Electrochemical Performance Testing

L. Walker, D. Robertson, J. Basco, P. Prezas and I. Bloom
Argonne National Laboratory

June 2015

Washington, DC

2015 DOE Annual Merit Review

Project ID:
ES201

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

Overview

Timeline

- Facility established: 1976
- End: Open – this is an on-going activity to test/validate/document battery technology as technologies change and mature

Budget

- DOE Funding FY15: $1.7 M
- FY14: $2.0 M
- FY13: $2.3 M

Barriers

- Performance (power and energy densities)
- Cycle life (1,000-300,000 depending on application)
- Calendar life (15 y)
- Low-temperature performance

Collaborations

- US battery developers
- Idaho National Laboratory, Sandia National Laboratories
- CATARC (China)

Relevance

Objective

- To provide DOE and the USABC an independent assessment of contract deliverables and to benchmark battery technology not developed under DOE/USABC funding
- To provide DOE and the USABC a validation of test methods/protocols
- To utilize test data to project battery life

Approach

- Apply standard, USABC testing methods in a systematic way to characterize battery-development contract and benchmarking deliverables
- Characterize cells, modules and packs in terms of:
  - Initial performance
  - Low temperature performance/Cold cranking
  - Cycle life
  - Calendar life
- Compare test results to DOE/USABC goals
- Adapt the test facility hardware and software
  - to accommodate programmatic need
  - to accommodate the unique needs of a given technology and/or deliverable

Program Milestones

- All deliverables below were characterized in terms of initial performance, calendar and cycle

Milestone	Due date	Status
Present test results at quarterly meeting	12/19/2014	Complete
Present test results at quarterly meeting	3/31/2015	Complete
Present test results at quarterly meeting	6/30/2015	On schedule
Present test results at quarterly meeting	9/30/2015	

Technical Accomplishments: Progress and Results - Testing Contract Deliverables

- Test deliverables are mostly cell-oriented and include developments in
  - Lithium-ion battery chemistry (graphite anodes)
  - Silicon anodes
  - Lithium metal anodes
  - Separators
  - Advanced cell chemistries (beyond Li-ion)
- Deliverables are characterized in terms of initial capacity, resistance, energy and power. They are then evaluated in terms of cycle and calendar life for the given application
- Results are used to show progress toward meeting DOE/USABC initial commercialization goals

Progress and Results – Testing Contract Deliverables

- Test deliverables come from many developers

Developer	Sponsor	Level	Quantity	Capacity (Ah)	Application	Status
JCI	USACB	Cell	6	27	PHEV 20	on-going
	DOE FOA	Cell	18	3	PHEV 20	complete
	DOE ARRA	Cell	6	41, 6	PHEV20, HEV	on-going
	USACB	Cell	18	36	PHEV 20	on-going
	DOE FOA	Cell	14	15, 3	PHEV 20	on-going
Xalt	DOE FOA	Cell	15	2.1	EV	on-going
Seeo	DOE FOA	Cell	6	0.00897	EV	complete
	DOE FOA	Cell	6	0.276	EV	complete
	USABC	Module	3	11	EV	on-going
Optodot	DOE FOA	Cell	9	2.1	EV	on-going
3M	DOE FOA	Cell	18, 6	1.7, 2.7	EV	on-going
	DOE FOA	Cell	21	2.4	EV	on-going
	DOE FOA (ABR-IC^{3}P)	Cell	14	2.1	EV	on-going
Navitas	DOE FOA	Cell	9	4, 2	EV	on-going
Tiax	DOE FOA (ABR-IC^{3}P)	Cell	12	1.8	PHEV 20	on-going
Daikin	DOE FOA	Cell	6	1	PHEV	on-going
Wildcat	DOE FOA	Cell	9	2	PHEV	complete
Leyden Energy	USABC	Cell	15	2.2	12V S/S	on-going
	USABC	Cell	2	40	12V S/S	on-going

Progress -- Protocol Validation/Effect of Fast Charge

- With further vehicle electrification, consumers may expect battery charging to take about the same amount of time that refueling an internal-combustion-engine-powered vehicle currently does at a service station
- This "fueling" does not have to be a full charge, but can be a partial charge
- The Fast Charge Test in the USABC EV Manual[1] determines the impact of charging a battery from 40 to 80% SOC at successively faster rates, starting from about twice the overnight rate. Since the manual was written for Ni/MH technology, the ideas were adapted for the higher-performing, lithium-ion cells
- Two commercial, lithium-ion cell chemistries, A and B, were chosen based on NMC materials in the form of 18650 cells
- The high charge rates used may introduce new degradation modes, causing the performance of the battery to decline faster than expected

- Post-test characterization of cells was conducted, results can be seen at poster ES166

[1]Electric Vehicles Battery Test Procedures Manual, Rev. 2, January 1996.

Effects of Fast Charging Lithium-Ion Cells

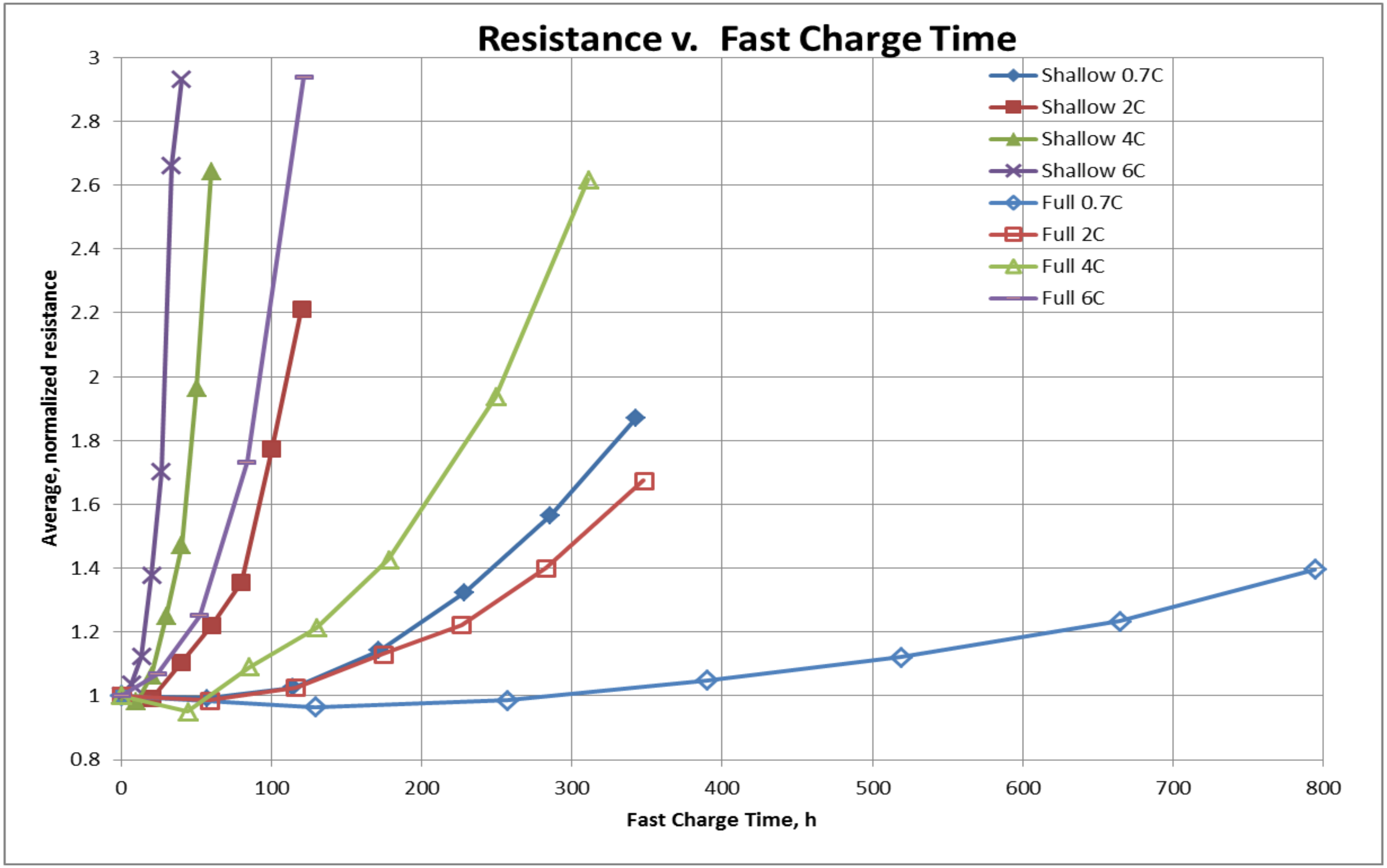
- Two sets of twelve lithium-ion cylindrical cells were used to investigate the effects of charge rate on life using EV cycle protocols
- Two cell chemistries

