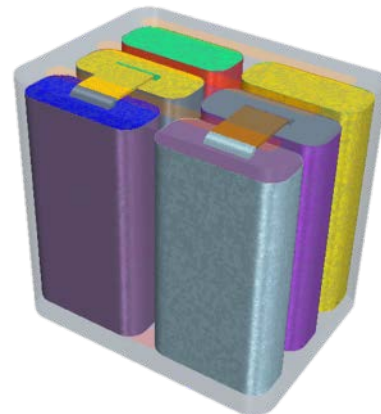


Figure III.E.4-7: Generic battery module using the generated wound cell models

Figure III.E.4-8 shows the maximum and minimum temperatures occurring within the 6 jelly rolls of the above module during 3 pulses of high rate discharge and then charge. This plot of the growing spread between maximum and minimum jellyroll temperature is a critical measure of how well the thermal management system and cell design copes with the imposed electrical loads. This shows the overall flow, thermal and electrochemical model operating in a complex 3D model.

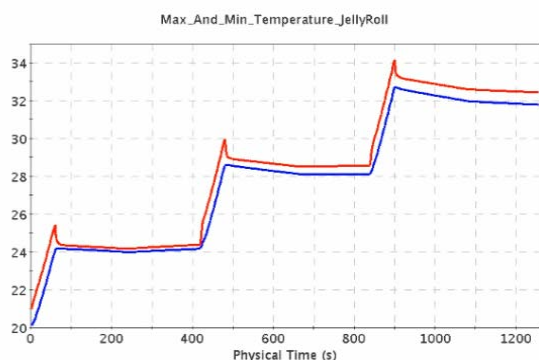


Figure III.E.4-8: Maximum and minimum temperatures occurring within the Jellyrolls

Furthermore, the predicted current density and potential on the electrodes that form the jellyroll can be plotted from the above simulation. The potentials are shown in Figure III.E.4-9 and this is a plot obtained from STAR-CCM+ plotting electrical quantities.

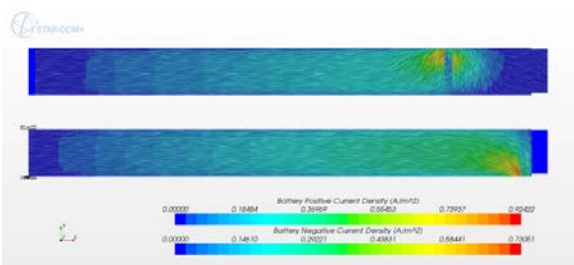


Figure III.E.4-9: Electrode current density for positive and negative electrodes from a generic cell

Due to the confidential nature of the commercial cells and modules used for validation with this project similar plots cannot be shown within this report.

Conclusions and Future Directions

The project is roughly 1/3 through its intended overall time and the overlying solution architecture is now complete. The electrochemical model has been re-implemented to take advantage of the parallel computing architecture that STAR-CCM+ offers and will be increasingly used in the larger module/pack simulations. The cell level test work has been largely completed and this work has been used to inform the input parameters which describe each of the wound cells to be validated. These cells have been generated in STAR-CCM+ to allow further, detailed investigation to continue through the subsequent years of the project.

The subcontractors would like to acknowledge the contribution and input that the National Renewable Energy Laboratory has made, particularly Kandler Smith.

FY 2012 Publications/Presentations

1. S. Hartridge, "Computer Aided Engineering of Electric Drive Vehicle Batteries in STAR-CCM+" DOE Vehicle Technologies Annual Merit Review, Washington DC, May 14-18, 2012.
2. R. Spotnitz, G. Yeduvaka, D. Schad, V. Gudimetla, J. Votteler, G. Poole, G. Damblanc, C. Lueth, E. Oxenham, S. Hartridge, "Electrothermal Simulation of Spirally-Wound, Lithium-Ion Cells", 222nd Meeting of ECS, Honolulu, HI, Oct. 7-12, 2012.

III.E.5 Development of Computer Aided Engineering Tools for Automotive Batteries (CAEBAT Contract - EC Power)

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Collaborators:
Ford Motor Company
Johnson Controls, Inc.
Pennsylvania State University

Start Date: May 2011
Projected End Date: May 2014

Objectives

- Support the DOE/NREL Computer-Aided Engineering for Batteries (CAEBAT) activity as one of the subcontract teams.
- Develop an electrochemical-thermal coupled model and associated computer code for large-format, automotive Li-ion cells and packs.
- Create a novel computational framework that allows for rapid and accurate performance/safety simulations. Algorithms will span across several length scales, ranging from particle size, to an electrochemical unit cell, to a 3D battery, and finally to an entire battery pack. This computational framework will model both wound and stacked-cell geometries.
- Develop a comprehensive materials database that is critical for accurate modeling and simulation of large-format Li-ion batteries.
- Test and validate the developed cell and pack models against a wide range of operating conditions relevant to automotive use, such as extreme temperature operation and complex power profiles.

Technical Barriers

- Lack of advanced computer-aided engineering tools to quickly design and simulate battery packs for electric-drive vehicles impedes optimizing cost-effective solutions. The large-format nature of automotive Li-ion batteries presents unique challenges that set them apart from the batteries used in cell phones, laptops, and other consumer goods. For example, high rates of charge and discharge in combination with the large surface area of the cell, lead to widely varied temperature distributions on the cell and throughout the packs. This non-uniformity causes a number of serious issues, including poor battery performance, increased degradation effects, potential safety concerns, and the inability to fully utilize the active material inside the battery. Creating actual cells and packs is time consuming and extremely expensive, which makes an efficient, high-fidelity simulation tool very desirable.
- However, the strongly coupled nature of electrochemical and thermal physics, the relevant scales of a battery cell or pack (ranging from sub-microns to meters), and the need for a comprehensive materials database, makes the creation and development of a Li-ion battery model a unique and challenging task.

Technical Targets

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

Accomplishments

In FY12, our team accomplished the following major tasks:

- Completed second version of our large-format software tool, “Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model” (ECT3D). Updates include electrochemical-thermal coupled pack simulation capability, parallel computing ability, the ability to model both rolled and stacked electrode designs, and a safety simulator that models nail penetrations/internal shorts.
- Tested more than 100,000 coin cells as part of the development of the materials database. The list of materials (relevant to the automotive industry) includes, but is not limited to: graphite and LTO (anode); NCM, LFP, and LMO (cathode)
- Validated initial model for extreme temperatures and high C-rates.
- Developed user-friendly GUI.

Introduction

To reduce greenhouse gas emissions and reduce U.S. dependence on foreign oil, developing hybrid electric, electric, and plug-in hybrid electric (HEV, EV, PHEV) vehicles is extremely important. These vehicles benefit greatly from advanced Li-ion battery chemistries, which can store large amounts of energy while maintaining a low weight relative to other battery chemistries. The design, build, and test process for batteries, however, is extremely time consuming and expensive. EC Power’s code, ECT3D, directly addresses the issues related to the design and engineering of these cells. Many technical characteristics of batteries and packs that are critical to battery performance and safety are impossible to measure experimentally.

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

Approach

EC Power is developing the large-format, Li-ion battery simulation software, ECT3D, to analyze battery cells and packs for electric vehicles (EV, PHEV, HEV). Team member Pennsylvania State University is primarily responsible for performing materials

characterization experiments and diagnostic experiments for multi-dimensional validation. The materials characterization experiments will supply data for the extensive materials database being incorporated into ECT3D. Significant progress has been made and is ongoing in this area.

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

Results

Figures III.E.5-1 and III.E.5-2 are plots generated by team member Pennsylvania State University during the ongoing development of the materials database. Figure III.E.5-1 shows the Li diffusion coefficient with respect to the SOC of the cell for both the cathode and anode. Figure III.E.5-2 is a parametric plot showing the relationship between LiPF₆ concentration and its conductivity with respect to temperature. These two plots are a small sample of the data that has been collected thus far. Many more materials are waiting to be characterized.

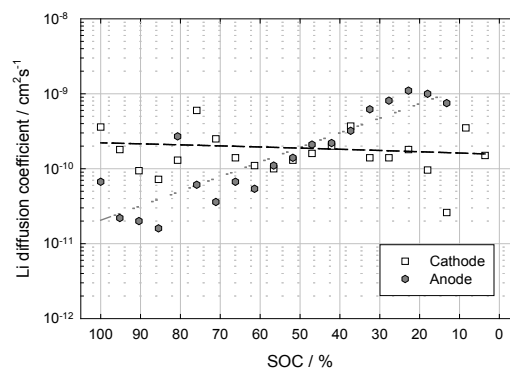


Fig III.E.5-1

Figure III.E.5-3 was generated for the 1C discharge of a 2P-12S configured 2.8-kWh pack with a parallel air-cooling system. The temperature distribution is accompanied by the electrochemical output of the cell in Figure III.E.5-4, both of which are calculated simultaneously, in real time. It is through this method of electrochemical-thermal coupling that the utility of ECT3D is demonstrated. The electrochemical performance is simulated in conjunction with the corresponding thermal behavior of the cell.

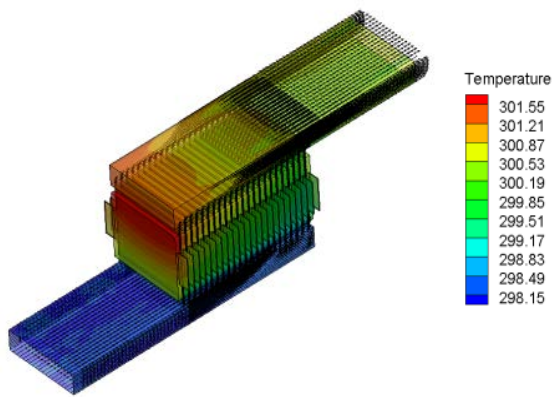


Fig III.E.5-3

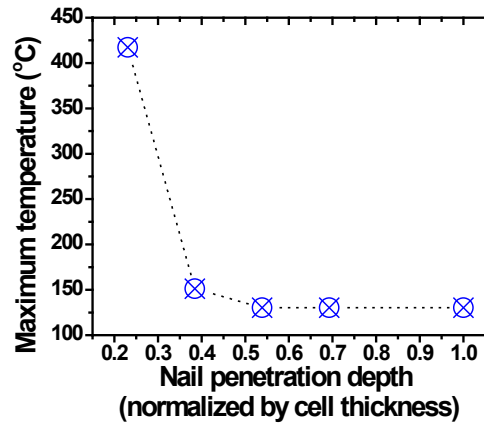


Fig III.E.5-6

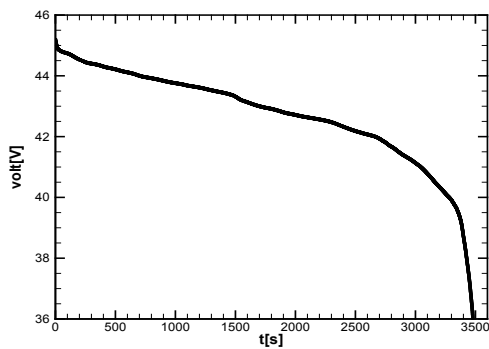


Fig III.E.5-4

Figures III.E.5-5 and III.E.5-6 show the temperature distributions resulting from a partially penetrated nail in a prismatic cell. In figure III.E.5-5, maximum local temperatures approach 400 °C within one second, almost certainly triggering thermal runaway and catastrophic failure of the cell. Figure III.E.5-6 shows the maximum temperature inside the cell with respect to the nail penetration depth.

