U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

Diagnostic Testing and Analysis Toward Understanding Aging Mechanisms and Related Path Dependence

Kevin L. Gering, PhD *Energy Storage & Transportation Systems*
Principal Investigator, Applied Battery Research

Contributors:

David K. Jamison, INL	Bor Yann Liaw, HNEI
Christopher J. Michelbacher, INL	Matthieu Dubarry, HNEI
Sergiy V. Sazhin, INL	Cyril Truchot, HNEI

May 9, 2011

Project ID ES096

2011 DOE Vehicle Technologies Program Annual Merit Review

www.inl.gov
Idaho National Laboratory

Overview

Timeline	Barriers
Project Start: April 2008 **Project End:** Ongoing **Percent Complete:** ≈ 50%. Extent of project completion depends on meeting key decision points and milestones built into schedule	**Cell/battery Life and related path dependence — lack of accurate life prediction capabilities**
Budget	**Partners**
Funding Received: **FY 10: $ 460K** **FY 11: $ 750K (All DADT, including subcontracts)**	**Hawaii Natural Energy Institute** **University of California at Pomona** **Argonne National Lab**

Relevance

Long-term usage of lithium-ion batteries in vehicle applications represents a significant warranty commitment. Yet, there is insufficient knowledge regarding aging processes in such batteries, particularly in cases of strong path dependence of performance degradation (aging).

Our objectives include*:

- Establish a platform of Developmental & Applied Diagnostic Testing (DADT) geared toward specific issues in EDV batteries.
- Employ DADT to examine mechanistic contributions to cell aging.
- Develop advanced modeling tools that will complement DADT.
- Develop/optimize an operational protocol to minimize the aging process (chemistry-specific, but with generalized approach).

This collective effort will allow us to answer fundamental questions for each specific cell chemistry regarding aging processes, path dependence thereof, and find ways to mitigate performance limitations over life.

*Performed under US DOE Applied Battery Research for Transportation (ABRT) Program

Milestones

Milestone	Status	Date
Initial cell characterization at INL and HNEI	completed	Sept.-Dec. 2009
Start of INL Path Dependence Studies 1 and 2	ongoing	Sept./Nov. 2009
Start/completion of HNEI Aging Study 1 (2C rate)	completed	Sept. 2010
Start/completion of HNEI Aging Study 2 (isothermal matrix)	ongoing	Dec. 2010
Validation of Incremental Capacity Analysis on Sanyo Y Chemistry (HNEI)	completed	Dec. 2010
Start of supplemental testing, INL (self-discharging)	ongoing	Oct. 2010
Start of INL Path Dependence Study 3 (current ramping as parameter)	ongoing	Dec. 2010
Development and validation of life modeling tools (INL)	completed	2007-2010
Development of generalized thermodynamic method for predicting aging path dependence (INL)	completed	Dec. 2010
Start of module or string-level studies (degradation path dependence tied to cell-to-cell interactions), using Sanyo Y cells or others (HNEI and/or INL)	pending	June 2011

Approach

☐ This work aims to bridge the gap between ideal laboratory test conditions and PHEV field conditions by isolating the predominant aging factors of lithium-ion cells in PHEV service, which would include, for example, the nature and frequency of duty cycles, as well as the frequency and severity of thermal cycles.

☐ Through DADT, these factors are then studied in controlled and repeatable laboratory conditions to facilitate mechanistic evaluation of aging processes and path dependence thereof.

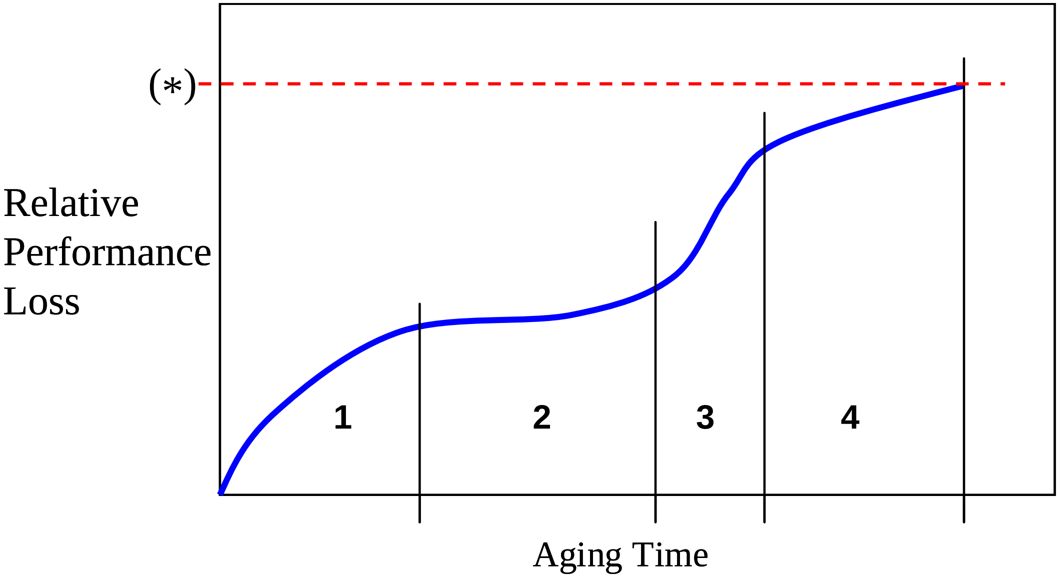
☐ Collaboration with the Hawaii Natural Energy Institute (HNEI) provides a synergistic basis due to the complementary histories of INL and HNEI in battery testing, research, and modeling.

☐ Modeling tools developed and employed are those that promote diagnostic analysis over multiple domains, looking at aging mechanisms and key performance issues. In some cases a lithium-ion cell is viewed as a batch reactor with aging processes modeled by sigmoidal mathematics.

Path Dependence of Cell Aging

INL aging models are easily adaptable to Path Dependence scenarios

- The extent and rate of cell aging over time depends on specific operational conditions (stress factors) encountered over the timeline. Path dependence asserts that the *sequence* of aging conditions (as well as the nature of conditions) has a direct influence on the rate of aging and net aging along the timeline. Think “batch reactor”.
- A change in aging conditions can accelerate or decelerate degradation mechanisms, and can initiate new ones. Reaction kinetics and thermodynamics are key to understanding the aging process along the path.
- Cell aging should be simultaneously judged from loss of capacity, rise in impedance, loss of power, self discharge, etc., where each require a standard basis.



Shown is an idealized projection of a path dependence involving four distinct aging conditions. An actual cell might encounter many times more unique aging conditions while in service.

Path dependence asserts that a randomized rearrangement of the four conditions will likely **not** reproduce the reference aging of (∗) by the end of the fourth period.

Approach

Modeling Aging Cells as Batch Reactors:

Current (I), heat (Q)

Chemical kinetics and thermodynamic considerations of degradation processes determine the effective rate that cells age, affecting losses in capacity, power, general performance, and ancillary quantities over service life of electrochemical cells. Sigmoidal expressions are well suited to describe these processes within a batch reactor scenario, e.g., for capacity loss at aging condition i (Ψ_i) we have:

$$\Psi_i = \sum_j 2M_j \left[\frac{1}{2} - \frac{1}{1+\exp\left(a_j t^{b_j}\right)} \right]_i$$

a_j : rate constant attributable to mechanism j,

b_j : related to the order of reaction for mechanism j,

M_j : theoretical maximum limit of capacity loss under mechanism j considering the thermodynamic limit of degradation under j for a batch system.

These mathematical expressions are self-consistent, properly bounded, adaptive, relevant to cell environments, and easily lend themselves to a comprehensive degradation rate analysis of performance data.

Li-ion Chemistry Used for Studies: Sanyo ‘Y’

Configuration: 18650
Cathode: {$LiMn_2O_4 + LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$}
Anode: graphitic
V_{max} = 4.2 V (100% SOC)
V_{min} = 2.7 V (0% SOC)
90% SOC = 4.07 V
70% SOC = 3.94 V
35% SOC = 3.65 V
Electrode Area: 800 cm^2 (estimated)
C_1/2 discharge capacity: 1.9 Ah,
C_1/1 discharge capacity: 1.86 Ah
Maximum recommended continuous discharge current: 5.7A
Maximum operating temperature during discharge: 60 °C.

These cells are high quality, showing good stability and low cell-to-cell variability.

Why Use Sanyo Cells?

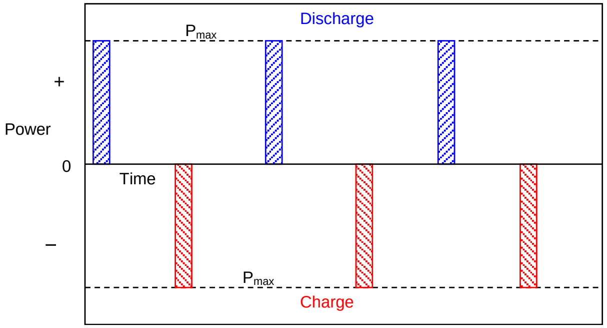
- High quality cells with low manufacturing variability.
- Available in a wide range of energy ratings.
- Relevant chemistries and performance for EDV studies.
- Commercially available (results are publishable).
- Economical to use in large test matrices.
- They serve as a reliable platform from which to develop DADT procedures and to validate related modeling methods.