  Cell A: NMC/graphite with organic-carbonate-based electrolyte (1.25 Ah)

  Cell B: Physical blend of NMC + Spinel/graphite with organic-carbonate-based electrolyte (1.5 Ah)

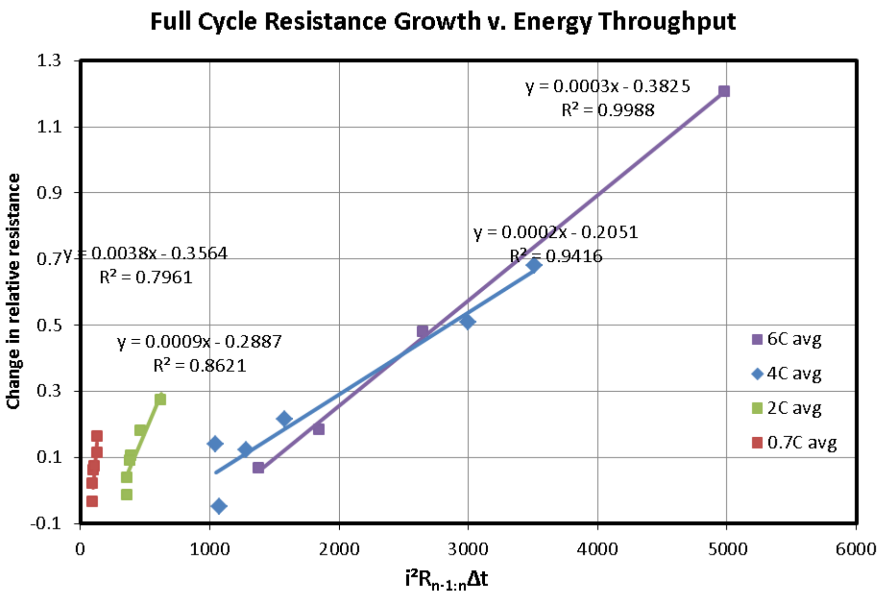
- Four test conditions with three cells per condition
  - Charge at manufacturer's suggested rate (0.7 to 1 C) rate
  - Charge at 2C rate
  - Charge at 4C rate
  - Charge at 6C rate
- Method
  - Two SOC-returned fast-charge windows: 40% (shallow) and 100% (full)
  - Full discharged at C/3 or C/1 rates, respectively
  - RPT every 100 cycles (~300-400 h)
    - One C/3 capacity test
    - One peak power test

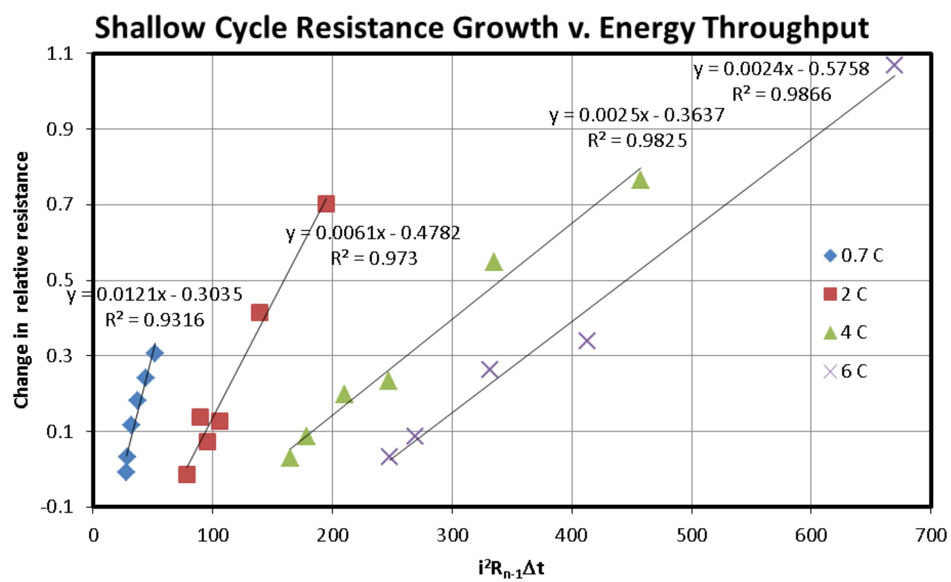
Fast Charge Cell A – Resistance at 80% DOD



Shallow charging and higher rates degrade the cell faster

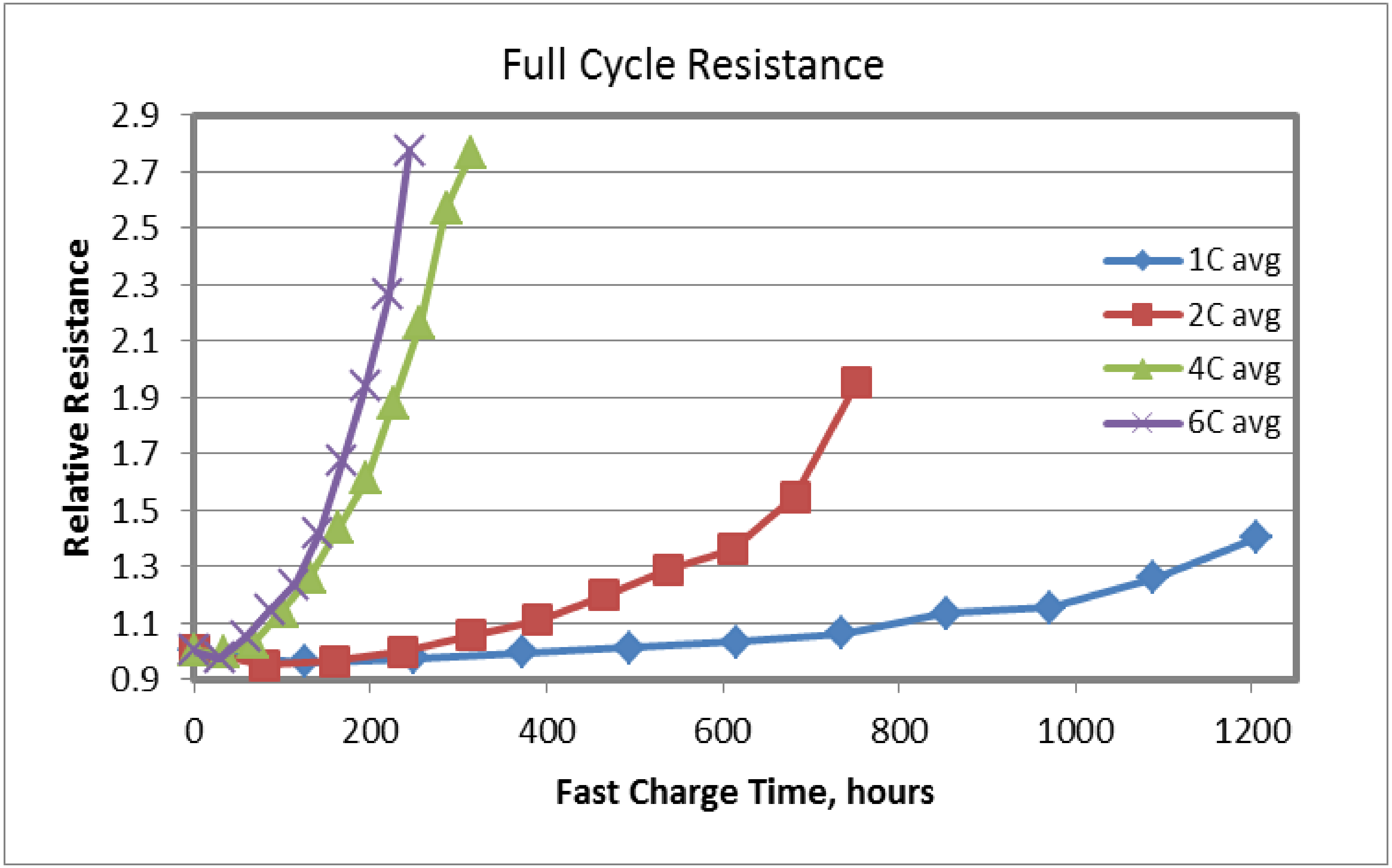
Fast Charge Cell A – Resistance Growth v. Energy Throughput