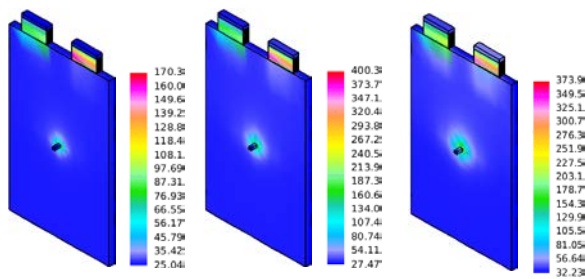


Fig III.E.5-5

Conclusions and Future Directions

Under the DOE/NREL CAEBAT activity, our team has successfully developed and demonstrated a vastly improved version of our ECT3D software. The capabilities to allow pack simulation, safety analysis, and parallel computing further increase the utility of our software in the private sector. Additionally, the ever-growing materials database will further enhance the accuracy of the model.

Our next steps include ongoing validation and testing of the updated features with industrial team members Ford and Johnson Controls, and ongoing development of the materials database. Further additions to ECT3D include blended electrode models for both the anode and cathode, in an effort to simulate blended materials that frequently are used in industrial applications.

FY 2012 Publications/Presentations

1. C.Y. Wang, “Breakthrough in Large-Format Li-ion Battery Safety Through Computer Simulation,” Battery Safety 2011, Las Vegas, NV, Nov. 9, 2011.
2. C.Y. Wang, C. Shaffer, G. Luo, “Progress of CAEBAT Project for EC Power Team,” Presentation to US Drive Electrochemical Energy Storage Tech Team, Dec. 13, 2011.
3. C. Shaffer, “Development of Cell/Pack Level Models for Automotive Li-Ion Batteries with Experimental Validation,” 2012 DOE Annual Merit Review, Arlington, VA, May 15, 2012.
4. C.Y. Wang, et al., “Fundamentals of Large-Format Lithium Battery Safety,” 13th Ulm Electrochemical Talks, July 5, 2012.

III.E.6 Battery Multi-Scale Multi-Dimensional Framework and Modeling (NREL)

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Start Date: April 2010
Projected End Date: September 2015

- Identify critical life- and safety-related mechanism and formulate mathematical expressions
- Develop numerical methods to reduce computational cost without compromising model accuracy
- Perform model study to expand knowledge on LIB performance, aging, and safety behaviors

Objectives

- Perform research and development to support the goal of the DOE/NREL Computer-Aided Engineering of Automotive Batteries (CAEBAT) activity
- Develop advanced cell- and pack-level model, method, code in context of the multiphysics, multi-scale, multi-dimensional (MSMD) framework
- Support CAEBAT subcontractors by providing technical guidance, and evaluate project outcomes

Technical Barriers

- Lack of comprehensive computer-aided engineering tools to quickly and cost-effectively develop and design cells and battery packs
- Complexity of multidisciplinary multi-scale physics interactions in intricate Li-ion battery geometries
- Computational cost for resolving widespread time and length scales in modeling physiochemical processes in Li-ion batteries

Technical Targets

- Support CAEBAT activity by further enhancing functionality and efficiency of the MSMD framework
- Improve scale bridging by providing advanced component models to better represent kinetic and dynamic behavior of Li-ion battery systems

Accomplishments

- By the end of FY11, NREL demonstrated cell-domain models for simulating large-format, stacked prismatic (pouch) and wound cylindrical cells using the “Orthotropic Cell Composite Continuum” models.
- In FY12, we focused on extending the MSMD model to simulate the response of large-format prismatic wound cells by adding new capabilities.
- NREL’s capabilities now include a complete set of cell-domain modeling tools to simulate all major LIB form factors: stacked pouch, wound cylindrical, and wound prismatic.
- Documented development of the MSMD framework was published in a peer-reviewed article for the *Journal of the Electrochemical Society*.

Introduction

Over the past several years, NREL has developed the MSMD model framework, which is an expandable development platform and a generic modularized flexible framework resolving interactions among multiple physics occurring in varied length and time scales in a Li-Ion cell. To respond to DOE’s CAEBAT objectives, NREL continues to develop battery models, methods, and codes in the context of the MSMD framework.

In past years, NREL has demonstrated cell-domain models for simulating large-format, stacked prismatic (pouch) and wound cylindrical cells using the “Orthotropic Cell Composite Continuum” models, including the Single Potential Pair Continuum (SPPC) model and the Wound Potential Pair Continuum

(WPPC) model. This year, NREL focused on the development of a new model capability to simulate the response of large-format prismatic wound cells. Wound prismatic cell formats are gaining increased attention from major electric vehicle battery manufacturers with the expectations of reduced production time over stacked-cell formats and improved thermal characteristics over cylindrical cell formats.

We developed a new cell-domain submodel to resolve complex electrical configuration in a wound prismatic cell with discrete electrical tabs, and wrote a code implementing the model into the NREL’s MSMD framework. Thermal, electrochemical, and electrical coupled simulations were performed to better understand the mechanisms and interactions between local electrochemical processes and macroscopic heat and electrical current transfer in large prismatic cells. The model was applied to predict impacts of form factors of cell designs, such as cell thickness and height, on performance of prismatic wound cells

With the successful completion of the new prismatic wound cell model, NREL’s capability includes a complete set of cell-domain modeling tools to simulate all major LIB form factors: stacked pouch, wound cylindrical, and wound prismatic. Table III.E.6-1 summarizes the NREL-developed “orthotropic continuum” cell-domain models for major cell formats.

Table III.E.6-1: 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

Approach

Based on its modularized architecture, the MSMD framework allows independent and parallel development of submodels for physics captured at each domain. NREL has developed several variations of orthotropic continuum modeling of cell composites to resolve cell-domain physics. In FY12, a new model capability to simulate the response of large-format prismatic wound cells was developed and applied to investigate cell behaviors for the impact of its form factors.

The schematic in Figure III.E.6-1 presents a typical jelly-roll wound structure. Multiple strata components of the cell composite are wound in a prismatic jelly-roll shape. The model geometry unit is defined as an orthotropic continuum composite including a pair of current collectors and two sets of electrode pairs with separators. Two distinguished electrode pairs are

resolved in the model geometry unit. An inner electrode pair is operated at potential difference between the paired current collector phase of the unit Wound Potential Pair Continuum (WPPC). An outer electrode pair is operated at potential difference across the unit WPPCs.

Figure III.E.6-2 shows the concept of the orthotropic continuum approach in the WPPC model. Cell composite strata volume is treated as a continuum with orthotropic properties. Individual component layers are not distinguished, but the wound structure geometry is still resolved. Temperature and two electric potentials at each current collector phase are evaluated at finite volume of WPPC. Charge transfer currents are calculated with current collector-phase electric potentials of WPPC volume units. The cell-domain model calls an electrode domain model twice at each discretized location of the cell composite.

The cell-domain model described here is linked with electrode-domain and particle domain models using the MSMD framework. The model choice used in the present study is summarized in Figure III.E.6-3.

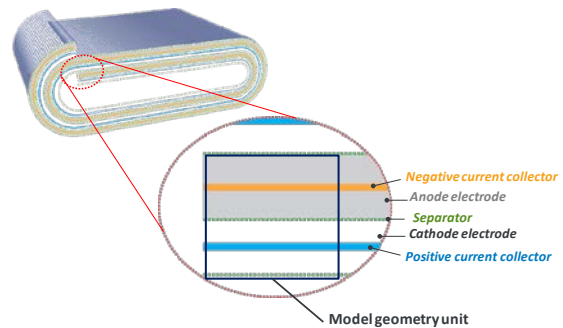


Figure III.E.6-1: Schematics of a typical jelly-roll wound structure

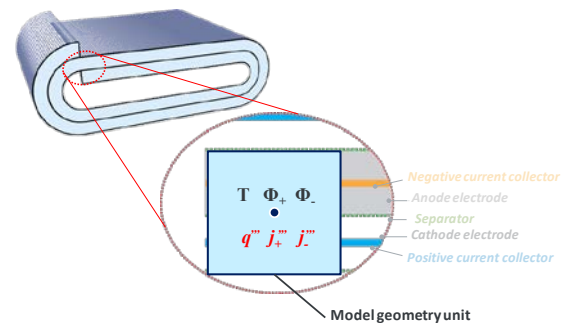


Figure III.E.6-2: Concept of orthotropic continuum approach in WPPC model

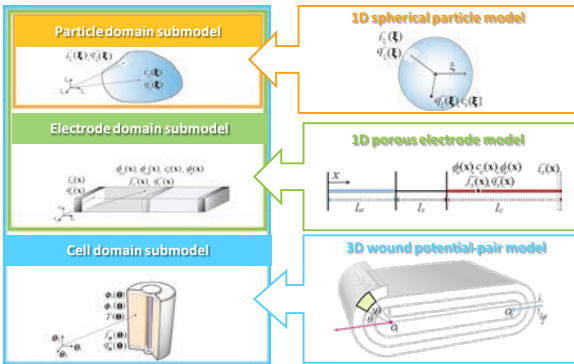


Figure III.E.6-3: MSMD submodel choice of present work

Results

Macroscopic cell design features regarding the thermal and electrical configuration greatly impact the overall cell performance and life, especially in large battery systems. The MSMD framework is employed to perform thermal and electrical design evaluations for a large-format wound prismatic cell. Microscopic aspects of cell design, including material compositions, electrode loading thicknesses, and porosities, are held constant. Rather, the impact of large-format cell design features such as the location and the number of electrical tabs and the aspect ratio of the wound jelly roll are varied. The schematic in Figure III.E.6-4 summarizes the nominal cell dimensions and electrical tab configuration investigated. The nominal capacity of the cells is 50Ah. Constant current discharge at 100A (2C-rate) cases are simulated. Cell discharge starts at 100% state of charge (SOC), and ends with voltage cut-off at 2.5V. The cell is initially at 25°C ambient temperature. The side walls of the cells are cooled with an effective heat transfer coefficient 50 W/Km during discharge. The width of the electrical tabs is 10 mm. Both the positive and the negative tabs are located on the same side of a cell. The tabs are extended from the electrode jelly in every winding turn to the terminals. Figure III.E.6-5 presents the simulated cases with variable form factors. Each design has a different external surface area for cooling, and a different number of winding turns and electrical tabs. The height of the wound electrodes is fixed to 110 mm. The length of the unwound electrodes is about 9.6 m.

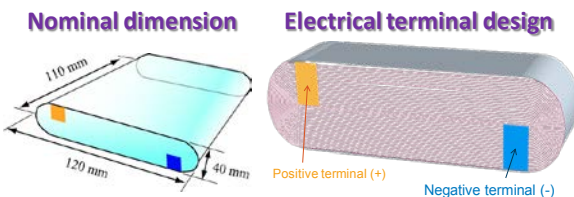


Figure III.E.6-4: Schematic description for nominal cell design and electrical tab configuration of the 50Ah wound prismatic cell

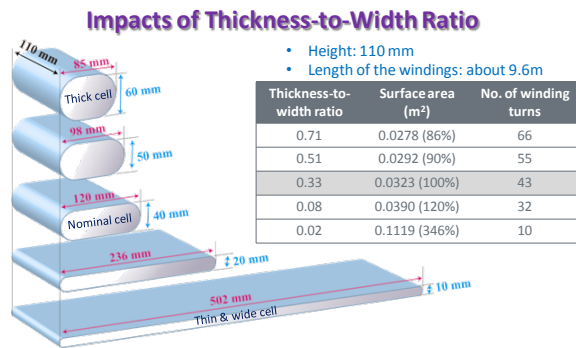


Figure III.E.6-5: Form factor case description investigated in present work

In Figure III.E.6-6, constant current discharge (100A) voltage curves are compared among the simulated designs. Due to the specific tab configuration used in this study, the thin and wide design has the least number of winding turns and consequently the least number of electrical tabs along the length of unwound electrode. The number of tabs (or the distance along electrode between the tabs) is the significant cause of difference in voltage curves. However, the discharge capacity at 2C discharge rate appears quite similar among the compared designs.