Approach

Path Dependence Studies *(two examples)*

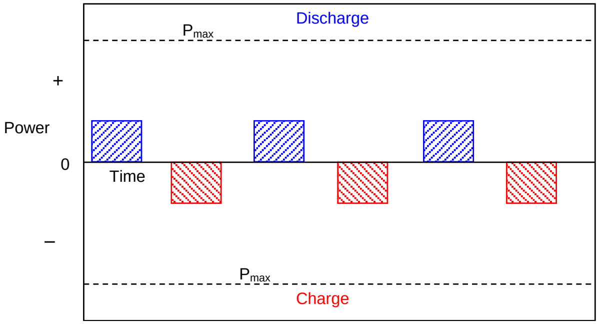
Study 1: Constant-power pulses of various magnitudes, using a time-average cumulative discharge energy that is equal for all scenarios.
Is there an aging path dependence due to severity and randomness of power pulses?

Scenario 1 (Baseline)

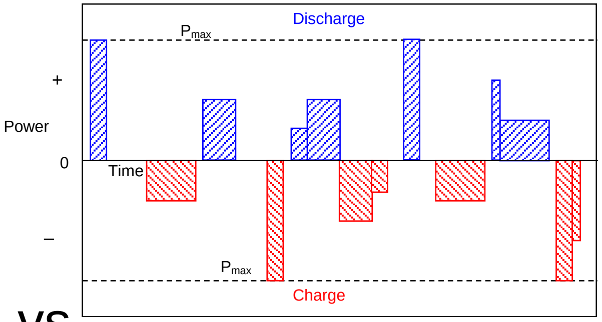


VS

Scenario 2

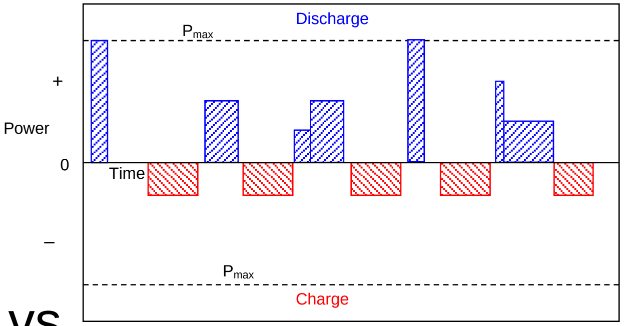


Scenario 3



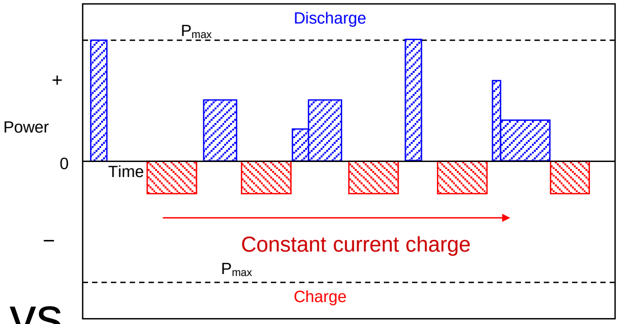
VS

Scenario 4



VS

Scenario 5

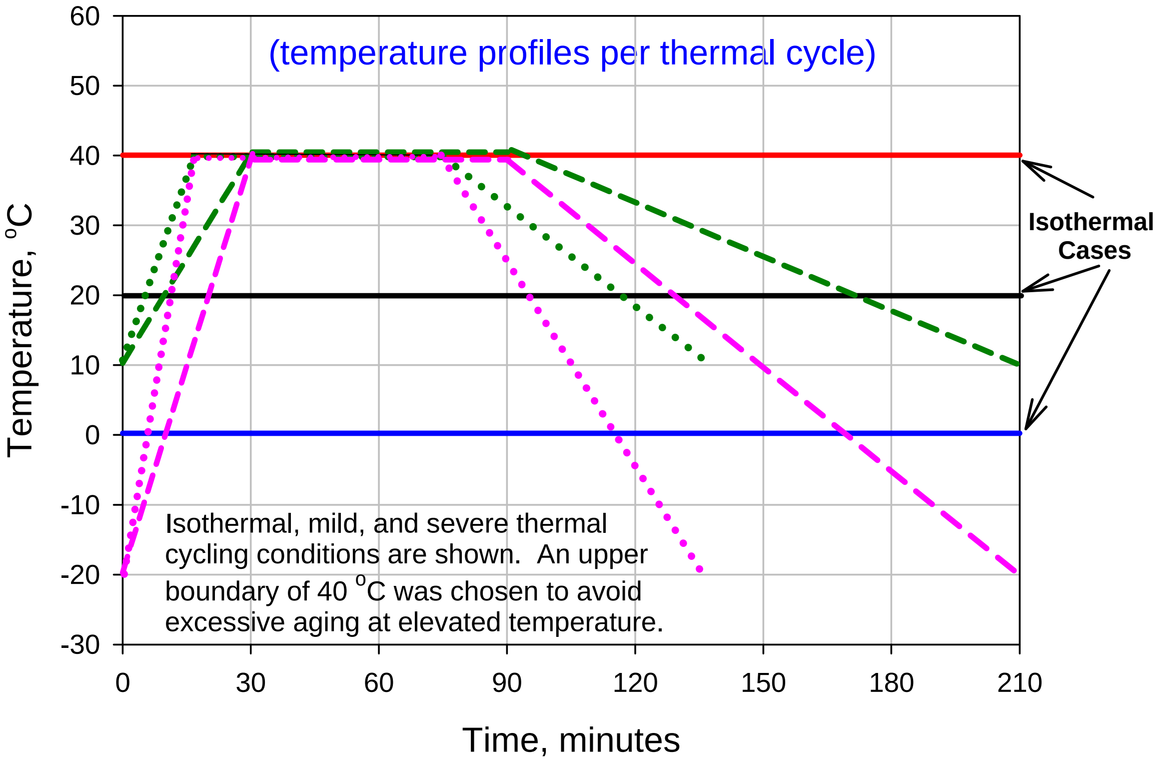


VS

Approach

Path Dependence Studies

Study 2: Combination of cell cycling (PHEV protocol, CD+CS) and thermal cycling. *Is there an aging path dependence due to cells operating under ambient temperature ramping?* Such thermal cycling will occur thousands of times during the projected life of a HEV/PHEV battery pack.



- This is a valuable study in transitioning between idealized lab data and actual PHEV field data.
- Temperature and cycling parameters can be tailored for specific regional targets.
- Added value is gotten through INL/HNEI synergy.

The main parameters are (1) the magnitude and frequency of the thermal cycling, looking at *isothermal*, *mild*, and *severe* scenarios, and (2) frequency of duty cycle.

Path Dependence Studies

<u>Study 2 cont.:</u> Duty Cycle: a *standard cycle-life profile* is defined here as consisting of one CD profile (360 s each) followed by ten CS profiles (90 s each), giving an overall profile duration of 21 minutes. Herein we define a *duty cycle* as three standard cycle-life profiles in sequence, that is, the <u>net profile represents a one-hour one-way commute</u>.