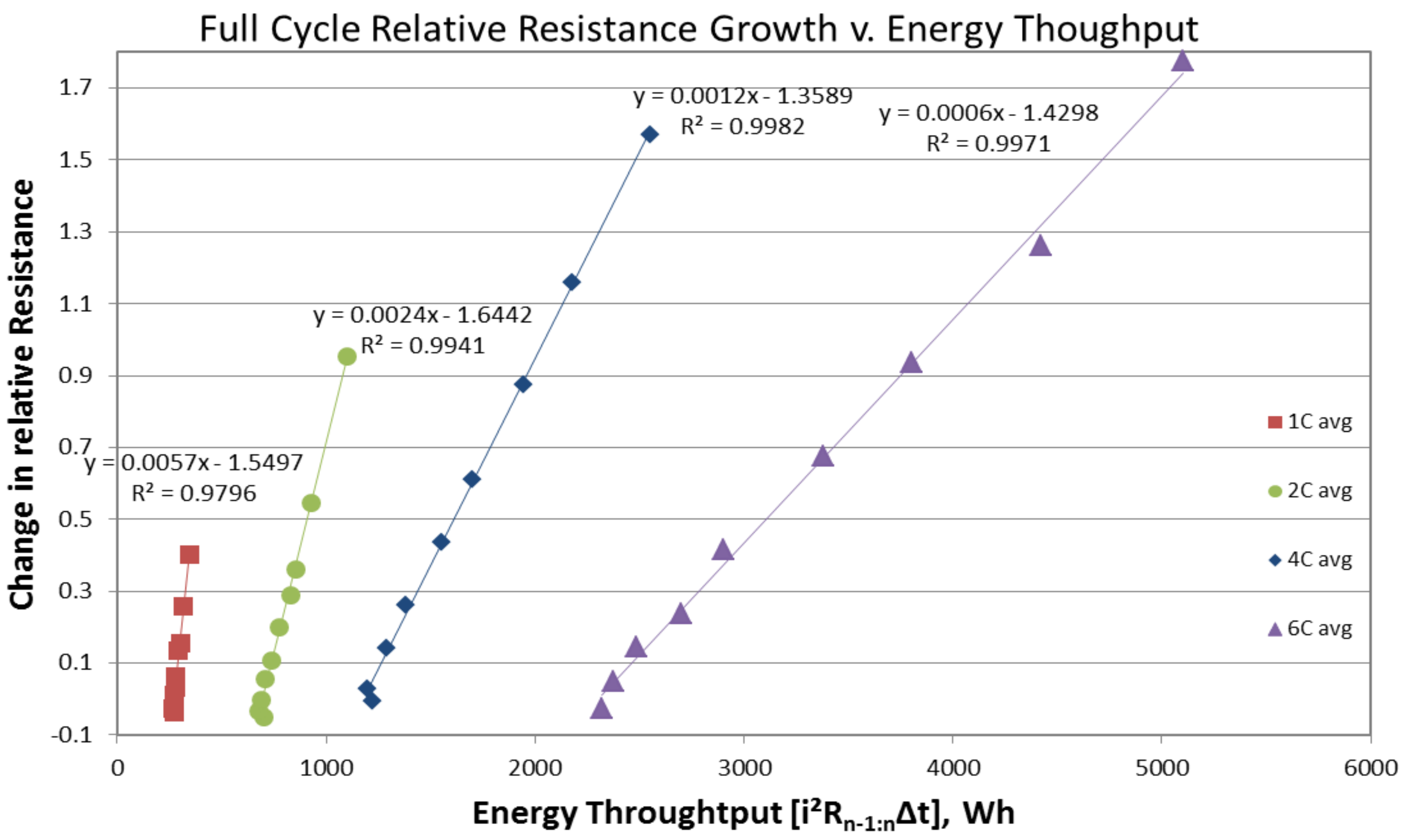


The rate of performance decline was proportional to the current used and to the resistance of the cell at the previous time interval. This implies that i^2R heating is a likely cause of the observed resistance increase

Fast Charge Cell B – Full Charge Resistance



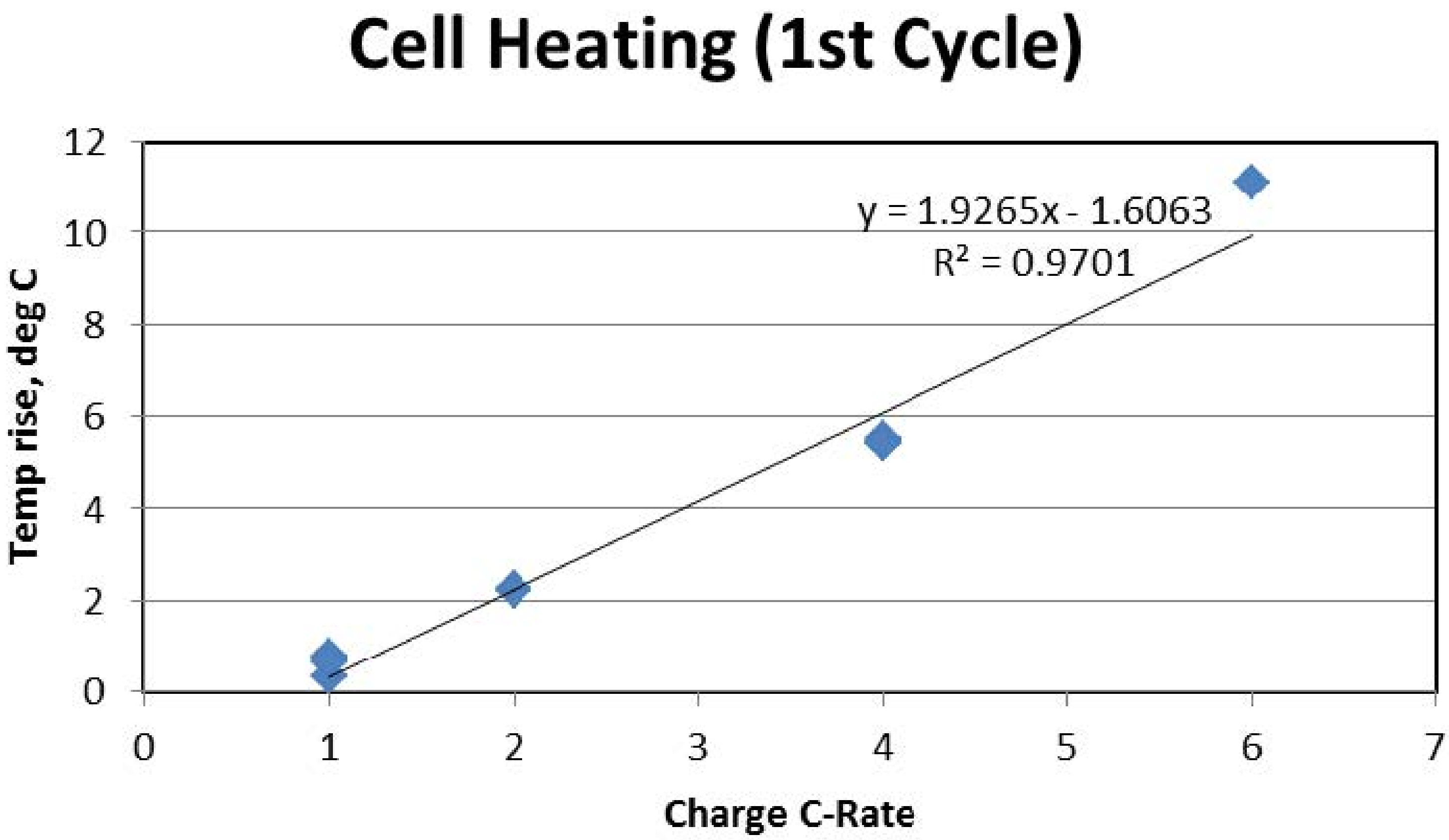
Fast Charge Cell B – Resistance Growth v. Energy Throughput



Similar to with Cell Chemistry A, the rate of performance decline was proportional to the current used and to the resistance of the cell at the previous time interval. This again implies that i^2R heating is a likely cause of the observed resistance increase

Fast Charge Cell B – Cell Heating Data

Cell heating is proportional to the charge rate



Progress and Results – Collaborative US/China Protocol Comparison

- Battery testing is a time-consuming and costly process
- There are parallel testing efforts, such as those in the US and China
- These efforts may be better leveraged through international collaboration
- The collaboration may establish standardized, accelerated testing procedures and will allow battery testing organizations to cooperate in the analysis of the resulting data
- In turn, the collaboration may accelerate electric vehicle development and deployment
- There are three steps in the collaborative effort

Step	Status
Collect and discuss battery test protocols from various organizations/countries	Complete
Conduct side-by-side tests using all protocols for a given application, such as an EV	Complete in US
Compare the results, noting similarities and differences between protocols and test sites	In progress