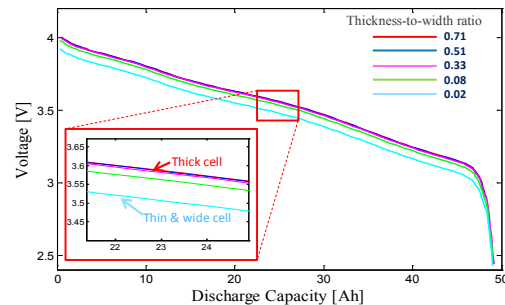


Figure III.E.6-6: Comparison of voltage outputs from the compared cases for constant current discharge at 100A

Thermal response of the cells is shown in Figure III.E.6-7. Due to the inefficiency originated from the poor electrical path design, the thin and wide cell generates the largest amount of heat. Therefore, this cell shows a fast temperature increase during the initial stage of discharge where heat generation dominates its thermal behavior. In the later stage of discharge, however, heat transfer becomes important. The thin and wide cell with the largest cooling surface reaches its thermal steady state quickly at relatively low temperature and ends up with the lowest end of discharge temperature. The contour plots in Figure III.E.6-7 show unwound views of temperature distribution at the end of discharge of each cell. Even though the thin and wide cell results in the lowest cell-averaged end of discharge temperature, the internal temperature imbalance is significant because of the

highly non-uniform heat generation in the cell. The thick cell shows increased temperature near the core region due to low layer-normal thermal conductivity and small surface area available for cooling. The thin and wide cell has hot spots near tabs for large convergence of electrical current and the consequent localized heat generation. The nominal cell design shows the most uniform temperature distribution.

Kinetics responses of the investigated cells are compared in Figure III.E.6-8. The unwound and wound views of the contours show the non-uniform kinetics occurring over the cell composite volumes in the cells investigated at 10 minutes after the start of discharge process. High kinetic current is still observed near the electrical tabs in the nominal and thick cells. However, the main cause of non-uniform kinetics of these cells is temperature imbalance. Higher temperature energizes the kinetics at the inner core of electrode rolls of the cells. Conversely, in thin and wide cell design, the location of the electrical tabs is the major cause of the imbalance of kinetics. More active kinetics and higher charge transfer currents result in vertical streaks of contour lines along electrode wound of the thin and wide cell.

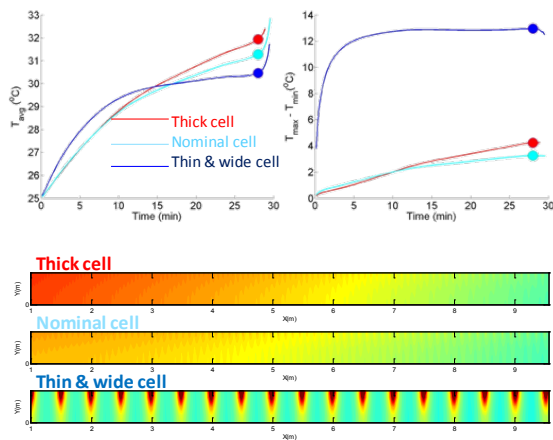


Figure III.E.6-7: Thermal behavior of the investigated cell designs

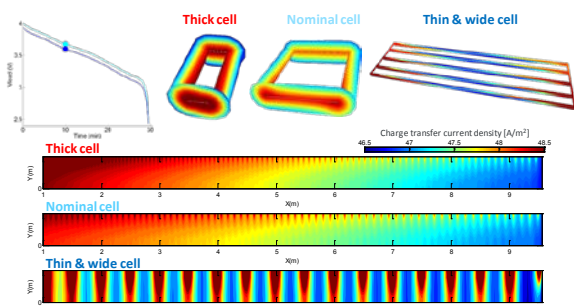


Figure III.E.6-8: Non-uniform kinetics during discharge of the investigated cell designs

Conclusions and Future Directions

NREL has developed the MSMD model framework, which is an expandable development platform providing “pre-defined but expandable communication protocol,” and a generic and modularized flexible framework resolving interactions among multiple physics occurring in varied length and time scales with various fidelity and complexity. In FY12, we focused on enhancement of framework functionality and development/documentation of cell-domain models/solution methods to be applicable to various cell formats such as stack pouch cells and wound cylindrical/prismatic cells.

Universal mathematical representation for dynamic and kinetic response of batteries is hard to define. Therefore, the modular framework of the MSMD provides critical benefits of applying various constituent models to properly simulate the battery response. We provided technical insight and based on our MSMD to the three CAEBAT subcontractors, particularly the GM/ANSYS/ESim team. The objectives of the FY13 task are to enhance the particle domain model capabilities, and to extend the MSMD paradigm to pack-level simulation.

FY 2011 Publications/Presentations

1. Gi-Heon Kim et al., “Orthotropic Continuum Modeling of Cell Composites for Multi-Scale Lithium-ion Battery Model,” 220th ECS meeting, Oct. 11, 2011, Boston, MA.
2. Kandler Smith et al., “Experimental Validation of 3D Electrochemical/Thermal Model of Large Li-ion cells,” 220th ECS meeting, Oct. 12, 2011, Boston, MA.
3. Kyu-Jin Lee et al., “3-Dimensional Thermal and Electrochemical Model of Prismatic Wound Li-ion Batteries,” 221th ECS meeting, May 9, 2012, Seattle, WA.
4. Ahmad Pesaran et al., “Computer-Aided Engineering of Batteries for Designing Better Li-Ion Batteries,” Advanced Automotive Battery Conference Battery Modeling Software and Applications Workshop, Feb. 6, 2012, Orlando, FL.
5. Gi-Heon Kim et al., “Multi-Domain Modeling of Lithium Ion Batteries Encompassing Multiphysics in Varied Length Scales,” International Meeting on Lithium Batteries, June 19, 2012, Jeju, South Korea.

III.E.7 Lithium-Ion Abuse Model Development (NREL)

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Start Date: October 2010
Projected End Date: Ongoing

Objectives

Build theoretical tools to:

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

Technical Barriers

- Safety concern for lithium-ion batteries in electric drive vehicles (EDV) is one of the major barriers to widespread adoption of EDVs.
- The large number of design parameters for lithium batteries and the complicated interaction among them makes it unfeasible to experimentally identify the weakest link by conducting case-by-case tests.
- Safety evaluation results for battery packs built with the same materials but by different manufacturers are very different. The costs associated with building and testing safety in large-format cells, modules, and packs are significant. Whenever such data is collected it is treated as proprietary, thus preventing other battery developers from using any lessons learned.
- Scaling-up a battery greatly changes the path of a system developing a defect and its consequent behaviors during fault evolution.
- Timely detection of fault signals in large-capacity battery systems is extremely difficult.

Technical Targets

- Build case studies for swelling of pouch cells, using the component-level models built in FY11.

- Explore alternate design for battery modules at the system level to enhance safety of lithium-ion batteries.
- Develop a design and method to reliably detect and isolate faulted cells within a pack.

Accomplishments

- Built a model for gas generation due to decomposition of the electrolyte during overcharge and linked the results from the electrode level model to the cell level to simulate swelling of prismatic (pouch) lithium-ion cells
- Conceived a “fail-safe design” for battery systems
- Built a mathematical model to demonstrate the concept of fail-safe design for a large-capacity lithium-ion battery system
- Published a study in a peer-reviewed journal and filed a U.S. patent for the resultant fail-safe design invention.

Introduction

In FY12, NREL’s modeling activity to improve lithium-ion battery safety focused on two topics, with the first part emphasizing safety models for components within the cell, and the second part detailing our recent modeling and studies on developing fail-safe design for battery packs.

The first part aims to bridge the gap between materials modeling—usually carried out at the sub-continuum scale, and the multi-scale-multi-domain models. In FY11, we developed a tool to incorporate the microstructure of battery electrodes from SEM images. In FY12, we employed the results from the previous year to demonstrate coupling of material response under abuse conditions to cell-level observations. Pressure build-up and distribution within the cell during overcharge is chosen as an example. Preliminary validation work with cells from Dow-Kokam and data from NASA-JSC support our findings that the degradation rates can be up to ten times faster than what the conventional models predict.

Preventing catastrophic failures of large battery systems resulting from latent internal defects in lithium-ion batteries is extremely difficult with the approaches currently considered state of the art, due to the inability to detect early indicators or adequately respond to them.

NREL proposes remedying this situation with a passive, chemistry-agnostic, pack-level electrical architecture for large-capacity batteries that can reliably detect and, more importantly, isolate faulty cells within a pack. Preliminary reduction-to-practice efforts have proven NREL's basic concept and shown that system-level benefits can easily exceed the implementation cost.

Approach

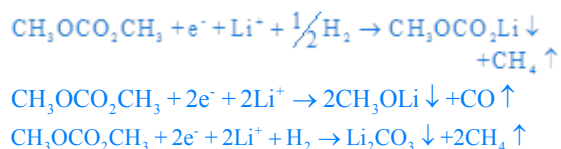
For the component models, the focus is to build mathematical descriptions more sophisticated than the traditional volume averaging approach to describe localized failure within the cells. In FY11, we developed a tool to incorporate the microstructure of battery electrodes from SEM images. The component models for the electrodes, interfaces, electrolytes, etc., incorporate the material properties calculated from micro-scale simulations. These component models are then integrated in to cell-level simulations. Building upon the framework from the previous year, we simulated the electrolyte decomposition mechanism as a case study and demonstrated the swelling of cells resulting from the pressure build-up due to accumulation of the gaseous products generated from decomposition of the electrolyte.

The solution proposed for the system-level safety enhancement is based on a novel battery pack architecture which can convert a localized fault response into a globally measurable signal. The passively amplified signal can be easily probed at the module/pack terminals under any operational condition to detect a fault occurring in any cell within the pack, providing information on both the status of an evolving fault and the location of the fault within the pack. The solution facilitates robust isolation of the fault by both passive and active limitation of its connectivity to surrounding cells, yet maintains partial power delivery from the pack following fault identification and isolation. Thus, a vehicle—even a series PHEV or BEV—still can be drivable if its battery has a faulty cell.

Results

Simulating Gas Evolution

As an example, the following decomposition reactions were considered in simulating the overcharge response when a lithium-ion cell is charged above the normal end-of-charge voltage (e.g., 4.2 V).



The gas generation rate and size of the bubble are influenced by the surface roughness, pore-size of the electrode, and parameters such as the vapor pressure, surface tension, and local density of the electrolyte. The size of the bubble corresponds to the region of the electrode surface that is unavailable for charge transfer. As a result, localized high-resistance spots develop across the electrode, resulting in a significant build-up of the local overpotential as shown in Figure III.E.7-1.

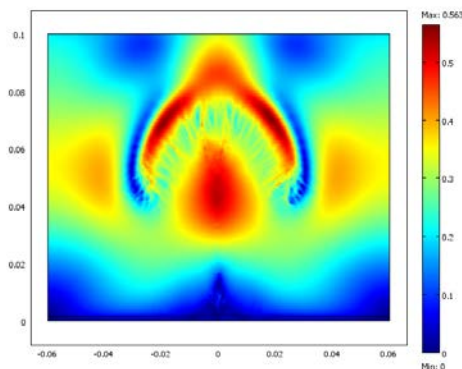


Figure III.E.7-1: Potential drop across the electrode/electrolyte interface due to the formation of a gas bubble on the electrode surface during overcharge: the ordinate $y=0$ represents the electrode surface.

The gas evolution rates on the electrode surface were then used to compute the localized buildup of pressure within prismatic cells. Sample results showing unequal distribution of reaction rates and swelling of pouch cells during overcharge are shown in Figure III.E.7-2. Such results enable the cell-designer to identify potential weak spots within the cell, which will likely initiate the failure of the cell under abuse.

Initial efforts to compare the pressure buildup within pouch cells to experimental data were started this year. NASA-JSC has testing capability to monitor cell pressure using micro-strain gauges. Order of magnitude estimates (24 bars from experiments versus 32 bars from models for C/5 rate, 70 bars from experiments versus 55 bars from models for the C/2 rate) indicate correct trends. A rigorous validation plan has been put together for future work.