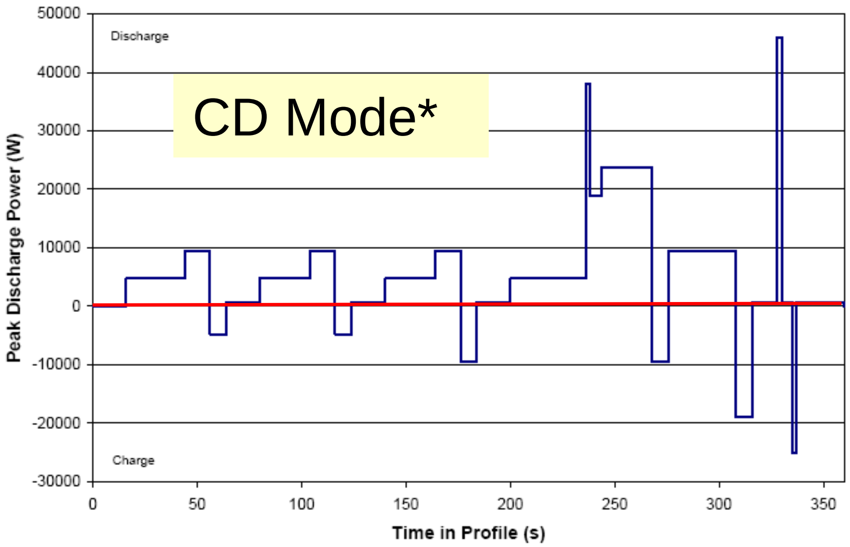
Duty Cycle

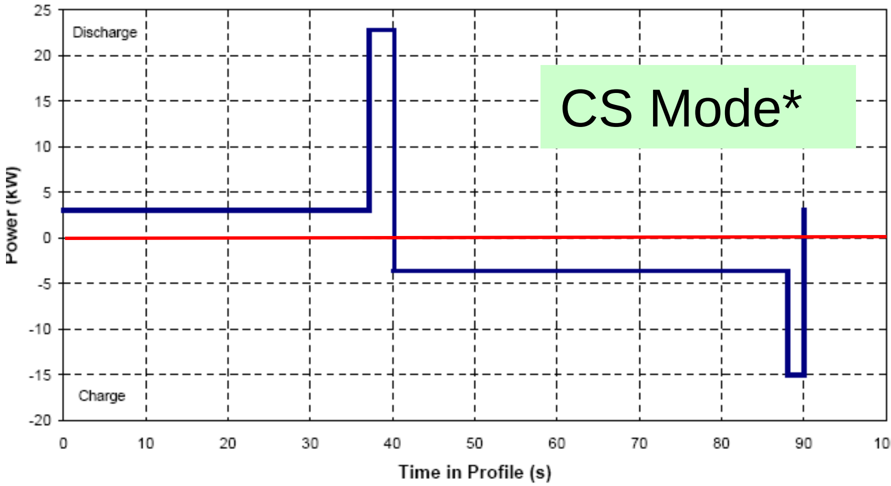
CD_1 (SOC_0 to SOC_1), then ten CS at SOC_1
\+ CD_2 (SOC_1 to SOC_2), then ten CS at SOC_2
\+ CD_3 (SOC_2 to SOC_3), then ten CS at SOC_3,*

Cycle-life Profiles

where

$SOC_0 > SOC_1 > SOC_2 > SOC_3$ ($\geq SOC_{min}$, here 35%)





Charge-Sustaining Cycle Life Test Profile (50 Wh) for Maximum PHEV Battery

Charge-Depleting Cycle Life Test Profile for Maximum PHEV Battery

* Battery Test Manual for Plug-in Hybrid Electric Vehicles (INL, March 2008, rev0).

Technical Accomplishments & Progress

- ❑ Parallel studies at INL and HNEI are ongoing that involve over eighty (80) commercial lithium-ion cells, with some sub-elements completed.
- ❑ INL Path Dependent Studies 1 and 2 (commenced Sept/Dec 2009) are providing data that aims to quantify the effects of foremost operational parameters on the aging path, such as magnitude of power pulses, and magnitude of thermal cycling during duty cycles. Complementary studies are being performed at HNEI. Collectively these studies will continue until adequate performance loss is seen to elucidate mature trends for diagnostic (mechanistic) analyses.
- ❑ Key computational methods have been developed and benchmarked to facilitate diagnostic analyses on performance and aging data. These include methods that cover:
    - ➢ Contributions to Capacity Loss over aging,
    - ➢ Contributions to Cell Conductance Loss over aging,
    - ➢ Cell Kinetic performance over multiple domains,
    - ➢ Incremental Capacity Analysis (ICA) over aging,
    - ➢ Thermodynamics-based approach to predicting Aging Path Dependence.
- ❑ An Interactive Battery Database Management System (BDMS) is under development to facilitate efficient and timely extraction of large and numerous datasets needed for more extensive diagnostic analysis by INL and collaborators.

Intellectual property from this work has been documented (patent applications)

Data Examples

INL Path Dependent Studies 1 and 2 commenced Sept/Dec 2009, giving interim aging trends at this time. HNEI aging studies have either been completed or are in progress.

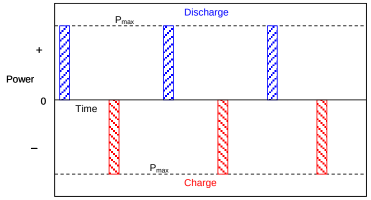
All studies will continue until mature aging trends or excessive performance losses are seen.

Tech. Accomp. & Progress

PD-1

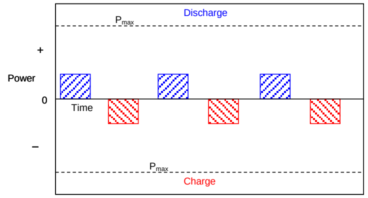
This slide will be updated to the latest RPT at the time of the Merit Review.

Scenario 1 (Baseline)