Conduct Side-by-Side Experiments

- A test plan based on an EV application was written and agreed to
- Commercially-available batteries based on $LiFePO_4$ and carbon were procured. The batteries were distributed to ANL, INL and CATARC (China). Each site received 10 cells.
  - ANL: Ira Bloom, David Robertson
  - INL: Jon Christophersen, Taylor Bennet
  - CATARC: Fang Wang, Shiqang Liu
- US/China testing protocols
  - The US cycle-life aging protocol consists of a dynamic, constant-power profile and constant-current charging
  - The Chinese cycle-life aging protocol consists of constant-current discharges and charges
  - USABC Reference Performance Test consists of 2 capacity cycles, peak power pulse test at 10% DOD increments and full DST capacity cycle. The cells are characterized using these performance tests every 50 cycles
  - China Reference Performance Test consists of 1 capacity cycle and 10 second discharge pulse at 50% DOD. The performance of the cells were characterized using these performance tests every 25 cycles
  - Both cycle-life protocols terminate discharge at 80% DOD
  - Add “no-power” pulse condition to mimic what was being done in China

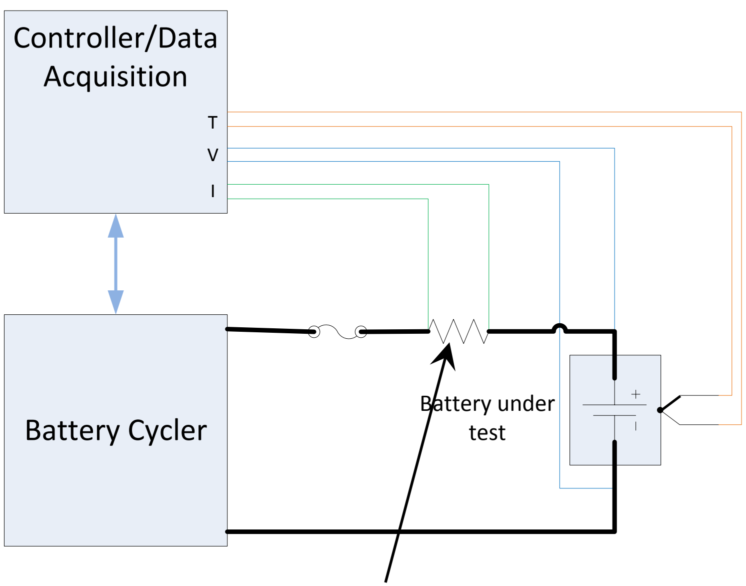
Comparing the Protocols Shows…

	USABC	China
DOD (Energy) Window	0-80% DOD	0-80% DOD
Temperature	25 °C	25 °C
Capacity measurement rate	C/3	C/3
End of Test criteria	80% of BOL	80% of BOL
Cycle Type	Dynamic, Power based	Constant-current
Power Capability Measurement	Peak Power Pulse Estimation at 80% DOD	Pulse Power Density at 50% DOD
Pulse duration	30 seconds	10 seconds
Pulse Current	75A	225A
RPT Frequency	50 cycles (10.5 days)	24 cycles (6 days)
RMS power of cycle	50-51 W	12-13 W
RMS current of cycle	15-16 A	3.5-4 A
Average Voltage of cycle	3.17V fading over time	3.27V without fading
Energy throughput of cycle	27 Wh	19.5 Wh

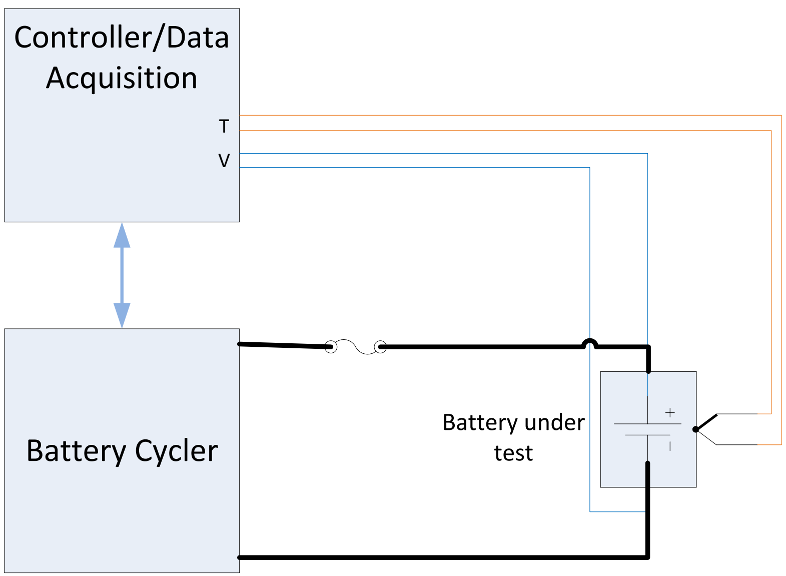
Comparing Test Hardware Configuration Shows…

- Schematic of a typical cycling channel

ANL+INL



CATARC

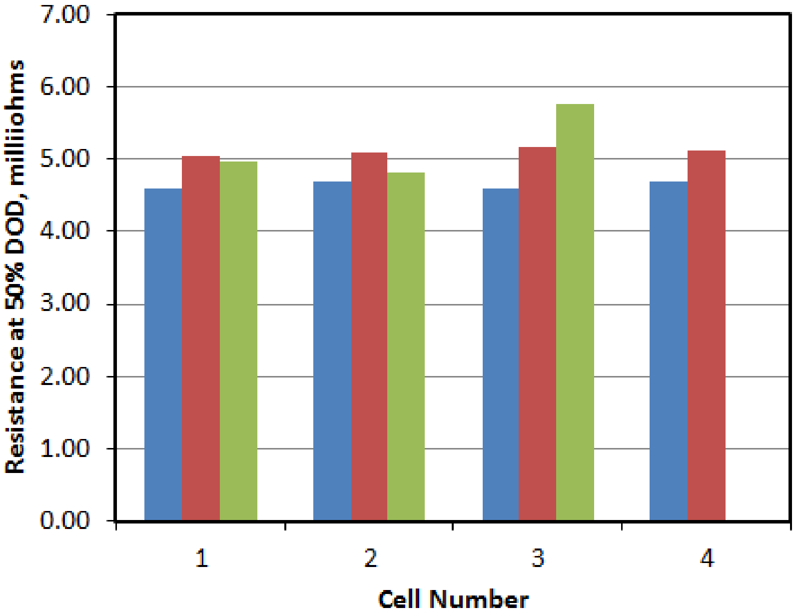


- Difference: the shunt resistor, which is used to quantify current

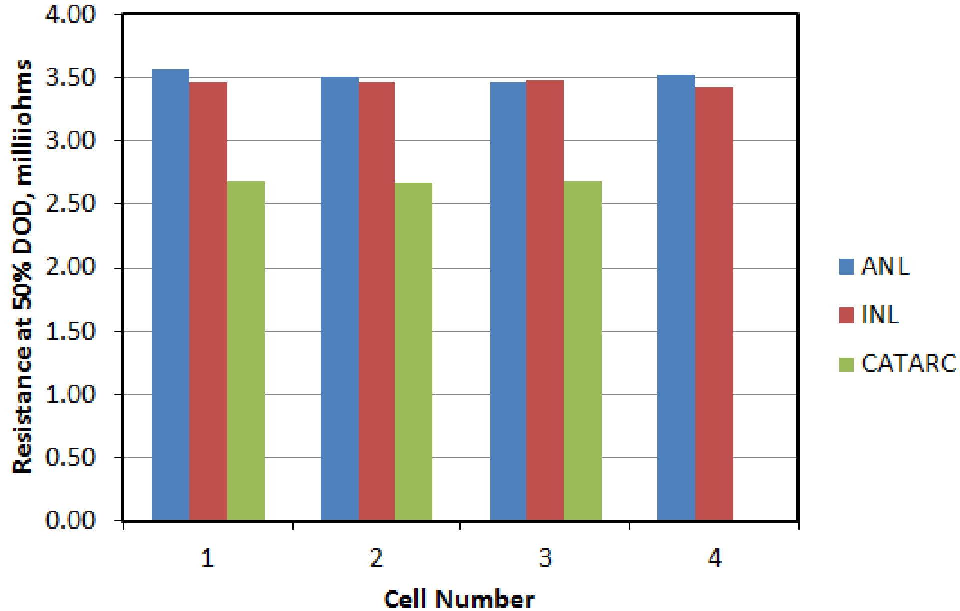
Initial Characterization of the Battery Population (continued)