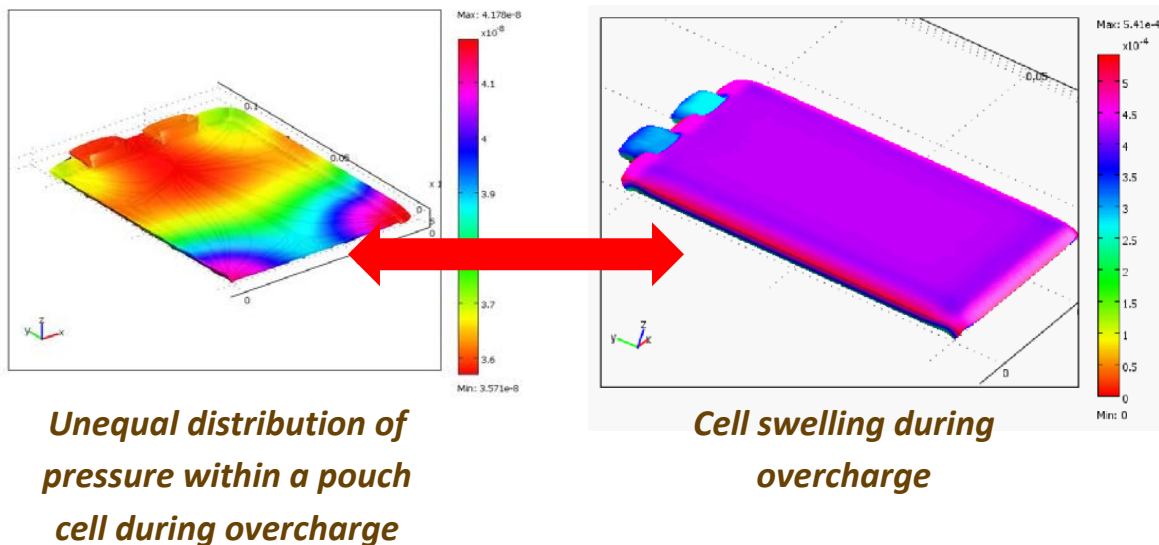


Figure III.E.7-2: Scaling up results from the component models to cell-level abuse simulations: This figure indicates the unequal pressure build-up across the interior of the cell during the swelling of a pouch cell. Notably, the region close to the tabs is highly constrained and is likely to suffer much more stress than the region far from it.

Fail-Safe Battery Design

At the pack level, we proposed an alternate way to connect cells within a module to enhance the safety of the battery. The proposed design claimed the ability to both detect an internal short circuit (ISC) in the early stages when its electrical resistance is still relatively high and before it evolves into a low-resistance hard short, as well as the ability to reduce current flowing through the short, and thereby reduce the risk of thermal runaway.

Computer simulations were performed to evaluate the viability of the proposed concept and to investigate the impact of the system design parameters and operating conditions. Multiple LIB cells were modeled in the fail-safe-design framework in the presence of various combinations of ISCs and pack-level power demands. The electric response of each LIB cell was predicted by resolving lithium diffusion dynamics and charge transfer kinetics using a model reduction technique.

Pack fault response model results indicate that the magnitude of the signal is shown to be a strong function of the resistance of the induced ISC. Therefore, a pre-developed database providing the relationship between the signal and the resistance of an ISC can be used to

determine the status of ISC evolution from an on-board control system. A viable signal of a fault should be detectable regardless of the use of a battery system. The model results show that the module output current does not greatly affect the signal. Therefore, the signal database for system control is not necessarily developed as a function of a module's output current. The signal is shown larger at the terminal closer to the faulted cell, because fewer balance paths are available around a faulted cell. The signal provides the information for identifying the faulted cell among the large number of cells in a module. Locating and isolating the defective cell in a module will provide a better chance to address the fault locally.

An experimental setup was used to demonstrate the proposed concept. The demonstration module consisted of two parallel sets of three Dow Kokam 8-Ah SLPB75106100 lithium polymer cells in series. Figure III.E.7-3 presents measured fault signals from 12 separate experiments for which faulted-cell location in the module, ISC resistance, and balance resistance are individually varied. Overall, the observations from the experimental demonstration of the concept confirm the model analysis for the functionality and viability of the proposed fail-safe design and method for large-capacity LIB systems.

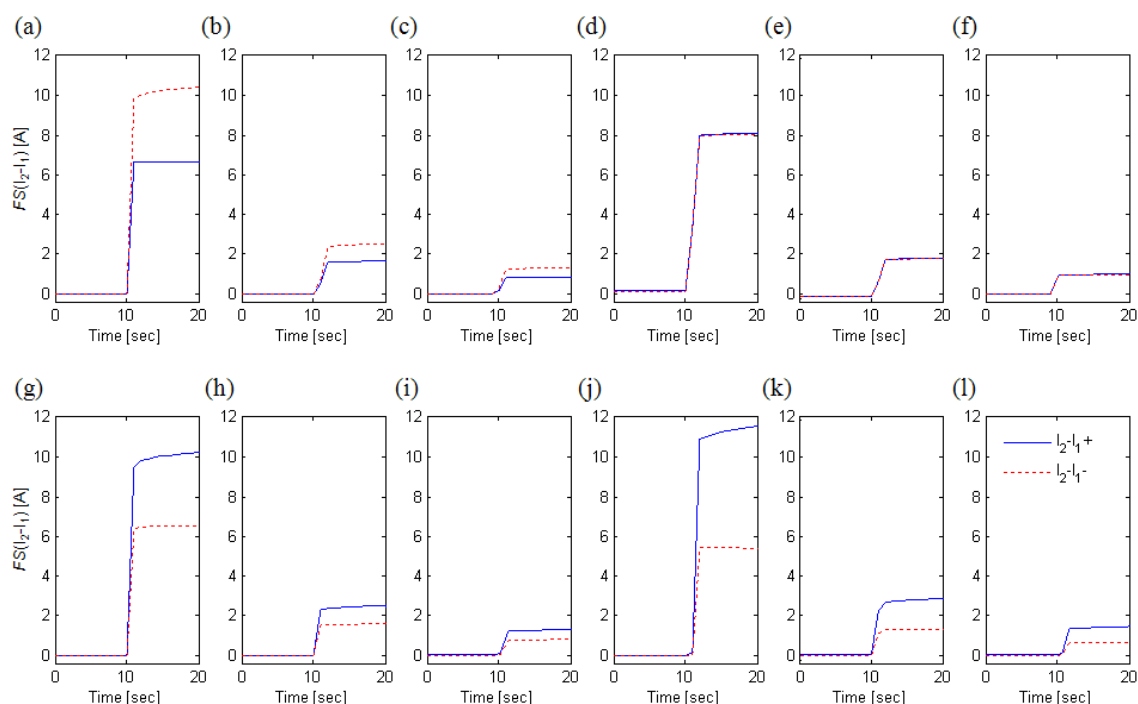


Figure III.E.7-3: Experimental results of fault signals (FS) at positive and negative module terminals (a) for 0.1- Ω ISC, (b) for 0.5- Ω ISC, and (c) for 1- Ω ISC induced in cell (1,1) in a module with conditions, $C_{mdl} = 16$ Ah (8 Ah + 8 Ah), $I_{mdl} = 0$ A, $N_s = 3$, $R_b = 0.2 \Omega$; same with (d), (e), (f) for ISCs induced in cell (1,2); same with (g), (h), (i) for ISCs induced in cell (1,3); same with (j), (k), (l) ISCs induced in cell (1,3) and $R_b = 0.1 \Omega$

Conclusions and Future Directions

Building detailed abuse models incorporating material properties provide a good insight for cell-designers. In this case study, multi-scale modeling with the pressure build-up in pouch cells helps identify weak spots within the cell. One of the biggest remaining challenges is determining the transport and reaction parameters to characterize the events happening inside the cell. Future work will include determining the model parameters and validating the key findings.

NREL developed a fail-safe design methodology for preventing catastrophic battery failures from latent internal defects in lithium-ion batteries. The solution proposed is based on a novel battery-pack architecture which can convert a localized fault response into a globally measurable signal. The passively amplified signal can be probed easily at the module/pack terminals under any operational condition to detect a fault occurring in any cell within the pack, providing information on both the status of an evolving fault and the location of the fault within the pack. A patent was filed with the concept, and a research article was published in the *Journal of Power Sources*. In FY13, we will demonstrate pack safety improvement with fail-safe-design concept applied to prototype module construction.

FY 2012 Publications/Presentations

1. S. Santhanagopalan, G.-H. Kim, K. Lee, K. Smith, and A. Pesaran, "Simulating Overcharge Reactions in a Lithium-Ion Cell," Presented at the 220th ECS Meeting and Electrochemical Energy Summit, Boston MA, Oct. 2011.
2. Shriram Santhanagopalan, Gi-Heon Kim, Kyu-Jin Lee, Kandler Smith, Ahmad Pesaran, "Effect of Microstructure on the Growth of the Solid-electrolyte Interface," Presented at the 2012 Spring Meeting & Exhibit of the Materials Research Society, San Francisco CA, Apr. 2012.
3. Venkatasailanathan Ramadesigan, Paul W. C. Northrop, Sumitava De, et al., "Modeling and Simulation of Lithium-Ion Batteries from a Systems Engineering Perspective," *J. Electrochem. Soc.* 159(3), R31-R45, 2012.
4. G.-H. Kim, K. Smith, J. Ireland, K.-J. Lee, and A. Pesaran, "Fail Safe Design for Large Capacity Lithium-ion Batteries," Presented at the 220th ECS Meeting and Electrochemical Energy Summit, Boston MA, Oct. 2011.
5. G.-H. Kim, K. Smith, J. Ireland, and A. Pesaran, "Fail Safe Design for Large Capacity Lithium-ion Battery Systems," *J. Power Sources* 210(2012) 243-253.
6. A. Pesaran, G.-H. Kim, M. Keyser, and K. Smith "Working Toward a Fail-Safe Design for Large Format Lithium-ion Batteries," Presented at Battery Safety 2011, Las Vegas, NV, Nov. 9-10, 2011.

IV.B.2.4 Development of Industrial Viable Electrode Coatings

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Start Date: January 2012
Projected End Date: September 2015

Objectives

To develop a deposition system for thin protective electrode coatings using a novel “in-line” atmospheric pressure atomic layer deposition (AP-ALD) reactor design that can be integrated into manufacturing to address needs for improvement in rate capability, cycle life, and abuse tolerance in a cost-effective manner.

Technical Barriers

Thin electrode coatings produced by atomic layer deposition (ALD) have been shown to lead to significant improvements in lithium-ion battery performance. At present, ALD is not likely suitable for large-format coating of deposited electrodes. This work seeks to develop new equipment for ALD that allows in-line deposition of coatings at room temperature.

Technical Targets

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

Accomplishments

- Demonstrated improved performance for an ALD alumina coated commercial electrode material.
- Demonstrated ALD alumina coatings on up to 6-in. by 6-in. substrates.
- Demonstrated atmospheric pressure ALD deposition on a moving substrate.
- Designed a new in-line ALD system for deposition on porous substrates.

Introduction

Recent work conducted by NREL and the University of Colorado at Boulder (CU-Boulder) has demonstrated improved performance for both anode and cathode materials following deposition of thin protective Al_2O_3 (alumina) coatings using atomic layer deposition. These protective ALD coatings have been shown to improve durability, rate capability, and operation at a higher potential versus Li/Li^+ and possibly can improve cell safety.

As an example, Figure IV.B.2.4-1 shows improved cycling performance for LiCoO_2 before and after ALD coatings. It is important to note that these samples were cycled from 3.3V to 4.5V which is considered an abusive condition for LiCoO_2 ; however the ALD coating appears to stabilize the electrode.