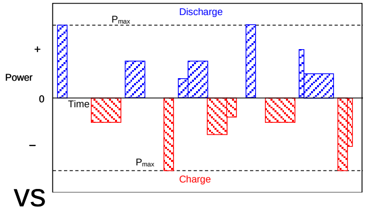


VS

Scenario 2

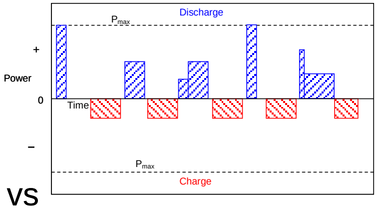


Scenario 3



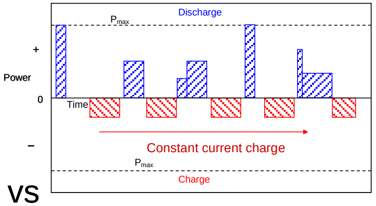
VS

Scenario 4

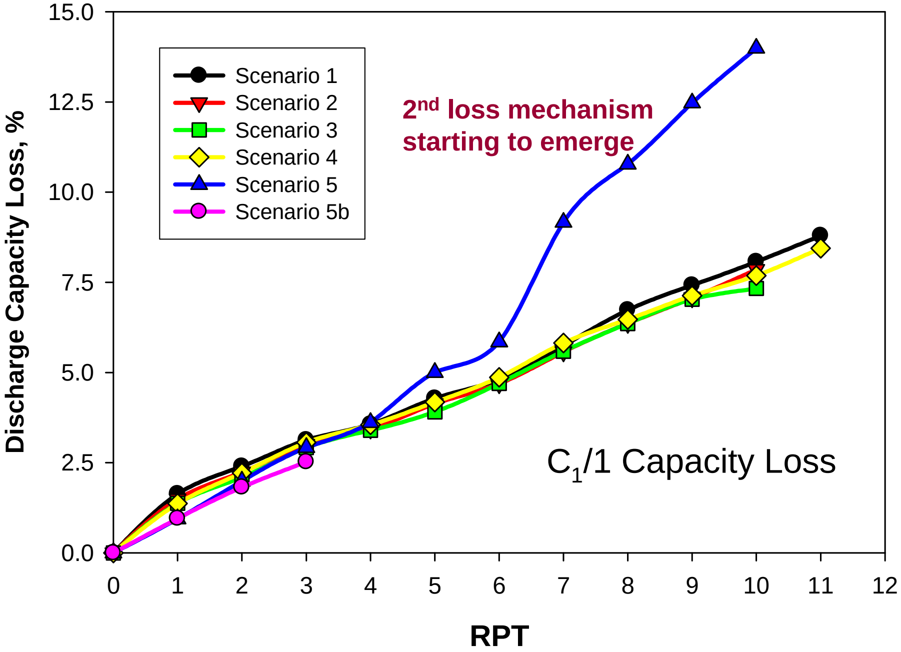


VS

Scenario 5

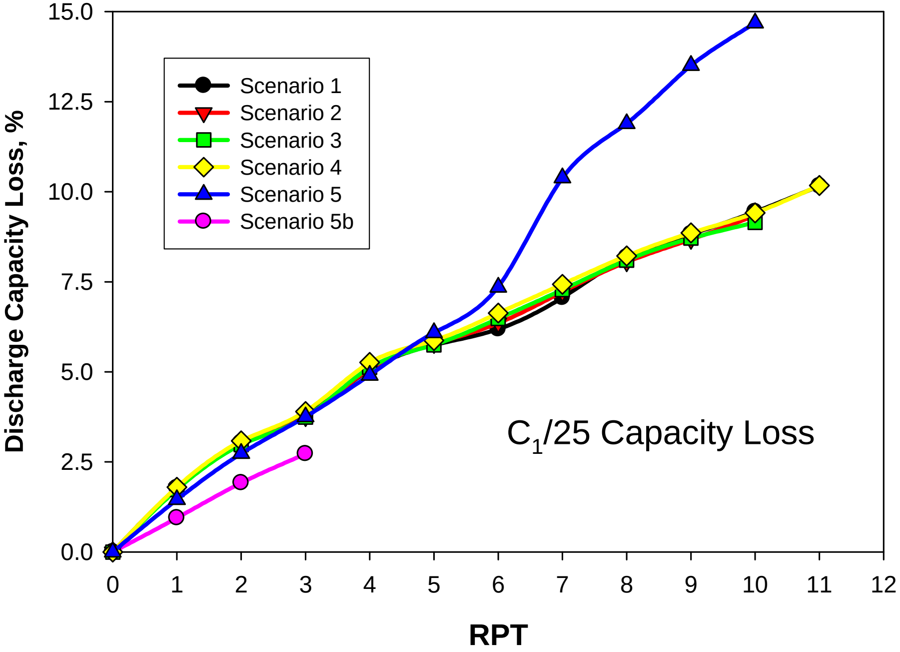


VS



2^{nd} loss mechanism starting to emerge

$C_1/1$ Capacity Loss



$C_1/25$ Capacity Loss

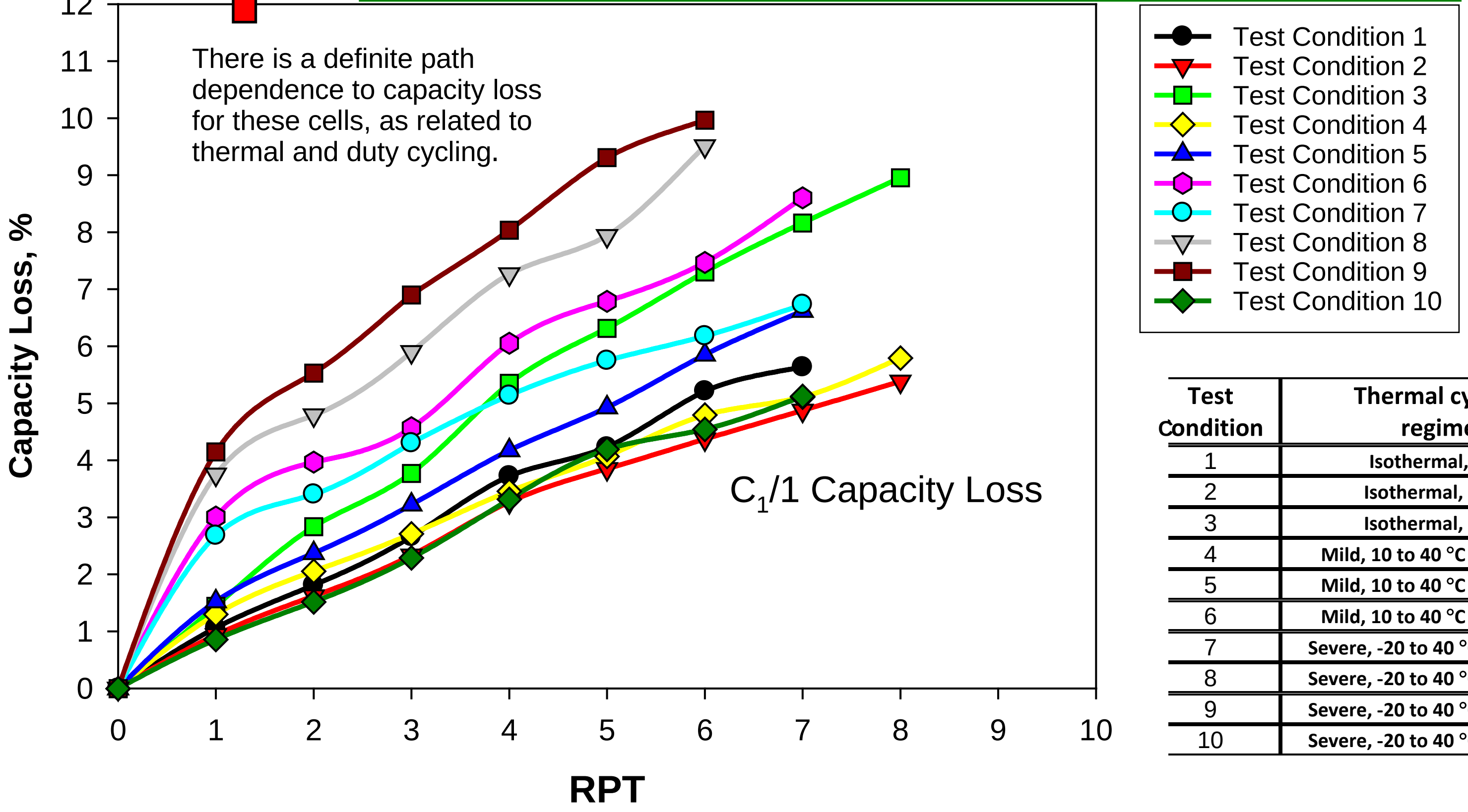
Scenario 5 is a condition where cells discharge from a full charge. The data here shows that these cells are charge sensitive, and age faster when operated near 100% SOC.

Tech. Accomp. & Progress

This slide will be updated to the latest RPT at the time of the Merit Review.

PD-2

These results suggest that EDV batteries operated at colder climates will survive a shorter time and should have more sophisticated thermal management.

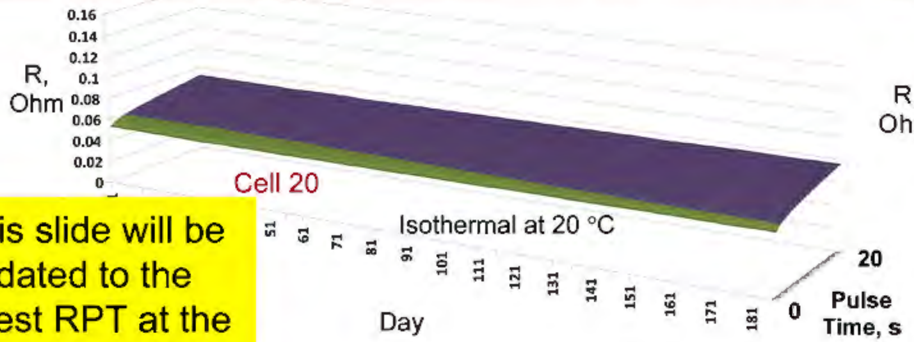


There is a definite path dependence to capacity loss for these cells, as related to thermal and duty cycling.

Test Condition	Thermal cycling regime	Duty cycle frequency
1	Isothermal, 0 °C	Continuous
2	Isothermal, 20 °C	Continuous
3	Isothermal, 40 °C	Continuous
4	Mild, 10 to 40 °C in 30 min.	1 Round trip/day
5	Mild, 10 to 40 °C in 30 min.	Continuous
6	Mild, 10 to 40 °C in 15 min.	Continuous
7	Severe, -20 to 40 °C in 30 min.	1 Round trip/day
8	Severe, -20 to 40 °C in 30 min.	Continuous
9	Severe, -20 to 40 °C in 15 min.	Continuous
10	Severe, -20 to 40 °C in 30 min.	None (cal-L)

Thermal cycling effects on capacity loss are more evident for those cells actively undergoing duty cycles. In contrast, cells under calendar-life conditions and thermal cycling experience slower aging (Condition 10).

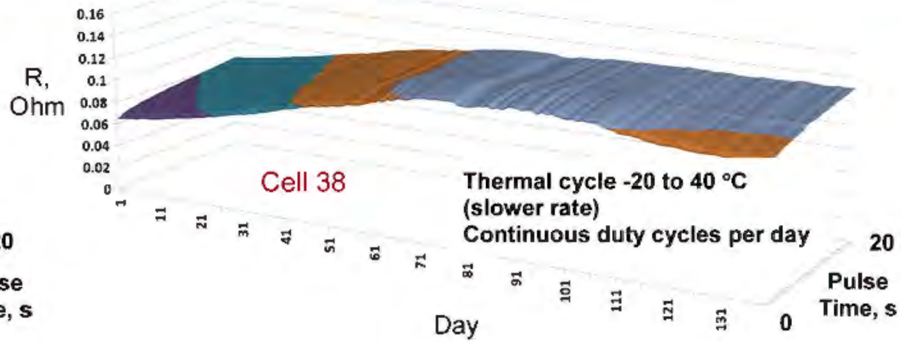
PD-2, Pulse-per-Day Discharge Impedance Data at 30 °C, Sanyo Y (selected conditions)



Cell 20

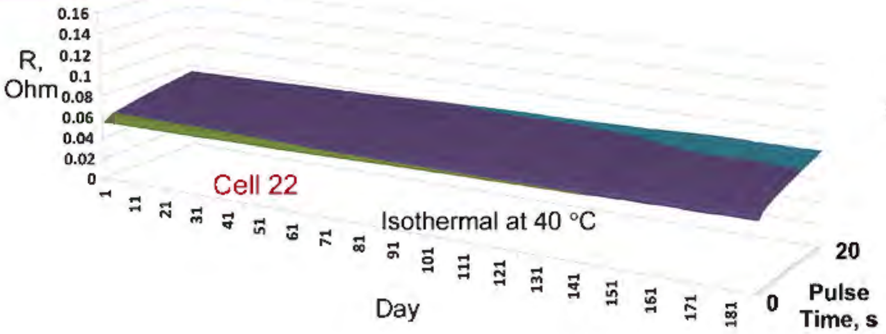
Isothermal at 20 °C

This slide will be updated to the latest RPT at the time of the Merit Review.