- Resistance at 50% DOD depends on measurement method as well as on the cell

USABC



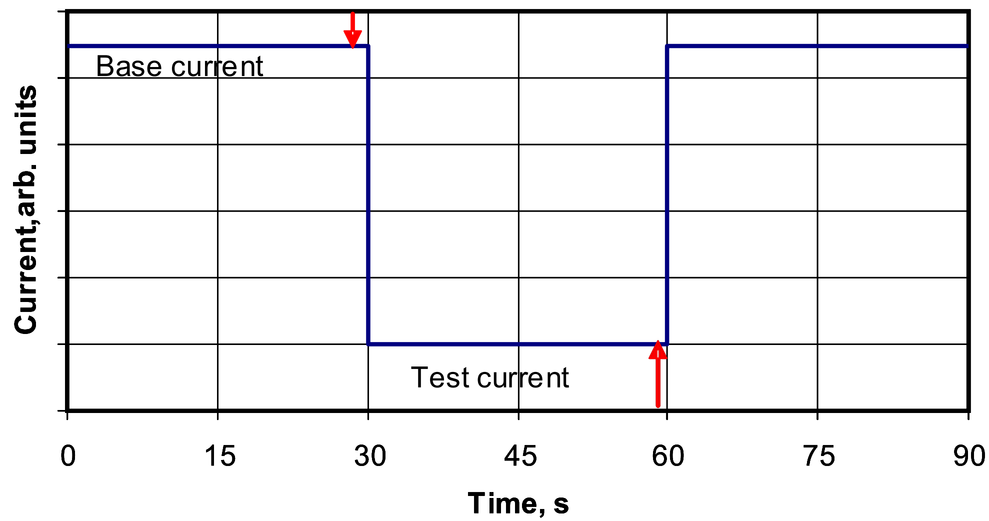
QT/C 743



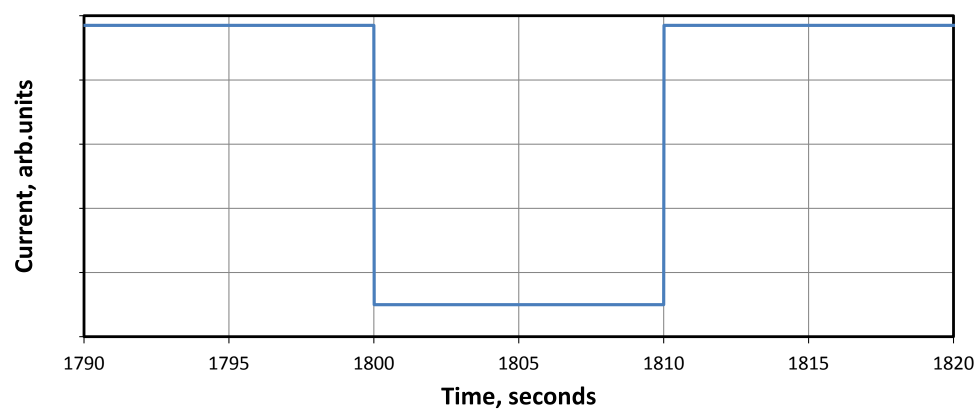
- Difference between measurement methods produces a 2-3-fold difference
- Variance (USABC protocol, mΩ): 3.06×10^{-3}, 2.44×10^{-3},2.54×10^{-1} for ANL, INL, and CATARC, respectively

Initial Characterization of the Battery Population (continued)

- Measurement methods
  - USABC: Peak power test
  - Each pulse is 30-s long
  - Magnitude: 75 A



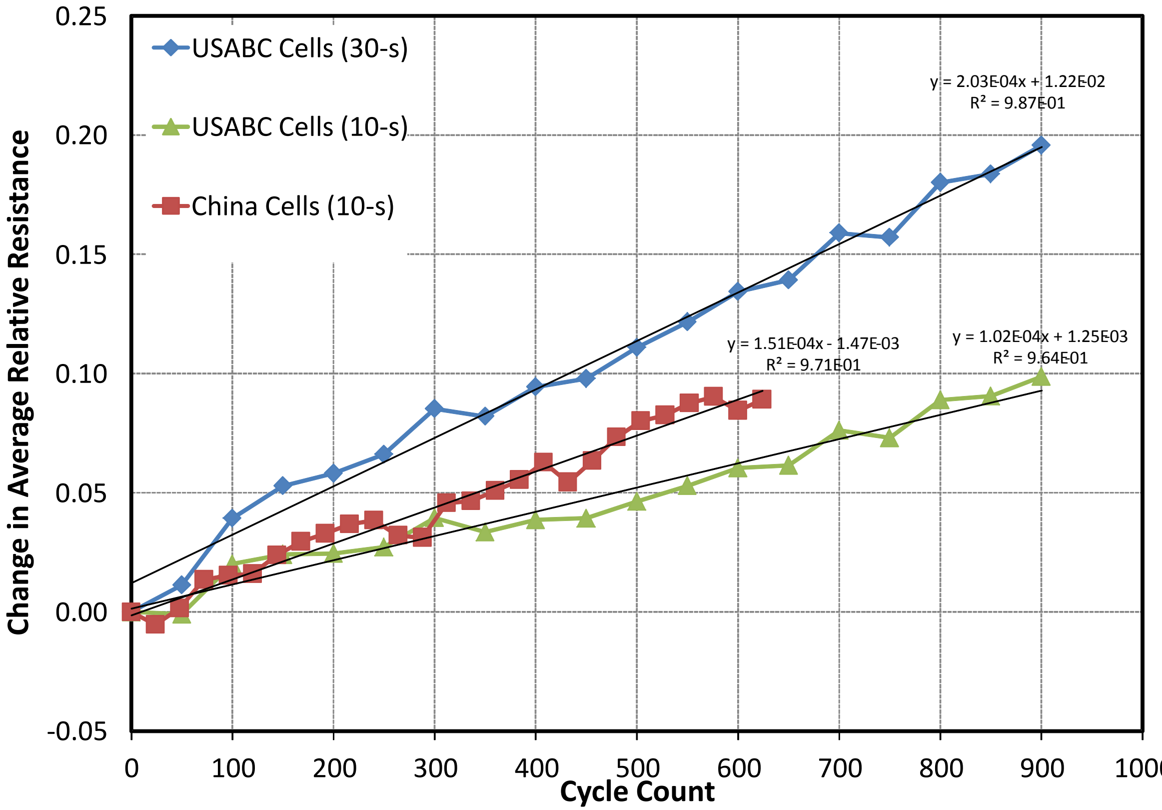
  - QT/C 743: Single 10-s, pulse at 50% DOD



- Pulse magnitude and width produce different amounts of electrode polarization, which affect the resistance observed

As the Cell Ages, Resistance Increases

- Relative change in cell resistance at 50% DOD
- Calculate resistance from peak power test at *t*=10 and 30 s.
- Initially, the 10-s USABC values compare well to those calculated from the QT/C 743 protocol.
- The 30-s USABC values are significantly higher
- Resistance increase seems to be linear with time

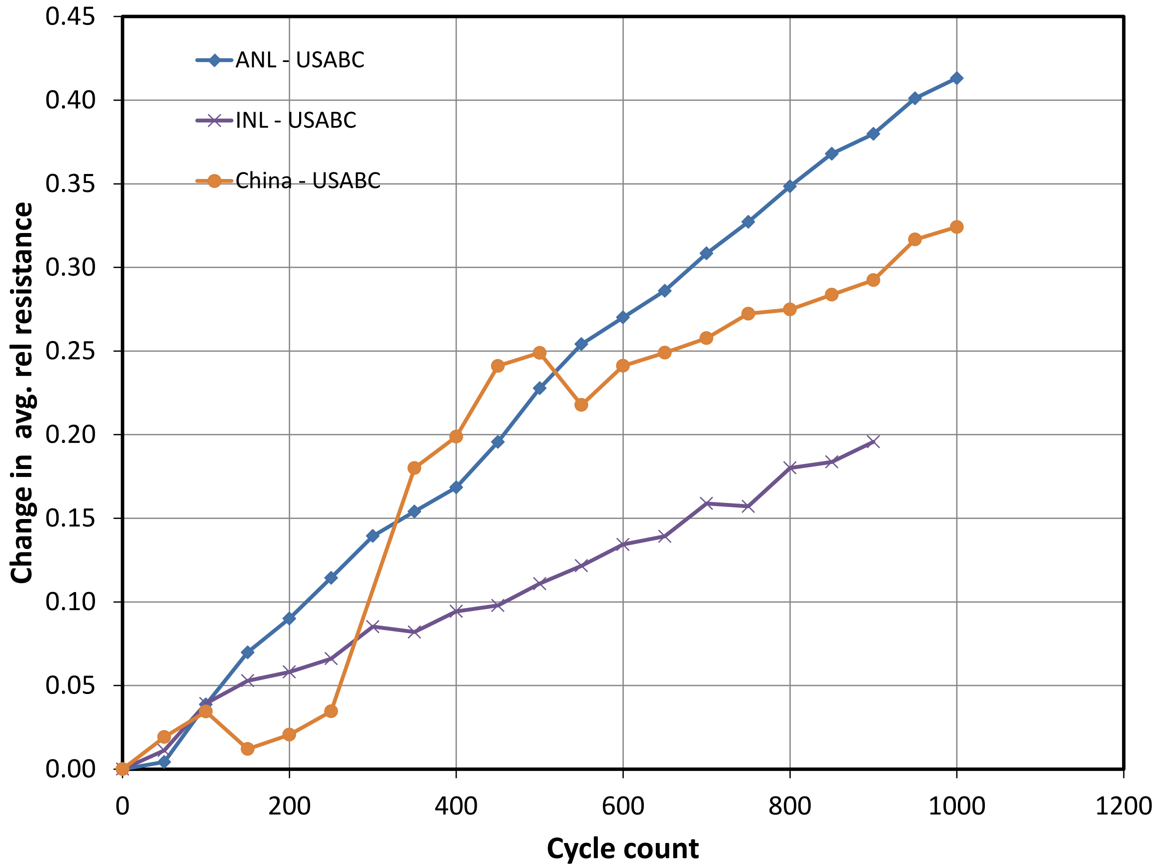


- From slope of least-squares fits, resistance increase in the 30-s USABC data is 1.3 that of the 10-s China data and about twice that of the 10-s USABC data