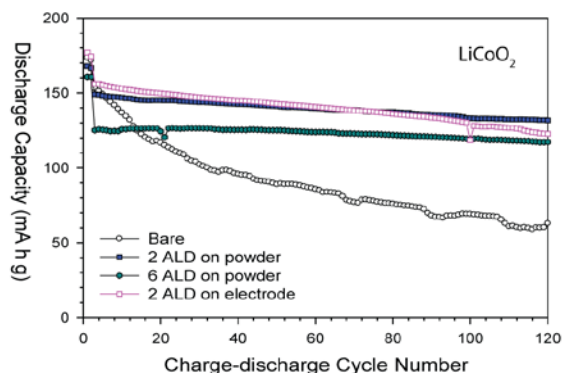


Figure IV.B.2.4-1: Cycling performance for ALD alumina coated samples of LiCoO_2 cycled between 3.3V and 4.5V

ALD is performed using sequential separate exposures of two (or more) reacting species to a stationary substrate at temperature and under a moderate vacuum (100 mTorr). Extensive purging is required between precursor exposure steps to eliminate the possibility of cross reaction in the gas phase. ALD

is not likely compatible with present battery manufacturing processes based on the need for vacuum as well as sequential static exposures of precursor materials and subsequent purging steps. NREL is developing a new reactor design that will enable ALD to be performed not only at increased pressures, but also on moving substrates.

Approach

As discussed above, ALD methods are conducted by sequential and separate exposure of a sample substrate surface to gas phase precursors which react to form a film. Deposition is typically performed in a closed reactor system at mild vacuum as shown in Figure IV.B.2.4-2. Precursor exposure steps are conducted in a single chamber and are separated *in time*. In a typical exposure “cycle,” a sample is exposed to one precursor and the chamber is then purged with inert gas prior to exposure to the second precursor and completing the coating reaction. The “cycle” ends with another extensive inert gas purging step before the process can be started again. Film growth takes place by repeating this cycling precursor exposure process multiple times. The sequential and separate exposures are the keys to achieving the excellent conformal film deposition on highly textured substrates for which the ALD technique is known.

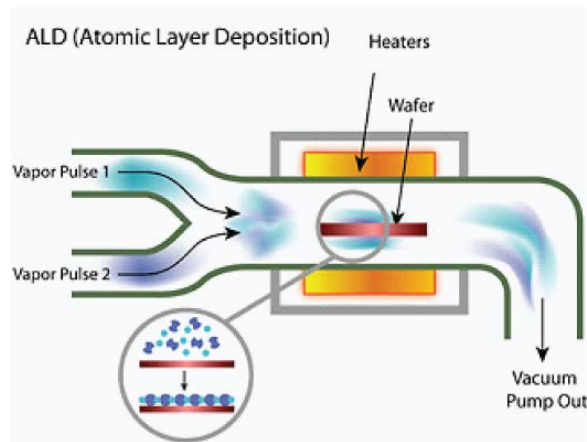


Figure IV.B.2.4-2: A typical ALD chamber with sequentially separated precursor exposure which draws out overall processing time

As an alternative to the temporal separation of precursor exposure in the same reaction chamber, our work proposes a *spatial* separation of precursor exposure steps that is more consistent with “in-line” processing techniques. Figure IV.B.2.4-3 shows a simplified conceptual schematic of our proposed apparatus.

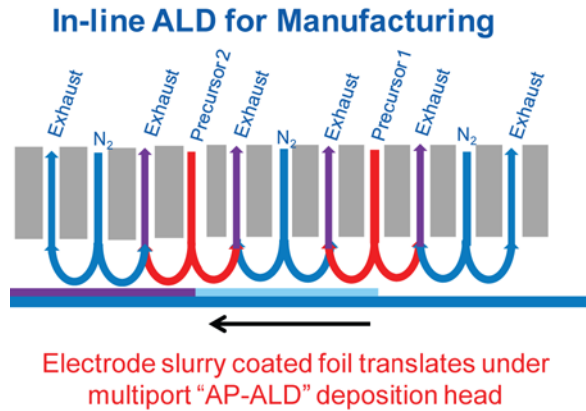


Figure IV.B.2.4-3: A simplified schematic demonstrating the in-line spatial ALD concept

Our “spatial” ALD approach employs a multichannel gas manifold deposition “head” that performs sequential exposure of precursor materials as an electrode foil translates beneath it. It is important to note that similarly designed deposition heads are currently employed by glass manufacturers for production of a variety of coated-glass products using high-volume, in-line atmospheric pressure chemical vapor deposition (AP-CVD). Our approach leverages this existing knowledge base as well as our ALD expertise to enable in-line ALD coating that will allow the transfer of our previously demonstrated ALD-based performance improvements to larger-format devices.

Results

Our initial project focus has included two main thrusts. The first involves studies of the effect of ALD alumina coatings on a variety of commercial cathode materials. The second focuses on scaling of the ALD process. We have demonstrated ALD coatings on electrode foils up to a size of 6-in by 6-in and also conducted work on an improved design for in-line ALD on porous electrode substrates. All of these areas are discussed in more detail below.

Development of In-Line ALD

Leveraging and building upon previous work by our collaborators at the CU-Boulder, we recently completed a preliminary design for an in-line ALD system specific for deposition on porous substrates. The majority of our previous work focused on the deposition of aluminum oxide via the reaction of trimethyl aluminum with water vapor. More recent work performed by Professor Steven George’s group at the CU-Boulder showed that aluminum oxide could be deposited onto flat silicon substrates using an in-line atmospheric pressure ALD (AP-ALD) format.

Figure IV.B.2.4-4 shows the design for the initial in-line AP-ALD demonstration from our collaborators at CU-Boulder. The deposition system consists of a multichannel gas manifold that creates separated exposure zones for both trimethyl aluminum and water. For the demonstration, a silicon wafer was placed on a heated substrate which was translated underneath the gas flow head. The wafer substrate was moved back and forth below the deposition head to drive two full ALD alumina deposition cycles per translation. All deposition was performed at atmospheric pressure. An example of an alumina film deposited on a silicon wafer using in-line AP-ALD is shown in Figure IV.B.2.4-5.

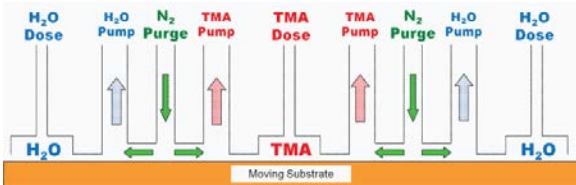


Figure IV.B.2.4-4: A preliminary design from the George group for demonstration of in-line AP-ALD

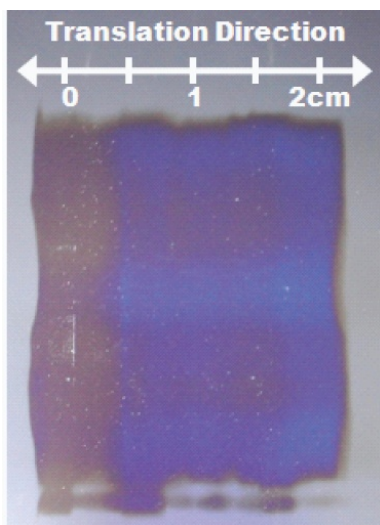


Figure IV.B.2.4-5: Demonstration of in-line deposition of aluminum oxide onto a silicon wafer at atmospheric pressure

Design of In-Line AP-ALD for Porous Substrates

Although the work described has demonstrated the feasibility of in-line AP-ALD, a crucial factor for successful coating of battery electrodes using this technique is the ability to coat *porous* substrates. Coating of a porous substrate presents a specific technical challenge, as precursor materials must be able to fully penetrate as well as be removed from the porous film as rapidly as possible. This requires that the porous film be exposed to alternating high and low gas-pressure regimes. Under viscous flow (high pressure) conditions, a high number of gas phase collisions drives

penetration of precursor gases into the film, while molecular flow conditions (low pressure) allow rapid removal of unreacted precursor prior to the next precursor exposure step. Figure IV.B.2.4-6 shows a recently completed improved design that allows in-line deposition to be performed with alternating pressure regimes.

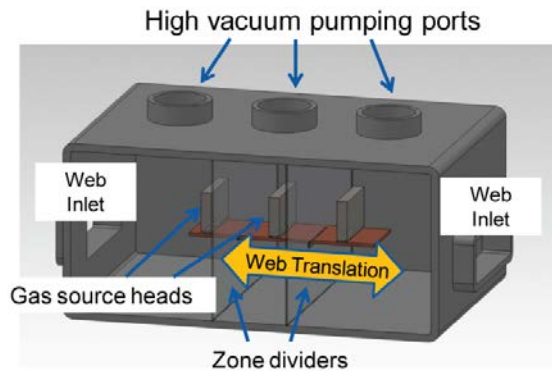


Figure IV.B.2.4-6: Initial design of an in-line ALD reactor for deposition on porous substrates

As shown in this new design, the coated electrode foil translates underneath multiple gas-source heads similar to the gas head designs shown above, but these gas deposition heads are contained in a larger chamber at a reduced pressure to facilitate removal of unreacted precursor. We are currently in the process of completing the hire of a post-doctoral researcher who will construct and test the initial prototype for this new reactor.

Deposition on Large-Format Samples

In addition to work related to in-line AP-ALD, NREL also recently has acquired a larger format ALD system. This system allows ALD to be performed on electrode foils of up to 6-in. by 6-in. This system will be used to facilitate larger format pouch cell testing while the in-line depositions systems are completed. Figure IV.B.2.4-7 shows a 6-in. by 6-in. foil of TodaHE5050 provided by the Argonne Cell Fabrication facility that has been coated with five cycles of ALD alumina. Cells fabricated from this sample currently are being tested and larger format cells will be provided to external parties for testing once initial efficacy of the coating method is established.



Figure IV.B.2.4-7: A 6-in by 6-in foil of Toda HE5050 following coating with 5 cycles of ALD alumina; Photo credit: Rob Tenent, NREL

Initial Screening of Commercial Electrode Materials

NREL has obtained a variety of electrodes and electrode materials (powders) from collaborators at Argonne National Laboratory (Bryant Polzin and Andy Jansen) and Sandia National Laboratories (Chris Orendorff) to enable preliminary investigation of the effects of ALD coatings. Table IV.B.2.4-1 lists the materials received.

Table IV.B.2.4-1: ABR Electrode Materials Received for Coating with ALD Alumina

A12 Graphite
Toda HE5050 NMC
Toda NCA
AML Made LiNiMnO
Toda NMC111
Toda NMC 523

All materials have been under extensive evaluation initially on a coin cell format level at NREL prior to coating with aluminum oxide using ALD. At present, ALD alumina depositions have been performed on formed electrodes of Toda NMC111 from Sandia as well as Toda HE5050 from Argonne, and samples currently are being tested.

Toda NMC111

In collaboration with Sandia, NREL performed ALD alumina coating on electrode foils of Toda NMC111 and CP A10 graphite. These foils were used for fabrication of 18650 cells and subsequent thermal analysis to determine the effect of ALD coatings on suppression of high-temperature thermal runaway. Figure IV.B.2.4-8 shows coated foils and 18650 cells fabricated at Sandia. These electrode foils were coated by rolling up the foils and placing them in a standard

ALD deposition system. Upon return to Sandia, 18650 cells were fabricated and tested. Cells were formed with coated anode or coated cathodes paired with uncoated electrodes to ease the determination of the effect of ALD coating on either electrode. Upon initial testing, we found that several cells failed. The cause was attributed to damage due to the electrode rolling process that was used to enable deposition in the existing (not in-line) ALD systems. Cell failures were found to predominate with the coated cathode cells; however, several coated anode cells were functional and subjected to accelerated rate calorimetry (ARC) testing at Sandia to examine the effect of ALD coatings on thermal runaway. Figure IV.B.2.4-9 shows ARC data from Sandia for one of the coated anode cells. Comparison of measurements made for an identical cell fabricated without any ALD coating appears to show an approximately 20°C increase in the onset temperature for high-rate thermal runaway. This likely indicates that the ALD coatings stabilize the anode and suppress high temperature decomposition.