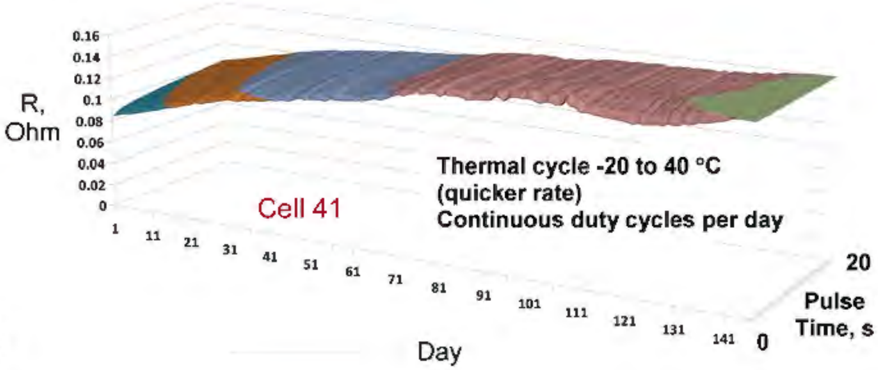
Cell 38

Thermal cycle -20 to 40 °C (slower rate)
Continuous duty cycles per day



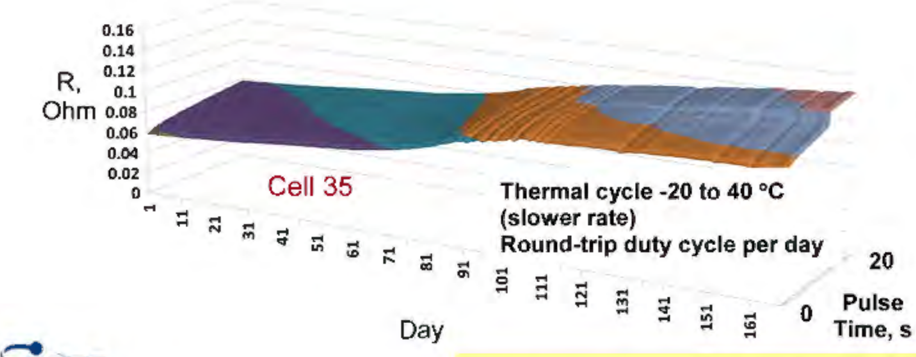
Cell 22

Isothermal at 40 °C



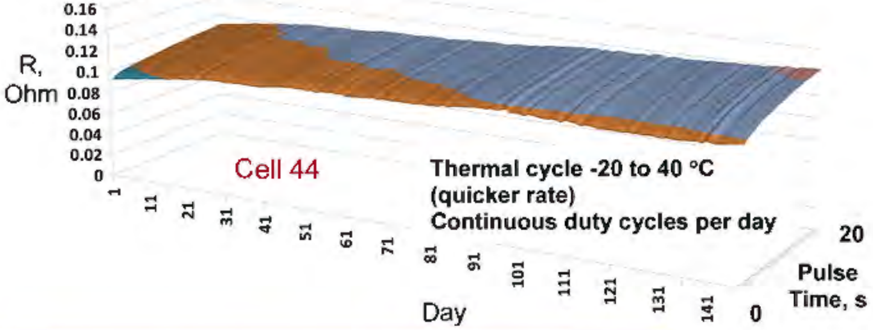
Cell 41

Thermal cycle -20 to 40 °C (quicker rate)
Continuous duty cycles per day



Cell 35

Thermal cycle -20 to 40 °C (slower rate)
Round-trip duty cycle per day



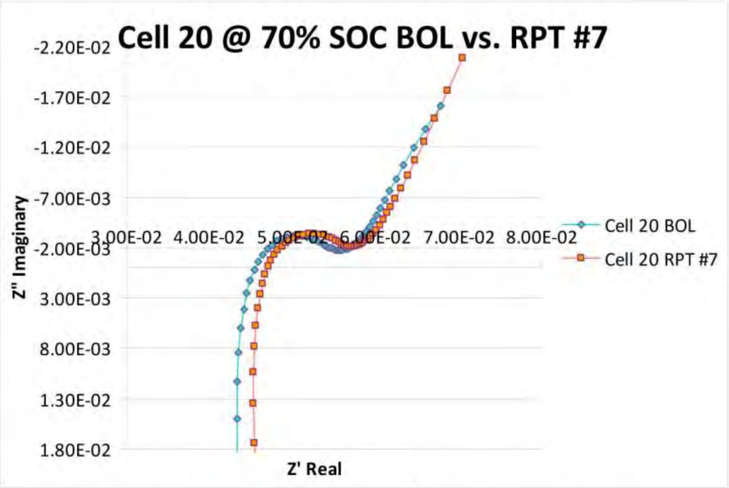
Cell 44

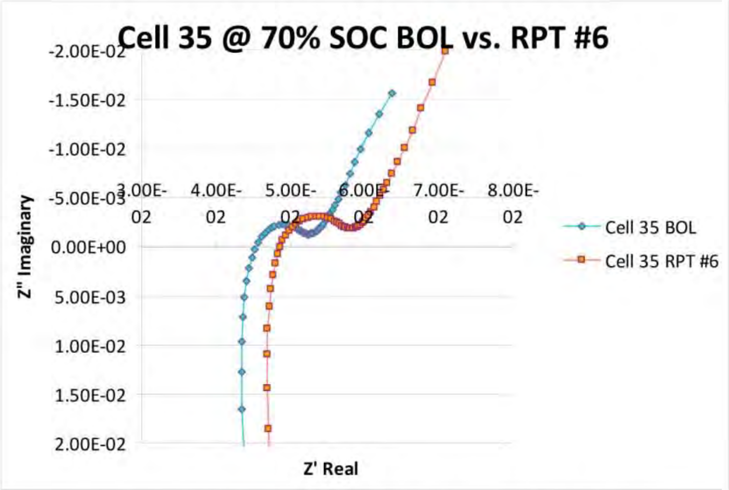
Thermal cycle -20 to 40 °C (quicker rate)
Continuous duty cycles per day

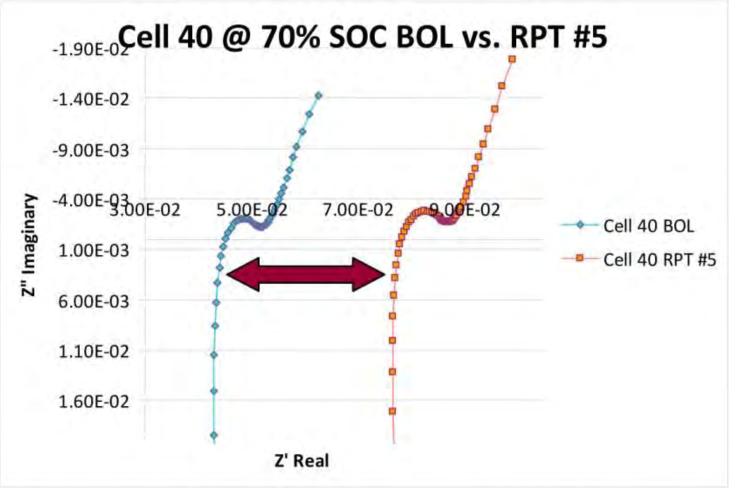
Cell impedance rises faster for cells cycled under greater thermal gradients!

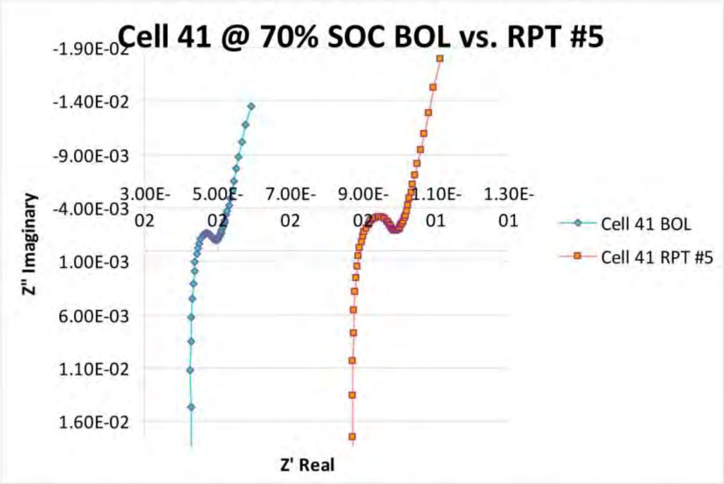
EIS for selected cells in PD-2

30 °C









There is an *increase of ohmic impedances* that tracks with severity of thermal and duty cycling. This is a strong aging effect that surpasses the increase of interfacial impedance. Does the combination of thermal and duty cycling cause a degradation of the electronic properties or mechanical structure of cell materials? Such trends will yield greater power limitations.