Data from INL

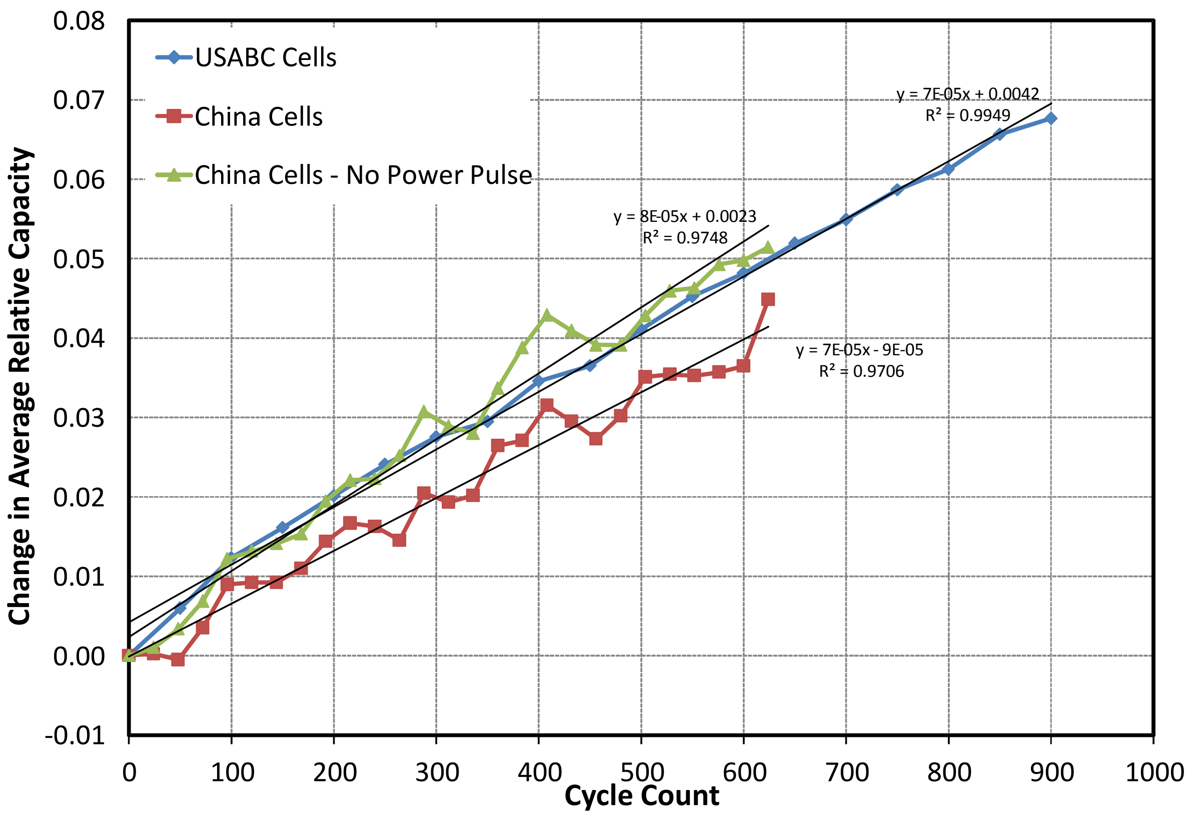
Comparing Resistance Values vs. Time Shows Differences

- Resistance values combine cell-to-cell variation and measurement errors between the sites
- Since the CATARC measurements were performed differently, it may not be an easy site-to-site comparison



As Cell Ages, Capacity Fades

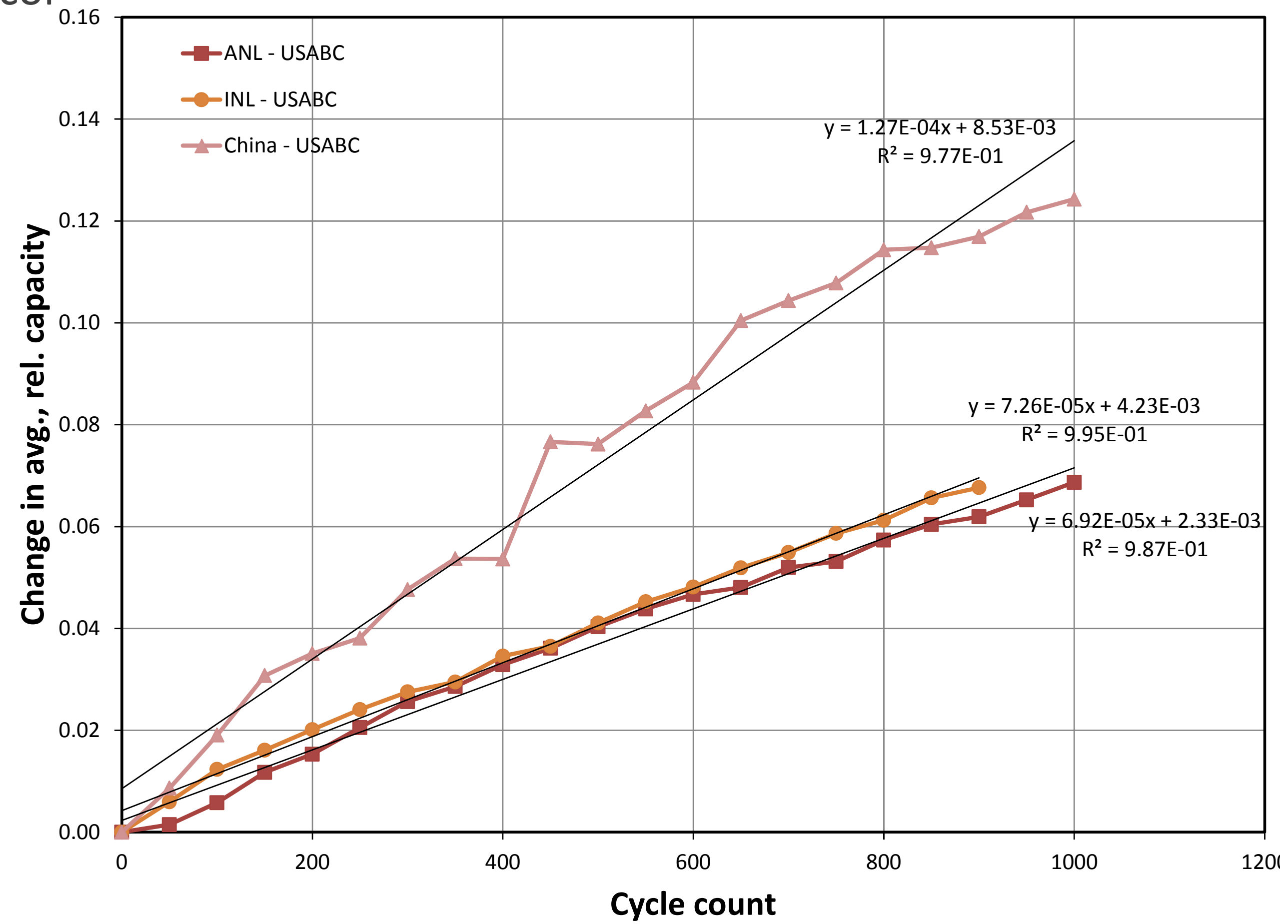
- Capacity fade appears linear-with-time for the three protocols
- Capacity fade does not seem to depend strongly on testing protocol