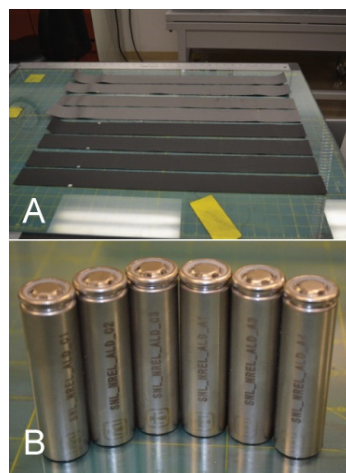


Figure IV.B.2.4-8: (A) Samples of NMC 111 and A10 Graphite provided by Sandia and coated with ALD alumina by NREL/CU (B) 18650 cells fabricated from coated ALD foils for testing at Sandia; Photo credit: Rob Tenent, NREL

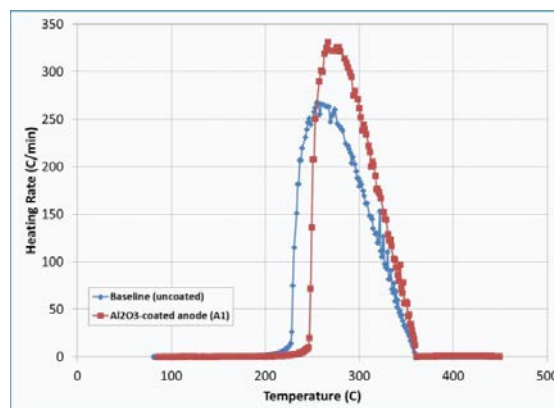


Figure IV.B.2.4-9: Accelerated rate calorimetry data for cells with and without an ALD alumina-coated anode

Although these data suggest that ALD coatings might improve safety, significant further work is needed and planned to assess this. To avoid the previous issues of damage to electrode foils, NREL is currently developing coating processes for powders of NMC 111 and 523 that can be used for further studies.

Toda HE5050

In addition to testing the NMC 111 material, NREL is working on characterizing the performance of ALD coatings on Toda HE5050 using already formed electrodes provided by the Argonne Cell Fabrication Facility (Bryant Polzin). Work in this area has been conducted to date using standard, single-chamber, ALD systems to perform initial screening experiments. The HE5050 material was chosen for further experimentation due to interest in understanding how ALD coatings can impact the voltage-fade phenomenon observed for this material.

Figure IV.B.2.4-10 shows initial cycling capacity data for HE5050 electrodes tested in a half-cell format under a variety of conditions with and without ALD alumina coatings. The samples for the data shown in Figure IV.B.2.4-10 consist of an untreated sample that was tested as received (bare) and two samples that were coated with either 5 or 100 cycles of ALD alumina. In addition to these coated samples, another control sample was placed in the ALD reactor and exposed to an identical process temperature profile, but without *deliberate* precursor exposure. The data in Figure IV.B.2.4-10 appear to show that the ALD coated and ALD control samples give better cycling durability than that of the uncoated sample.

Interestingly, the ALD control sample that was only exposed to heating appears to give a similar response to the 5 ALD cycle sample. We also note that similar experiments with 10 and 20 cycles of ALD alumina showed nearly identical behavior to the five-cycle sample. This result is inconsistent with multiple previous observations that an increase in the number of ALD cycles leads to a decrease in initial capacity. In an attempt to further understand the situation, coating experiments were performed with 100 cycles of ALD alumina on an HE5050 electrode. The 100-cycle sample does show the initial capacity loss as well as apparently improved cycling durability as compared to a bare sample.

Based on the current data, our hypothesis is that although it is certainly possible that the thermal treatment of the HE5050 sample in the ALD chamber might well play a role in improving performance, the absence of the expected capacity decreases with the 10- and 20-cycle samples likely indicates incomplete coverage of the electrode at low cycle number under the deposition conditions used. Issues with nucleation of ALD films are not uncommon and NREL is currently

conducting further experiments based on modifying deposition conditions as well as performing “post mortem” analysis of existing samples to understand these issues. At present, the observed behavior is not clearly understood.

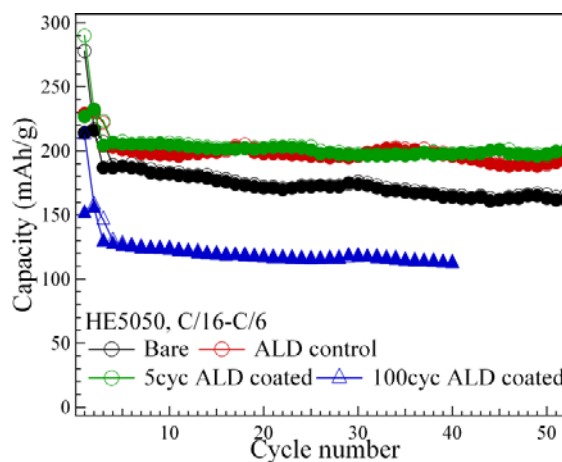


Figure IV.B.2.4-10: Cycling capacity performance for a variety of HE5050 samples with and without ALD coatings (condition details are provided in the accompanying text)

Conclusions and Future Directions

Significant progress was made this year on the development of an in-line ALD coating system compatible with coating on formed electrodes. By leveraging existing expertise with our collaborators in the George group at CU-Boulder, we have been able to significantly reduce the amount of time required to demonstrate in-line atmospheric pressure ALD, and move toward design refinement specific to battery materials. We have completed an initial design for a new battery-specific in-line reactor and are currently completing hiring a post-doctoral staffer to begin work on prototype system construction and demonstration. We anticipate work on this new system to initiate in early CY13.

NREL will continue to work with other Applied Battery Research (ABR) PIs not only to supply ALD coated materials (both powders and electrodes), but also to further understand the role that these materials can play in a variety of systems.

FY 2012 Publications/Presentations

1. 2012 DOE Annual Peer Review Meeting Presentation.

IV.B.2.5 Evaluate Impact of ALD Coating on Li/Mn-Rich Cathodes (NREL)

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Collaborators:
C. Ban, NREL

M. Alamgir, LG Chem Power, Inc.

D. King, K. Buechler, ALD Nanosolutions

Start Date: June 2012

Projected End Date: Projected September 2013

Objectives

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

Technical Barriers

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

Technical Targets

- Demonstrate capacity loss of less than 20% at C/2 rate over 500 cycles at 45°C for the high-voltage manganese-rich cathode.
- Demonstrate scalability of the ALD process by coating batches up to 500g of the manganese-rich

cathodes with alumina, to reproduce cell-level performance observed at the lab scale.

- Build capabilities to directly coat electrode sheets of up to 6-in. by 6-in.

Accomplishments

- Collaborated with LG Chem Power Inc. and obtained commercial samples of Li-Mn-rich cathode materials.
- Collaborated with ALD NanoSolutions—a leading company for coating ALD on battery materials—to scale-up ALD coating using alumina on high-capacity Mn-rich cathode material.
- Initial evaluation of the coated powders show little to no reduction in cell capacity over 50 cycles.
- Initiated modification of reactor to coat electrode sheets.
- Initial results indicated that 2- to 3-cycle ALD coatings with Al_2O_3 could decrease the Li/Mn-rich fade rate.

Introduction

Extending the driving range of PHEVs requires the use of high-voltage cathodes that offer consistent performance over 5,000 cycles or 15 years of battery life without compromising safety. The Mn-rich cathode is an excellent choice of material for these specifications, and has been shown to have the potential to be stable over a wide voltage window of between 4.5 and 2.7 V. Preliminary work at the laboratory scale performed by NREL and LG Chem Power Inc. indicates that although ALD coating of the cathode improved its cycling performance, no enhancements were observed for coating carbon-based anodes. In the current effort (initiated in June 2012), we demonstrate the scalability of the ALD process and reaffirm findings from the preliminary study, using large-format pouch cells. We also are exploring the viability of coating sheets of electrodes directly.

Approach

Powders

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

Electrodes

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

Results

In FY12, the focus was on scaling-up the ALD coating of powder samples. Two different samples of cathode powders were provided by LGCP. Each of these samples was subjected to two different ALD coating profiles (Run 1 and Run 2) to assess the uniformity of the coating and the resistance as a function of the number of cycles. The profiles were chosen based on the preliminary investigation of these cathode materials carried out earlier at NREL.

ALD Coating

The pre-processing step included drying overnight. No unusual off-gassing or decomposition reactions were observed. The coating process involved the following steps.

1. Loading the bed of powders into the fluidized bed reactor (shown in Figure IV.B.2.5-1).
2. Fluidizing the powders at the coating temperature and pressure.
3. Introducing the ALD precursors sequentially. Each cycle comprised of the routine A-purge-B-purge, and the process was repeated for the desired number of cycles.

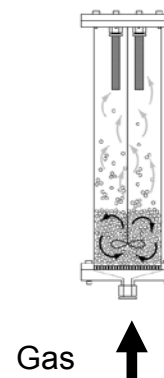


Figure IV.B.2.5-1: Fluidized bed reactor to coat powders with ALD cycles: the existing reactor at ALD Nanosolutions can process up to 8L of powder per batch; Photo credit: Shriram Santhanagopalan, NREL

The coating was carried out at the vendor's (ALD Nanosolutions') facility in Broomfield, Colorado. ALD Nanosolutions has been performing ALD coating of battery materials and has the capability to process multiple batch sizes from tens of grams to tens of kilograms. The samples were fluidized at 10 cm^3 per minute after the initial drying. The coating time per batch was about 2.5 hours. The initial trials focused on alumina coatings, because we had demonstrated the proof-of-concept with alumina on the Mn-rich cathode material.

Characterization

The baseline sample consisted of spherical particles with a D_{50} of 11 and 12 μm for the two batches (Sample 1 and Sample 2). The SEM images before and after coating are shown in Figure IV.B.2.5-2. A uniform coating is observed for both the cycle profiles. Upon coating, the alumina content after Run 1 and Run 2 is as shown in Table IV.B.2.5-1. Run 1 employed fewer cycles to form a thin ALD coating and Run 2 involved a thicker coating.

Table IV.B.2.5-1: Composition of Alumina on Different Batches of Mn-Rich Cathode Material Coated with Al_2O_3 Using ALD

Sample ID	Run 1	Run 2
1	0.98%	1.86%
2	1.12%	1.91%

Physical observations showed that the alumina on Sample 2 tends to flake off readily (perhaps due to a different surface treatment on the baseline particles). Neither sample showed any degradation or discoloration when stored in the electrolyte at 60°C for two weeks.

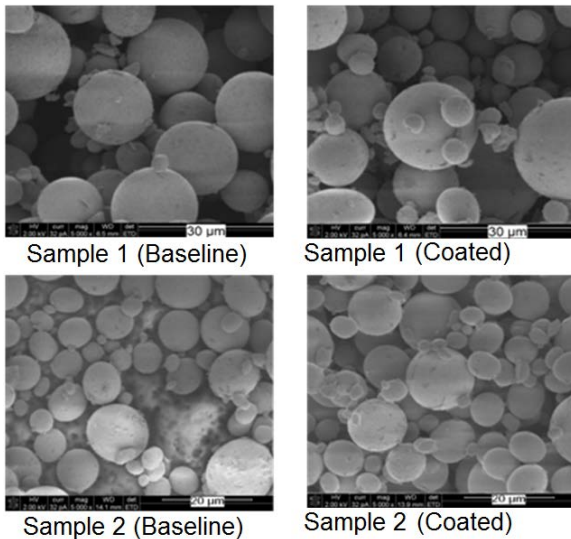


Figure IV.B.2.5-2: SEM images of two different batches of Mn-rich cathode powders coated with alumina; the coatings are uniform and conformal over a range of baseline particle sizes

Cell-Evaluation

The coated material was evaluated using coin cells at NREL and pouch cells at LGCPI. The sample coated in Run 1 showed good cyclability and low IR-drop during the 1C discharge pulses (Figure IV.B.2.5-3). The cells fabricated with the samples coated in Run 1 showed almost no degradation after 50 cycles at 100% depth of discharge (DOD), when cycled at 25°C at the C/2 rate. As shown in Figure IV.B.2.5-4, the baseline samples showed a detectable loss in cell capacity under identical conditions.