Diagnostic Studies by HNEI

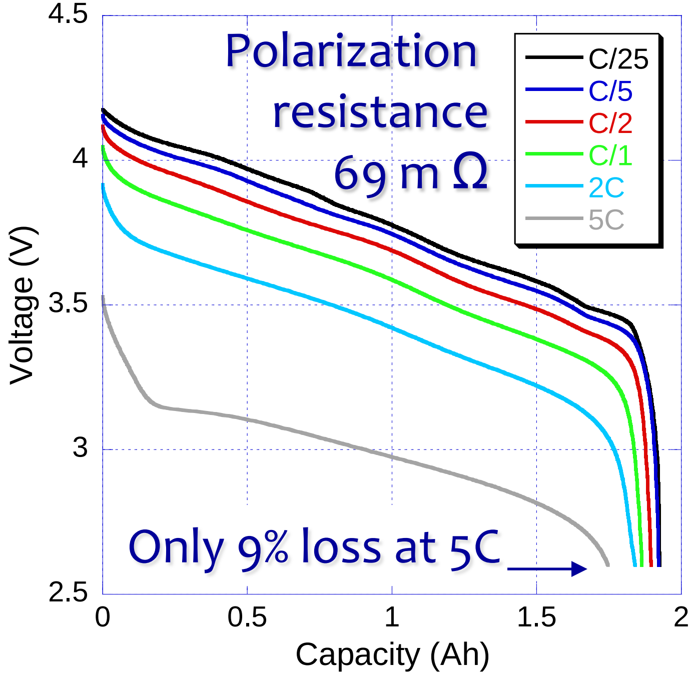
- A small population of Sanyo Y cells was subjected to additional diagnostic testing to gain a deeper knowledge of performance attributes.
- Duty cycle consisted of 2C cycling at RT.
- Aging regimes were detected: Stage 1 (1-500 cycles); Stage 2 (500-950 cycles).
- Analysis of capacity retention and incremental capacity (dQ/dV) provides a basis for assigning mechanisms of performance loss. Data suggests early capacity fade is due to loss of lithium inventory (SEI growth), followed by loss of active material. These findings complement INL modeling tools.

Initial Conditioning and Characterization Tests

Performance Analysis

- Capacity from C/25 to 5C rates

Discharge



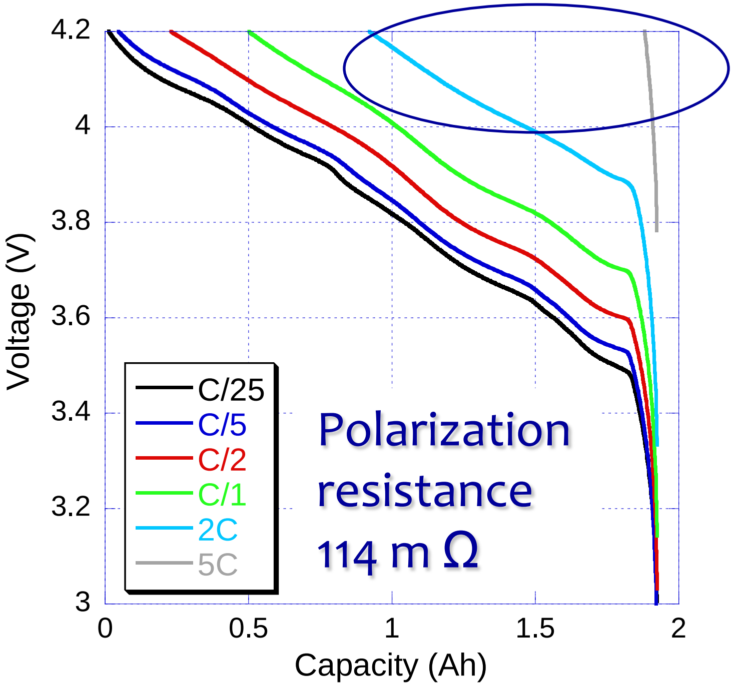
Polarization resistance 69 m Ω

Only 9% loss at 5C

- Good rate capability

Charge

Operating window hampers recharging at high rates



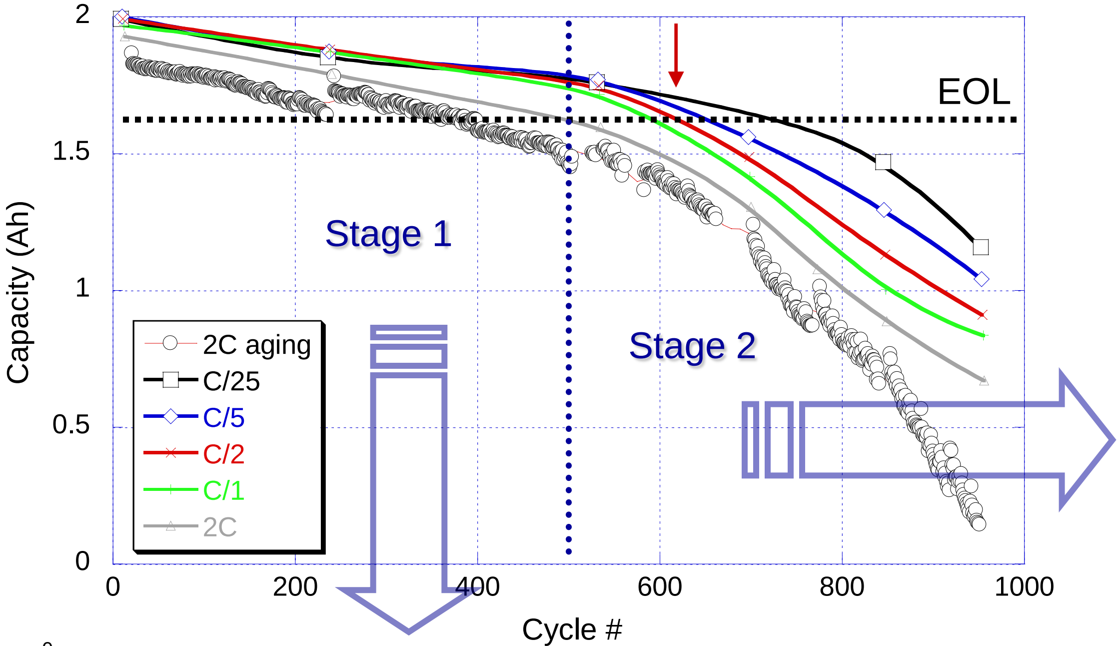
Polarization resistance 114 m Ω

- Limited rate capability

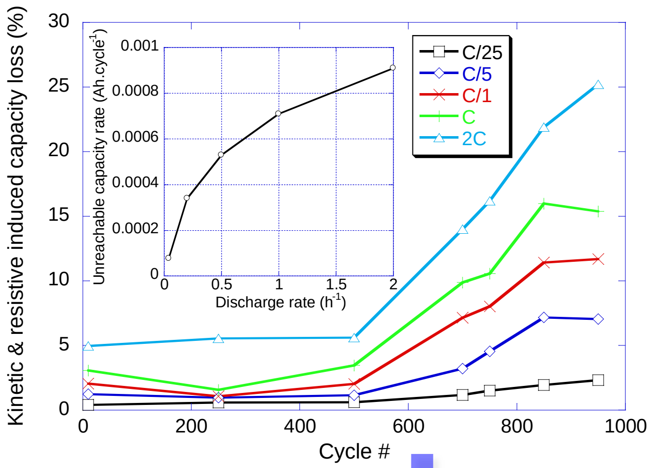
Cell may be capable for high rate pulsing but not fast charging (>C)

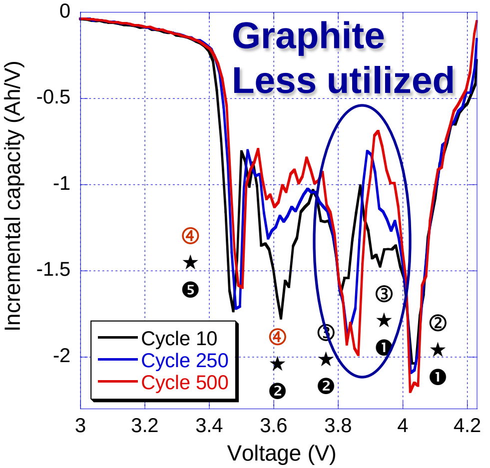
Capacity Retention upon 2C Cycle Aging

- EOL ($Q_{C/2}<80\%Q_{nom}$) after 600 cycles

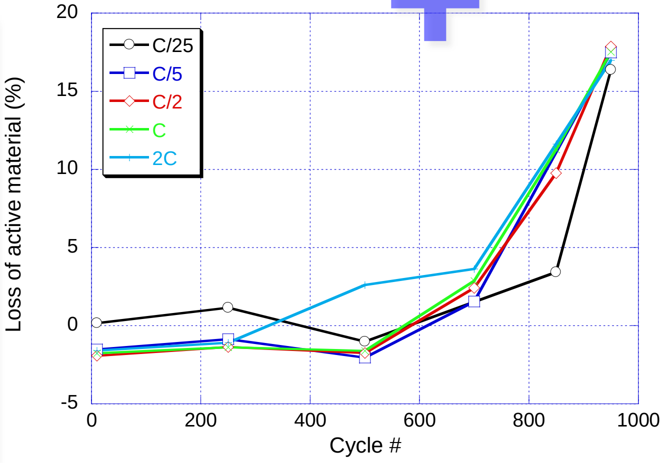


- Degradation in two stages, separated at about 500 cycles





- **Stage 1**
  - **- Loss of lithium inventory**
  - **- No capacity loss induced by kinetic/resistive effects**
- **Stage 2**
  - **- Loss of lithium inventory**
  - **- Kinetic degradation**
  - **- Loss of active material**