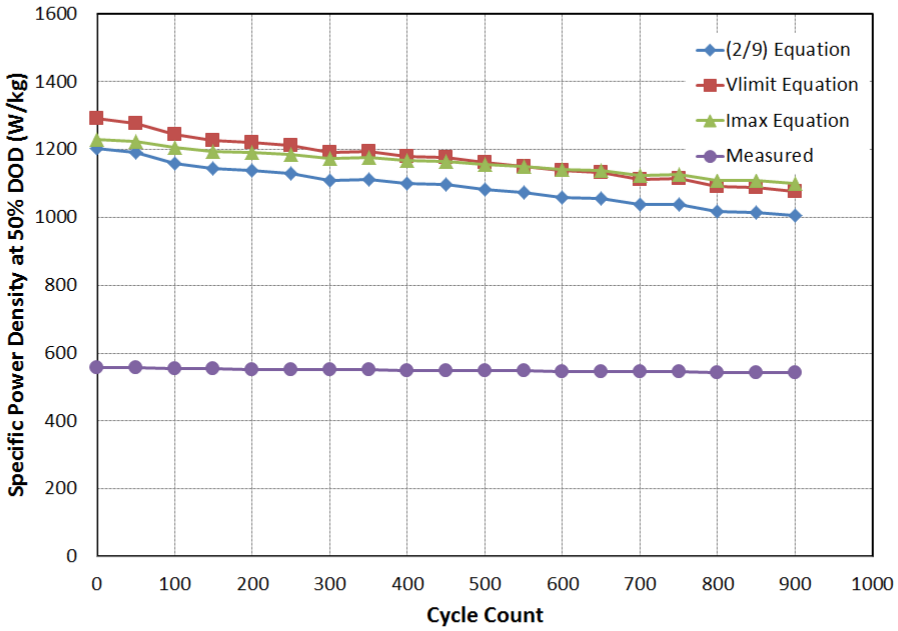
Data from INL

As Cell Ages, Capacity Fades

- There are differences between US and China test sites, performing USABC protocol

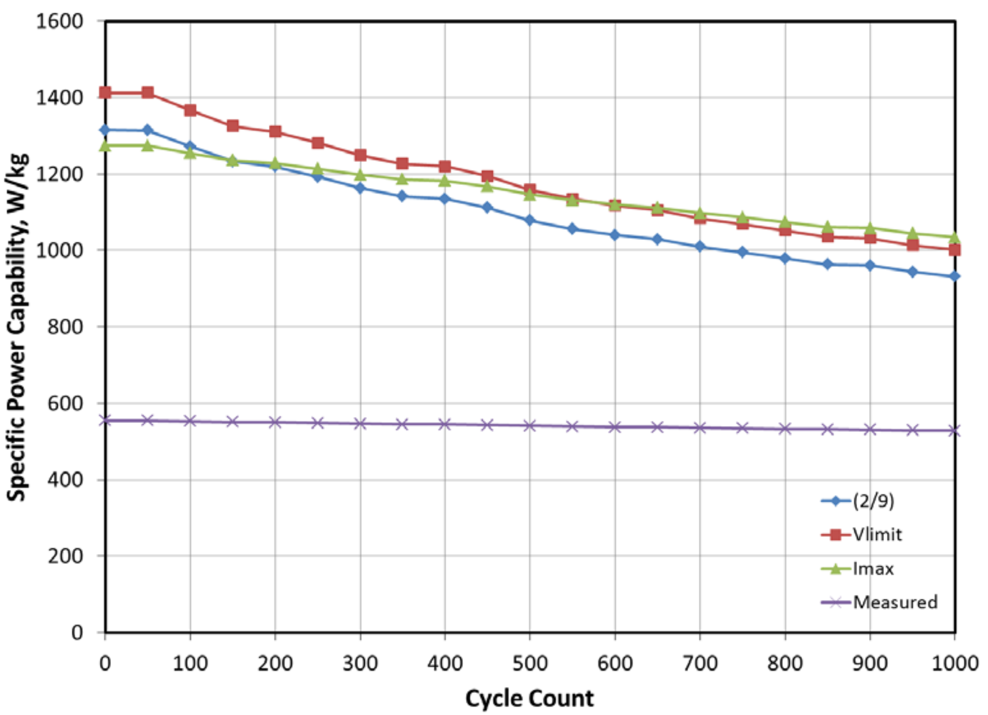


Comparing USABC Results at 50% DOD from INL and ANL Shows They Are Similar



INL

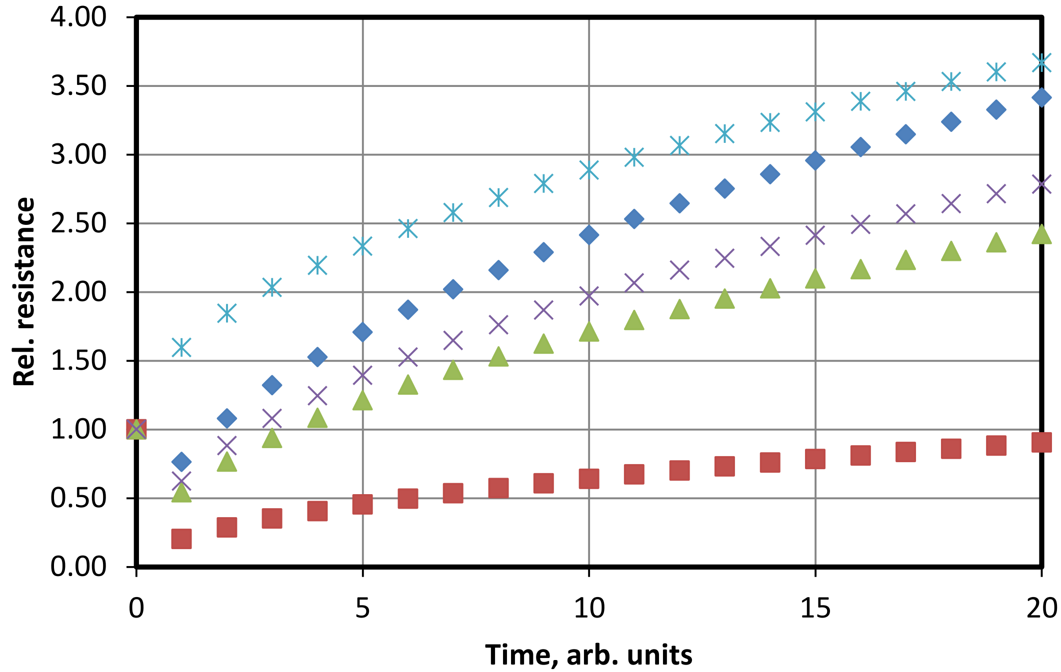
ANL

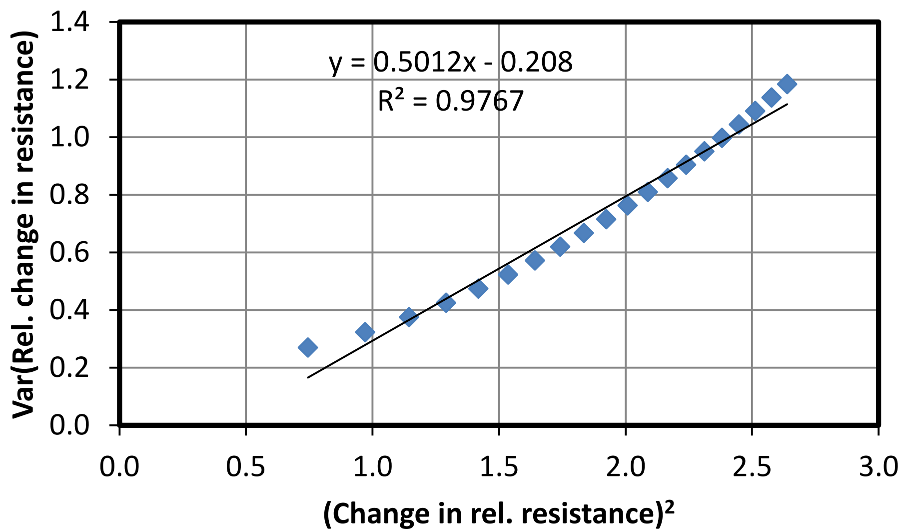


- Data are similar
- Differences may be due to cell-to-cell variation

Basis of Error Model*

- Each observation contains a factor for cell-to-cell variability and measurement error
- If have time-base degradation behavior, such as resistance increase, each observation can be written as $Y_i=\delta_i(\mu_i-1)+\pi_i$, where δ_i=cell-to-cell proportional effect, μ_i is the mean of the observations, and π_i is measurement error
- $Var(Y_i)=\sigma_\delta^2(\mu_i-1)^2+\sigma_\pi^2$, where σ_x^2 is the variance of that parameter