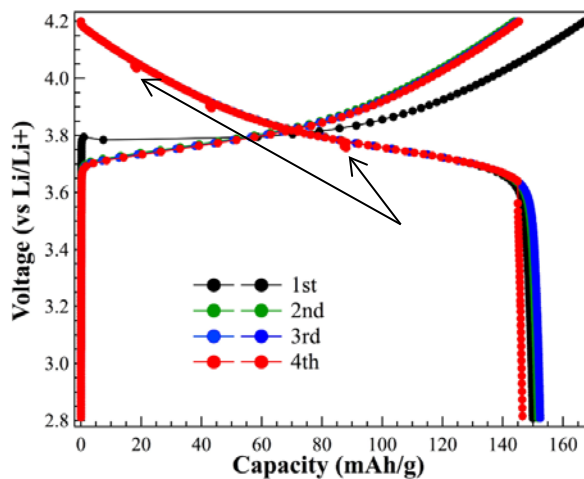


Figure IV.B.2.5-3: Initial evaluation of Sample 2 coated with Al₂O₃ in Run 1 using coin cells at NREL: Charge and Discharge at C/5 (250C) with 1C-discharge pulses for 20s after every 10% discharge

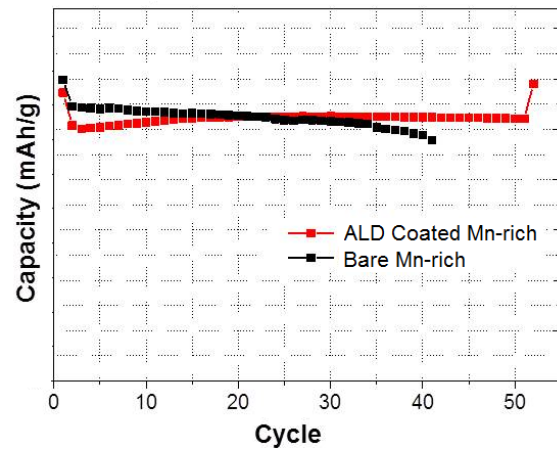


Figure IV.B.2.5-5: Cycling performance of pouch cells at 25°C subjected to 100% DOD cycles at the C/2-rate

The samples coated in Run 2 showed higher resistance versus the baseline material as confirmed by electrochemical impedance measurements (Figure IV.B.2.5-5) possibly because the coating thickness is greater.

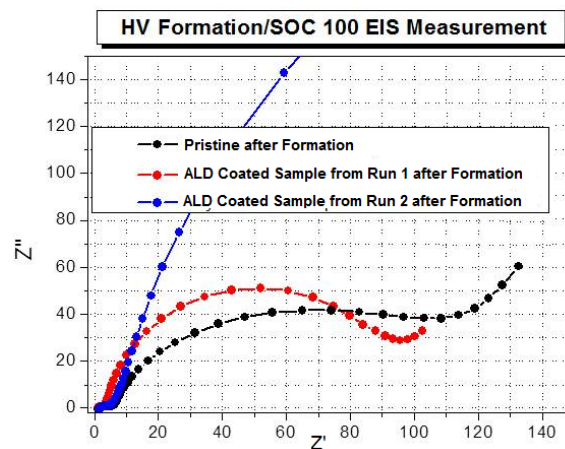


Figure IV.B.2.5-5: EIS measurements on Mn-rich cathode material coated with different ALD layers of Al₂O₃: the powders coated in Run 2 show larger impedance build-up compared to the baseline

Conclusions and Future Directions

The initial results indicate that the ALD technique is quite scalable with the cathode powders. A semi-continuous production option has also been validated for large-scale manufacturing that will facilitate industry adoption. Initial results indicated that 2- to 3-cycle ALD coatings with Al₂O₃ can decrease the Li/Mn-rich fade rate. The initial cycles of the baseline particles coated Al₂O₃, show a gradual increase in the cell capacity. This is indicative of the need for optimizing the coatings and the cathode properties, to enhance mutual compatibility, and maximize the cell performance. A predictive roadmap is an integral

feature to expedite the commercialization of the technology. Future runs will focus on such optimization based on these initial results.

The second part of the project focuses on coating electrode sheets directly with ALD cycles. Toward this end, modification of the reactors to coat electrodes is underway. NREL has been working with ALD Nanosolutions to install electrode-racks to facilitate coating of electrodes as large as 6-in. by 6-in. Future work will include coating of sheets of electrodes.

FY 2012 Publications/Presentations

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

V.C.10 Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes (NREL, University of Colorado)

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Start Date: October 1, 2010
Projected End Date: September 30, 2014

Objectives

- Develop a novel conductive and elastic framework for Si anodes using atomic layer deposition and molecular layer deposition (MLD).
- Demonstrate durable cycling performance of thick Si anodes by using new ALD/MLD coatings and electrode designs.
- Investigate effects of atomic surface modification on irreversible capacity loss and structural evolution during cycling.
- Explore the importance and mechanism of various coatings via the BATT Coating Group.
- Collaborate within the BATT program with the aim of developing high-rate plug-in hybrid electric (PHEV) 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

- Stabilize the high-capacity silicon anodes by employing the advanced surface coating techniques, ALD and MLD.
- Demonstrate the stable high-rate cycling performance of Si anodes.
- Relevant to USABC goals: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3,000 cycles (PHEV 40 mile requirement). Calendar life: 15 years.
- Improved abuse tolerance.

Accomplishments

- Successfully developed the Si thick electrode ($\geq 15 \mu\text{m}$) with a highly reversible capacity of at least $2,000 \text{ mAh g}^{-1}$ at C/20 (175mA/g).
- Demonstrated the high-rate capability (at C/3, $\sim 1200 \text{ mA/g}$) for Si-polyacrylonitrile (PAN) composite electrodes.
- Demonstrated mechanistic information about ALD coatings via in-situ synchrotron X-ray diffraction, and ex-situ X-ray photoelectron spectroscopy and time of flight secondary ion mass spectrometry (TOF-SIMS).
- Greatly improved cycling performance of full cells by applying Al_2O_3 ALD coating on electrodes and separators.
- Performed density functional theory simulations of lithiation in silica through partial reduction.

Introduction

Significant advances in both energy density and rate capability for Li-ion batteries are necessary for implementation in next-generation EVs. Due to the high theoretical capacity of Si, 3579 mAh g^{-1} for $\text{Li}_{15}\text{Si}_4$, and its natural abundance, silicon has attracted much attention as a promising Li-ion anode material. However, progress towards a commercially viable Si anode has been impeded by Si's rapid capacity fade caused by the large volumetric expansion. Such a massive volumetric change can result in cracking and pulverization of the Si particles, which leads to the interruption of electronic transport pathways and the electrochemical isolation of pulverized particles.

Using an ALD conformal nanoscale coating of Al_2O_3 on nano- MoO_3 has greatly improved the performance of these electrodes despite the volumetric expansion of nano- MoO_3 electrodes ($> 100\%$). The nanoscale conformal coating of Al_2O_3 is believed to stabilize the surface and enhance the mechanical integrity of MoO_3 electrodes. These past results suggest that new ALD and MLD coatings can be developed to accommodate the volumetric expansion of Si anodes, and ensure the electronic paths through the electrodes.

Both high rate and durable cycling of Si will be achieved by employing the ALD coating and new elastic (polymer-like) coatings with low elastic moduli that are similar to polysiloxanes. We collaborated with multiple outside organizations to investigate the effects of the ALD/MLD coatings and to demonstrate nano-structured materials. Ultimately, we are enabling the development of both high-capacity anodes and cathodes within the BATT program that exhibit durable high-rate capability.

Approach

Chemical vapor deposition via silane decomposition on a hot filament was used to synthesize the amorphous silicon particles. Recently, a nanocrystal RF plasma reactor has been utilized to synthesize silicon/alloy nanocrystals with uniform size and shape. Size can be tuned from < 10 to ~ 100 nm by varying the plasma conditions that will allow the study of how Si nanocrystal size affects the electrochemical performance. Conventional electrodes containing active material, conductive additive, and binder have been fabricated to evaluate the cycling properties.

ALD was employed to coat both Si particles and Si electrodes to enhance the surface stability and electrode integrity. Further, MLD was applied to develop a novel conductive and elastic framework to accommodate the volumetric changes in Si particles. Besides an Al-based precursor, other metal precursors are used to enhance the conductivity in the MLD flexible coatings.

Results

Development of Si-Cyclized PAN Composite Electrode

Greatly improved cycling performance was achieved by using Si-cyclized polyacrylonitrile hybrid material as an Li-ion anode. Optimal performance was achieved through the use of low-temperature heat-treated composite electrodes. The mechanical properties of the Si-cyclized PAN hybrid material were studied by nanoindentation. Figure V.C.10-1 exhibits the hardness and reduced elastic modulus (E_r) of the cyclized PAN at different synthesis temperatures. The E_r of the cyclized-PAN, calculated by using nanoindentation, remains consistent below 500°C . It confirms that the low-temperature cyclized-PAN keeps the similar mechanical properties as the pristine polymer. However, an abrupt increase in hardness was found at temperatures $\geq 300^\circ\text{C}$. This sudden increase in hardness is due to the cyclization of PAN at $\sim 300^\circ\text{C}$. The cyclization of PAN has been verified with the results from Raman spectroscopy.

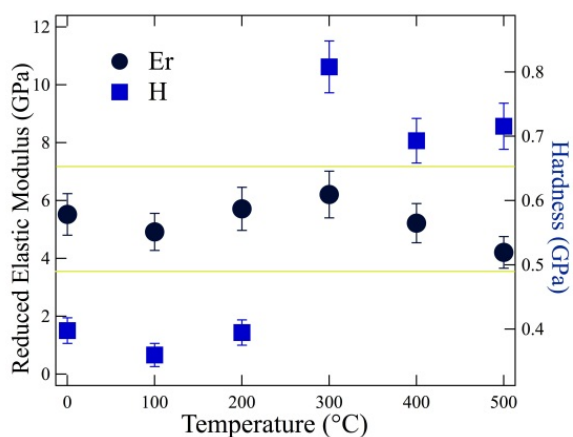


Figure V.C.10-1: Hardness and elastic modulus of PAN with increasing annealing temperature

The formation of the sp^2 bonding in the Si-PAN hybrid material was confirmed with Raman spectroscopy. Figure V.C.10-2 presents the Raman spectra for the pristine PAN, and Si-PAN cyclized at 300°C , and Si-PAN cyclized at 500°C . The two Raman shifts at $1,600 \text{ cm}^{-1}$ and $1,360 \text{ cm}^{-1}$ were obtained in both cyclized Si-PAN materials, which were attributed to the G band and D band from a graphite-like structure. However, these two peaks are absent in the Raman spectrum of the pristine PAN. The observation of both the D and G bands attests to the existence of graphite-like domains with varying degrees of crystallinity. The peaks in the cyclized PAN were fitted with a Gaussian-Lorentzian function to compare the relative intensity of the G band (crystalline graphite-like structure) and D bands (disordered graphite-like structures). As indicated

in Figure V.C.10-2 b and c, a stronger relative G band for the sample treated at 500°C indicates a graphite-like structure with a higher degree of order than that for the sample treated at 300°C. The evolution of a cyclized pyridine-ring structure occurs at a low temperature of ~300°C. These cyclized pyridine rings have sp² bonding with delocalized π bonding, which enables good electronic conductivity.