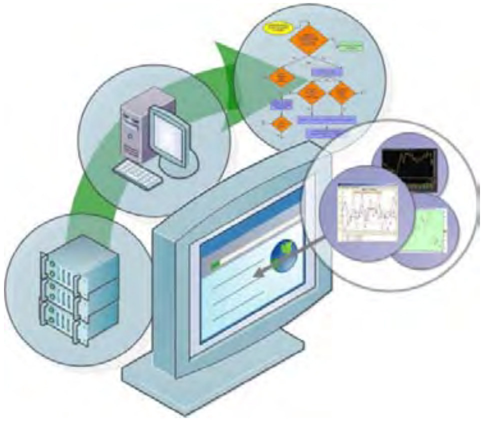
Battery Database Management System (BDMS)

(in collaboration with HNEI)

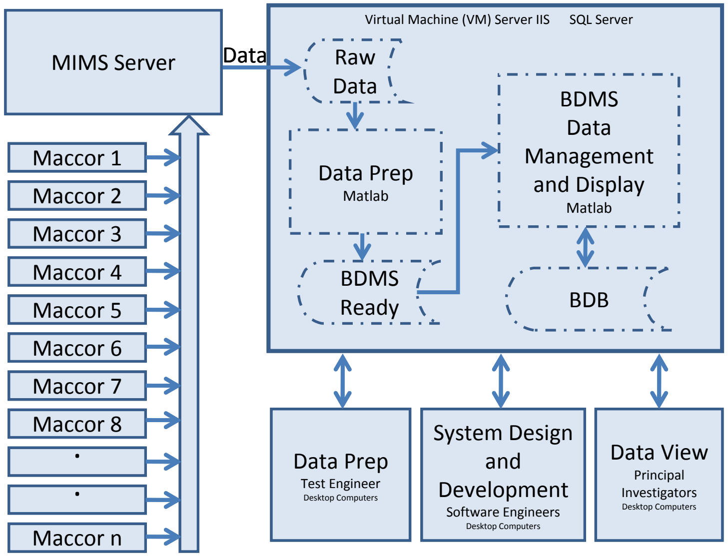
Purpose

To facilitate the efficient and timely extraction of large and numerous datasets needed for diagnostic analysis by INL and collaborators. Platform will reside within a virtual environment.

Good progress has been made in the recent quarter to build infrastructure for a dynamic database that is adaptable, expandable, trainable, and highly interactive.



Stage 1 Development



MIMS Server

Data

Maccor 1
Maccor 2
Maccor 3
Maccor 4
Maccor 5
Maccor 6
Maccor 7
Maccor 8
.
.
Maccor n

Virtual Machine (VM) Server IIS SQL Server

Raw Data

Data Prep
Matlab

BDMS Ready

BDMS Data Management and Display
Matlab

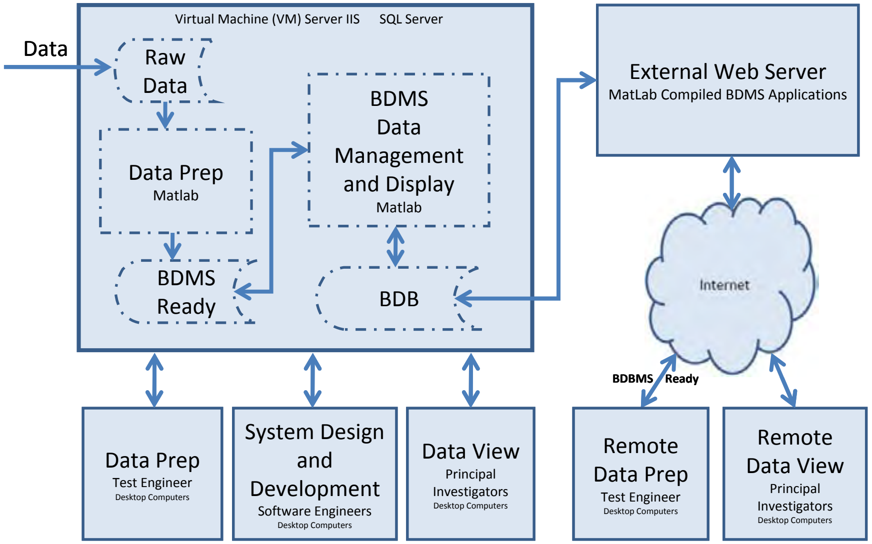
BDB

Data Prep
Test Engineer
Desktop Computers

System Design and Development
Software Engineers
Desktop Computers

Data View
Principal Investigators
Desktop Computers

Stage 2 Development and Deployment



Data

Virtual Machine (VM) Server IIS SQL Server

Raw Data

Data Prep
Matlab

BDMS Ready

BDMS Data Management and Display
Matlab

BDB

External Web Server
MatLab Compiled BDMS Applications

Internet

BDBMS Ready

Data Prep
Test Engineer
Desktop Computers

System Design and Development
Software Engineers
Desktop Computers

Data View
Principal Investigators
Desktop Computers

Remote Data Prep
Test Engineer
Desktop Computers

Remote Data View
Principal Investigators
Desktop Computers

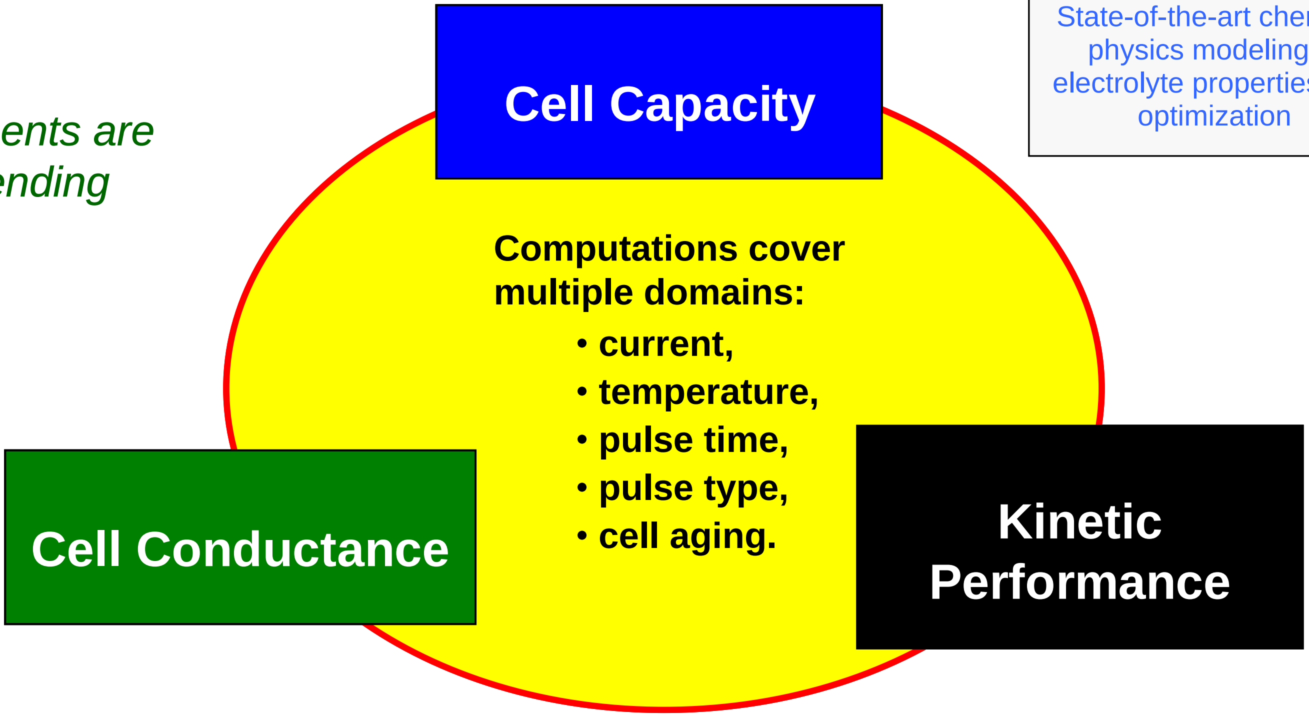
INL Essential Modeling Tools

Interpretation of Life and Performance Data

Key Elements are Patent Pending

Advanced Electrolyte Model (AEM)

State-of-the-art chemical physics modeling of electrolyte properties and optimization



Cell Capacity

Computations cover multiple domains:

- **current,**
- **temperature,**
- **pulse time,**
- **pulse type,**
- **cell aging.**

Cell Conductance

Kinetic Performance

These capabilities lend themselves to mechanistic analyses, cell design, and are amenable to aging path dependence modeling per INL protocol; complemented by Equivalent Circuit Models (ECMs).