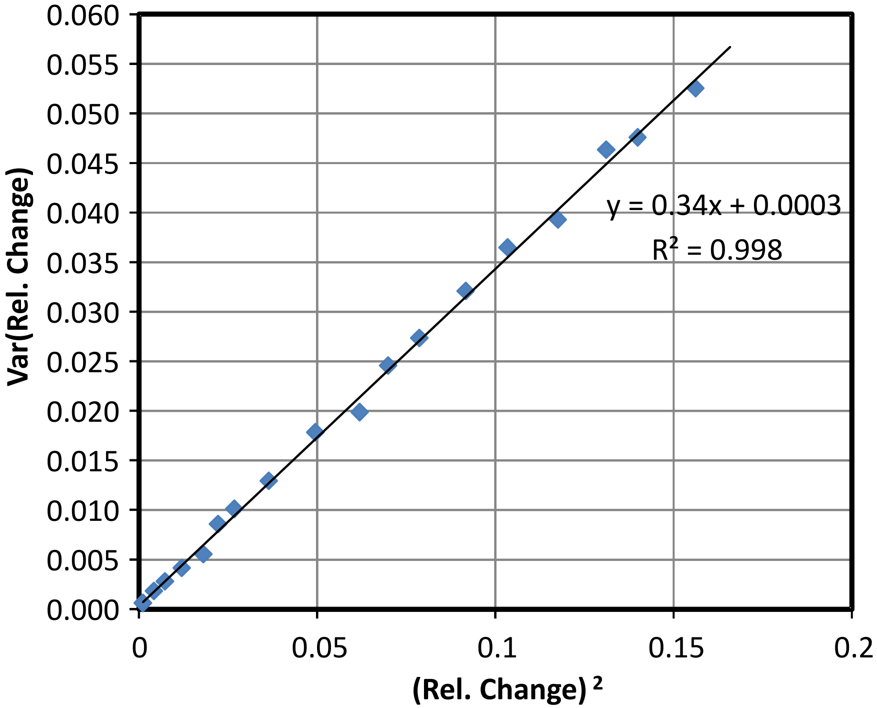




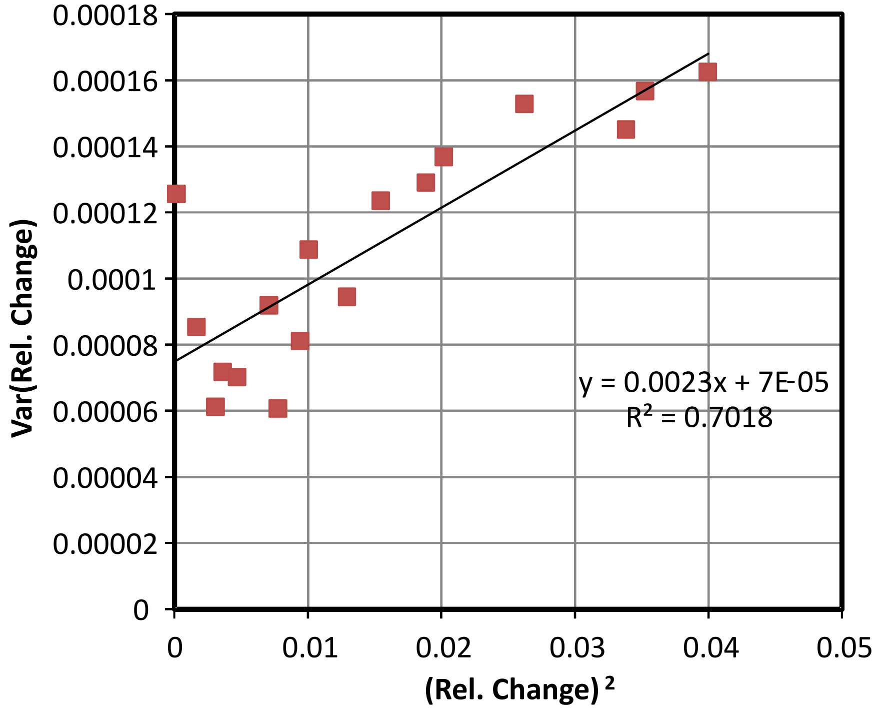
E. Thomas, I. Bloom, J.P. Christophersen, and V.S. Battaglia, *J. Power Sources*, 206 (2012) 378-382.

Error Models

- Measure resistance (in mΩ) using USABC protocol



ANL

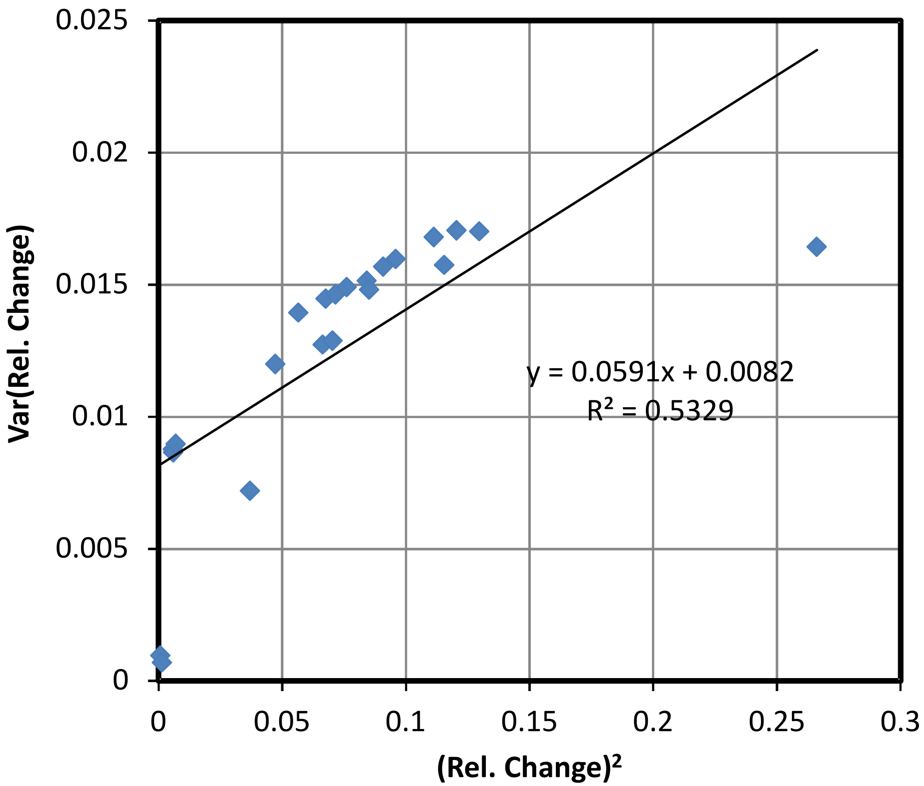


INL

- Estimated standard deviations/errors
  - Cell-to-cell: 0.58 | 0.05
  - Measurement: 0.01 | 0.006

Error Models (continued)

- Linear error model may not apply to data from CATARC



- Estimated standard deviations/errors
  - Cell-to-cell: 0.24
  - Measurement: 0.06

Comparing the Results Shows…

- There are similarities and differences in the test protocols
- Results indicate that:
  - There are significant differences in the way battery test channels are configured between the US and China. Site to site differences in control and measurement have resulted in variations in reported data. These differences may impact test results and life projections. US-China site-to-site comparisons may, therefore, be difficult
  - The initial capacities and resistances, measured using the USABC protocol, of the cells used were not very uniform. The non-uniformity may impact how the cells age
  - For capacity, the Chinese test protocol produced slightly more fading than the USABC at both ANL and INL
  - For resistance, the USABC test protocol caused a greater increase in cell resistance at both test sites

Summary

- Hardware deliverables from many sources have been tested at Argonne and continue to be evaluated for a variety of vehicle applications
- This testing directly supports DOE and USABC battery development efforts
- The fast charge test results have shown
  - Fast charging causes performance decline in lithium-ion batteries. The extent of decline is proportional to charge rate
  - In the field, infrequent fast charging of electrified vehicles, while not causing the effects observed here, may also introduce degradation modes
  - Post test characterization has shown the physical effects of charging at different rates.
- The US/China Protocol Comparison has shown
  - There are similarities and differences in the test protocols and hardware configurations
  - For capacity, the Chinese test protocol produced slightly more fading than the USABC at both ANL and INL
  - For resistance, the USABC test protocol caused a greater increase in cell resistance at both test sites
  - A better error model may be needed since some of the curves were clearly not linear. Error models should be developed for the set of data derived from using the Chinese protocol (with the power pulse)

Future Work

- Continue to support the DOE and USABC battery development efforts by performing unbiased evaluations of contract deliverables, using standardized test protocols
- The Fast Charge Testing
  - It may be possible to lessen these effects through effective thermal management of the vehicle battery pack which we will seek to study
  - Evaluation of Cell B (Physical blend of NMC+Spinel/graphite with organic-carbonate-based electrolyte) continues as samples are ‘Shallow’ cycled
- The US/China Protocol Comparison
  - The collaboration is working
  - Complete the manuscript on this work and submit for publication
  - Start a new, collaborative experiment focused on fast charge

The work at Argonne National Laboratory was performed under the auspices of the U.S Department of Energy (DOE), Office of Vehicle Technologies, under Contract No. DE-AC02-06CH11357. The program manager was Brian Cunningham.