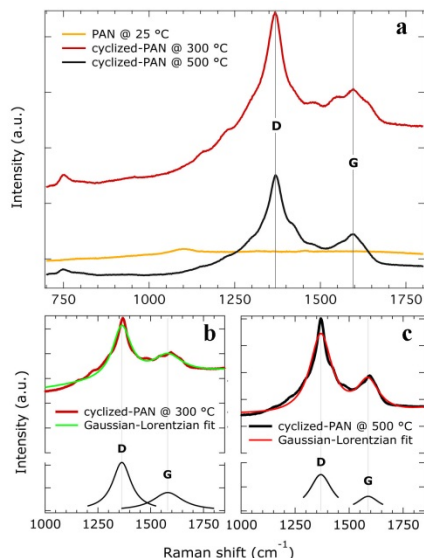


Figure V.C.10-2: Raman spectrum of pristine PAN and cyclized PAN

Rate Capability of Si-Cyclized PAN Composite Electrode

The development of the cyclic (ring) polymeric molecular structure at low temperatures enhances the electronic conductivity but also maintains the favorable mechanical properties of the polymer.

The Si-cyclized PAN nanostructure has demonstrated the stable cycling performance with minor degradation of the cycling capacity. Plotting the differential capacity as a function of voltage confirms the structural stability after the first lithiation process, and shows highly reversible Li-alloying/dealloying over 50 cycles without degradation, as indicated in Figure V.C.10-3. Electron energy loss spectroscopy (EELS) overlay mapping image of the Si-C core-shell nanostructure, seen in the overlay of Figure V.C.10-3, displays the cyclized-PAN shell covering the silicon core.

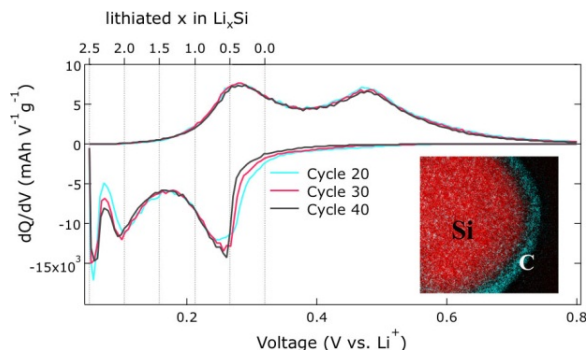


Figure V.C.10-3: Differential capacity vs. voltage curves represent the highly reversible cycling of Si-cyclized PAN electrodes, the inset shows EELS mapping image of the core-shell nanostructure

The rate-capability has been demonstrated in the half-cells with Li metal, as shown in Figure V.C.10-4. The cells were cycled at C/20, followed by 20 cycles at C/10, then finally cycled at C/3. The Si-cyclized PAN has a reversible capacity of 800 mAh g⁻¹ at a cycling rate of C/3 for more than 100 cycles, and retains a reversible capacity of 600 mAh g⁻¹ after 300 cycles. Moreover, coulombic efficiency of the Si/cyclized-PAN composite anodes approaches 100% after 150 cycles. The greatly improved cycling performance at a rate of C/3 is believed to be due to the enhanced electronic and mechanical properties of the Si-cyclized PAN composite material.

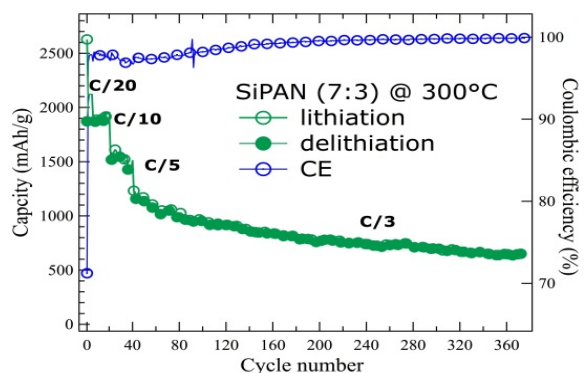


Figure V.C.10-4: Sustainable cycling performance of Si-cyclized PAN electrodes at the higher cycling rates

Effect of Al₂O₃ ALD Coatings on SEI Composition of Li-ion Electrodes

The effect of Al₂O₃ ALD coatings on solid electrolyte interphases (SEI) formation also was studied by using ex-situ XPS and TOM-SIMS. The full cell composed of LiCoO₂ (LCO) cathode and natural graphite anode (NG) was used as a platform. Figure V.C.10-5 summarizes the XPS results from NG (a-e) and LCO (f-j) electrodes before and after cycling. The presence of the Al₂O₃ ALD layer has been observed on coated-NG (c-NG) XPS (Figure V.C.10-5d and e). Unexpected peaks at ~286.2 eV for C 1s (Figure

V.C.10-5a) and ~ 686 eV for F 1s (Figure V.C.10-5b) on c-NG indicates a chemical interaction between Al_2O_3 ALD species and the carbon in NG or PVDF—chemically changing the PVDF by ALD. The signals from the cycled c-NG also show the SEI signatures except for the Li_2O . Additionally, the cycled c-NG does not show the Li_2CO_3 peak at ~ 290.3 eV for C 1s, but it is evident on bared NG (b-NG) (Figure V.C.10-5a). A much higher intensity of the Li 1s peak was observed for the cycled b-NG than that for the cycled c-NG (Figure V.C.1-5c).

These observations indicate that we have significantly mitigated side reactions by using Al_2O_3 ALD coating. Overall, the analyses of XPS signals from NG suggest that the c-NG has a markedly different SEI from that of the b-NG in terms of the amount and also the composition. Further, the Al_2O_3 ALD coatings on the NG anodes result in a suppression of the side reactions on the bare LCO cathodes. An LiF peak at ~ 685 eV for F 1s (Figure V.C.10-5h) is very intense for the b-LCO cathode paired with a b-NG anode. The peak is negligible for b-LCO paired with c-NG. The overall shape of O 1s spectra for b-LCO/b-NG is quite different from that for b-LCO/c-NG (Figure V.C.10-5j), suggesting that a b-LCO/c-NG pair leads to different SEI components from b-LCO/b-NG.

An ex-situ TOF-SIMS has been performed to confirm the effect of Al_2O_3 ALD on the thickness of SEI components. The depth profiling data of the ions on cycled NGs and LCOs by TOF-SIMS is shown in Figure V.C.10-6a-f. For NG electrodes, Al^+ signals and others (Li_2O^+ , Li_2F^+ , CH_3^+) contributed to Al_2O_3 ALD and inorganic (Li_2O^+ , Li_2F^+)/organic (CH_3^+) components of the SEI, respectively. Two dramatic differences between b-NG and c-NG are: (1) the thickness of Li_2F^+ on b-NG (~ 24 nm) is almost twice than that on c-NG; and (2) CH_3^+ signals are very intense only for b-NG (arrow). *The TOF-SIMS results strongly reflect a much thinner SEI layer with much less organics on c-NG than on b-NG.* In contrast, the signals for b-LCOs don't give any pronounced difference between b-LCO/b-NG and b-LCO/c-NG from the TOF-SIMS data (Figure V.C.10-6e, f). This observation could indicate that the key to govern the degradation of b-LCO might not be related to the thickness of the SEI. From the combined analyses by ex-situ XPS and TOF-SIMS, the following conclusions are possible: (1) The Al_2O_3 ALD coating significantly mitigates the surface reaction on NG, forming thinner SEI with significantly reduced organic species; and (2) compared with b-LCO paired with b-NG, b-LCO paired with c-NG shows similar thickness of the SEI but a different composition. Thus, improved durability has been achieved in the full cell of b-LCO/c-NG.

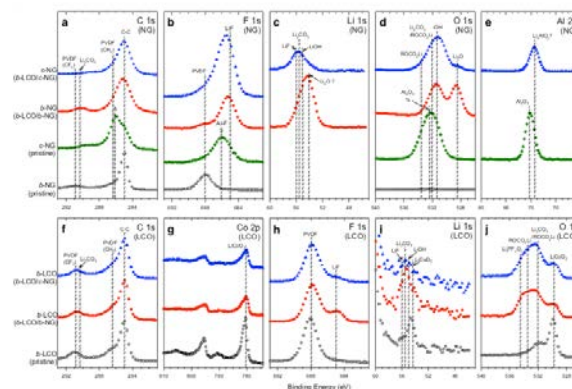


Figure V.C.10-5: XPS spectra of NG and LCO electrodes before and after the charge-discharge cycles

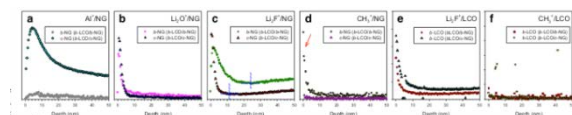


Figure V.C.10-6: Time-of-flight secondary ion mass spectrometry (SIMS) analyses of cycled NG and LCO electrodes from b-LCO/b-NG and b-LCO/c-NG full cells

Conclusions and Future Directions

By cyclizing commercially available polyacrylonitrile, a pyridine-based conjugated polymer is obtained to accommodate Si's volumetric expansion during lithiation. Pyridine also has delocalized sp^2 π bonding for intrinsic electronic conductivity. Good ionic conductivity of cyclized-PAN coatings is assumed based upon good electrochemical performance at fast cycling rates. For increased electrode energy density, cyclized-PAN coatings serve as both conductive additive and binder singly. Therefore, the cyclized-PAN acts both as a binder and conductive additive because of its good mechanical resiliency to accommodate silicon's (Si) large expansion as well as its good ionic and electronic conductivity. The Si-cyclized PAN electrodes exhibit a specific charge capacity of nearly $1,500 \text{ mAhg}^{-1}$ when cycling at C/10, and deliver the reversible capacity of 800 mAh g^{-1} at a cycling rate of C/3 for more than 100 cycles, and retains a reversible capacity of 600 mAh g^{-1} after 300 cycles. The enhanced electronic and mechanical properties of the Si-cyclized PAN composite material enable the durable cycling performance with greatly improved rate capability.

The effect of Al_2O_3 ALD coatings on the structure and SEI composition have been demonstrated by using in-situ synchrotron X-ray diffraction and ex-situ XPS and TOF-SIMS. Al_2O_3 ALD has mitigated the side reaction on the surface of electrodes and preserved the structure during severe cycling at higher voltage.

In FY13, our research will focus on developing a hybrid metal-organic coating on Si anode; optimizing the coating materials for ALD/MLD to reduce the

irreversible capacity loss; and demonstrating the effect of new coatings on the electrochemical performance and structural evolution of Si anodes.

FY 2012 Publications/Presentations

1. Y. Jung, L. Peng, A. S. Cavanagh, C. Ban, S. Lee, S. J. Harris, G. Kim, A. Dillon, "Unexpected Improved Performance of ALD Coated LiCoO₂/Graphite Li-ion Batteries," *Adv. Energy Mater.* DOI: 10.1002/aenm. 201200370.
2. C. Ban, B. Kappes, Q. Xu, C. Entrakul, C. V. Ciobanu, A. C. Dillon, Y. Zhao, "Lithiation of silica through partial reduction" *Appl. Phys. Lett.* (2012) 100, 243905.
3. Jung, Y. S., A. S. Cavanagh, L. Gedvilas, N. E. Widjonarko, I. D. Scott, S.-H. Lee, G.-H. Kim S. M. George, A. C. Dillon, "Improved Functionality of Lithium-Ion Batteries Enabled by Atomic Layer Deposition on the Porous Microstructure of Polymer Separators and Coating Electrodes" *Adv. Energy Mater.*, 2: 1022–1027 (2012).
4. 2012 DOE Annual Peer Review Meeting Presentation.
5. (Invited talk) Electrochemical and In-situ Structural Study of Coated Li[NMC]O₂ Cathodes for Durable High-Voltage Cycling, International Battery Association-Pacific Power Source Symposium, 2012, Hawaii.
6. (Invited talk) Improving Electrochemical Performance of Li-ion Electrodes via Advanced Surface Modification, 10X Advanced Battery R&D, 2012, Santa Clara, CA.
7. (Invited talk) Enabling Durable High Rate Capability for High Capacity Li-Ion Electrodes, Gordon Research Conference 2012, Ventura, CA.