Life Data + Mech. Models = Early Diagnosis and Predictive Analyses

Cell Sage

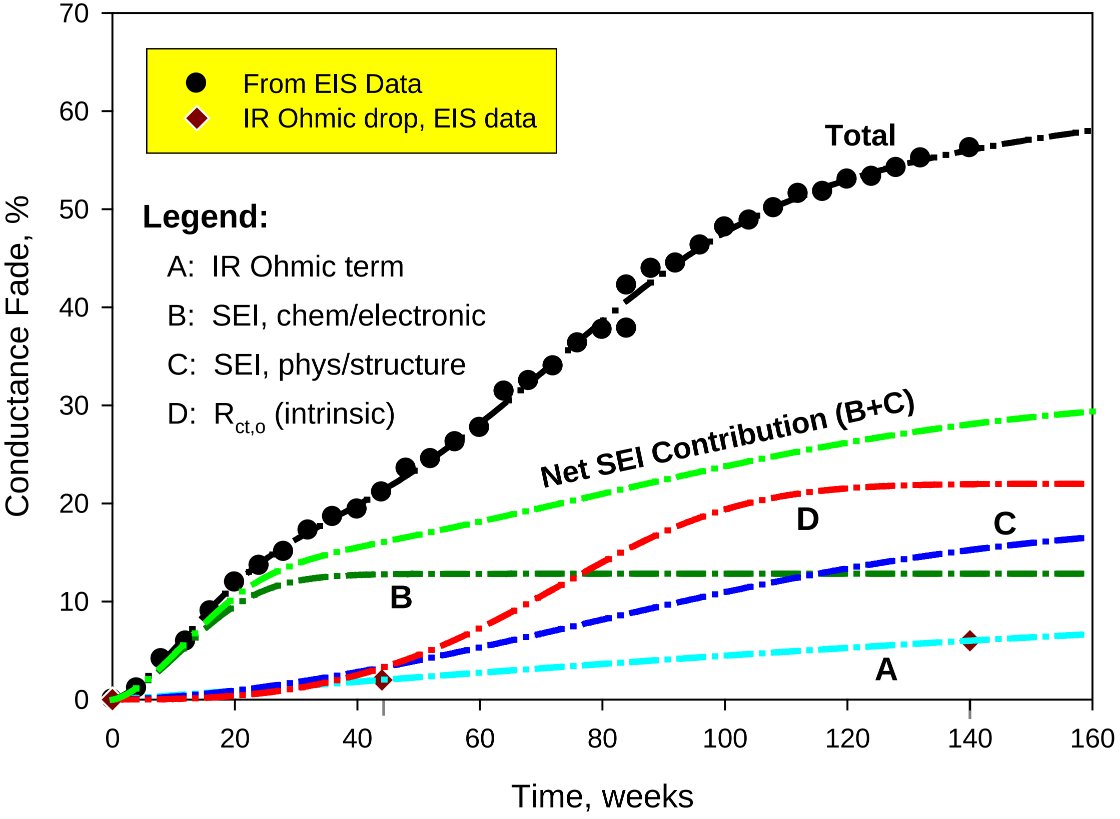
Battery Performance Diagnostics and Prediction

- ◆ A collection of novel computational tools useful toward cell design, performance characterization, and evaluation of aging trends, that could be integrated or embedded into numerous applications or within onboard device monitoring and control systems.
- ◆ This modeling suite will enable multi-tier analysis and prediction of several DADT performance parameters over aging.
- ◆ Core elements are copyrighted and patent pending, *and are demonstrated in following slides using Gen2 lithium-ion cell data as a baseline.*

CellSage demo is slated for 2011.

Modeling Cell Conductance Fade

Results from two-model synergy (MSM + θ-BV Kinetics)



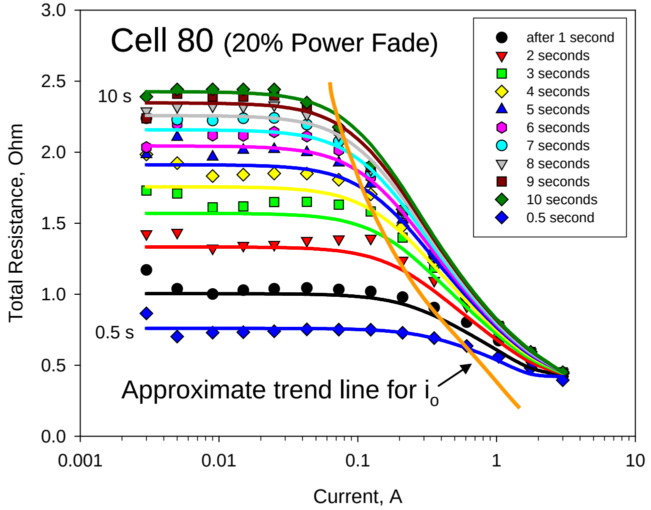
Based on data for EIS semicircle RHS edge, Gen2 cells cycle-life tested at 25 °C.

Cell conductance has a principal influence on attainable power, decreasing over the life of a cell.

Key insights into cell operation and rate-based mathematics allows accurate modeling and high-fidelity diagnostic analysis of conductance behavior in electrochemical cells.

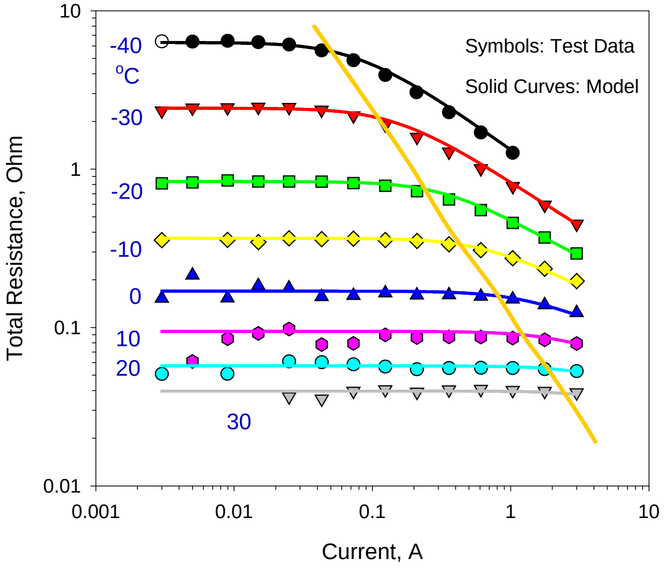
INL Kinetics Modeling

R_{total} at –30 °C along pulse timeline

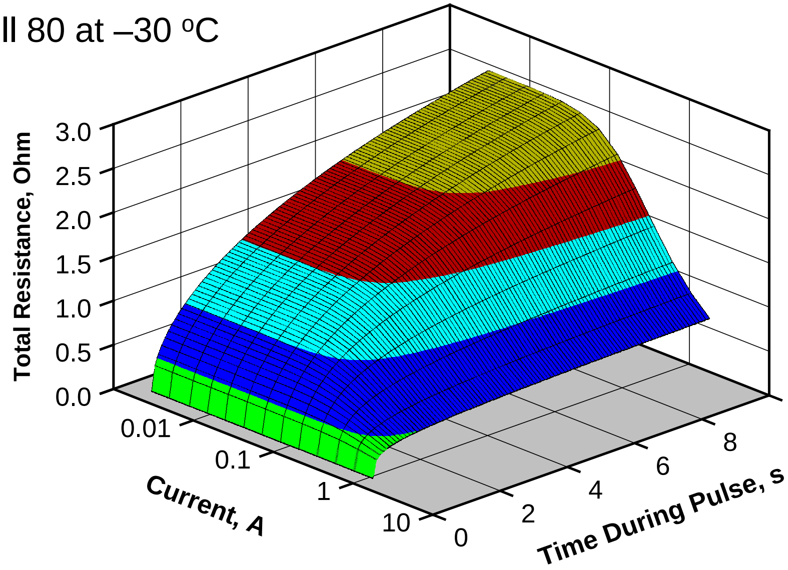


- **Based on an improved form of Butler-Volmer expression that is well-suited for Li-ion systems. Model gives extremely accurate predictions over (T, I, t_{pulse}, cell aging) when coupled with an advanced set rate expressions for charge transfer.**

R_{total} at 10 s over temperature

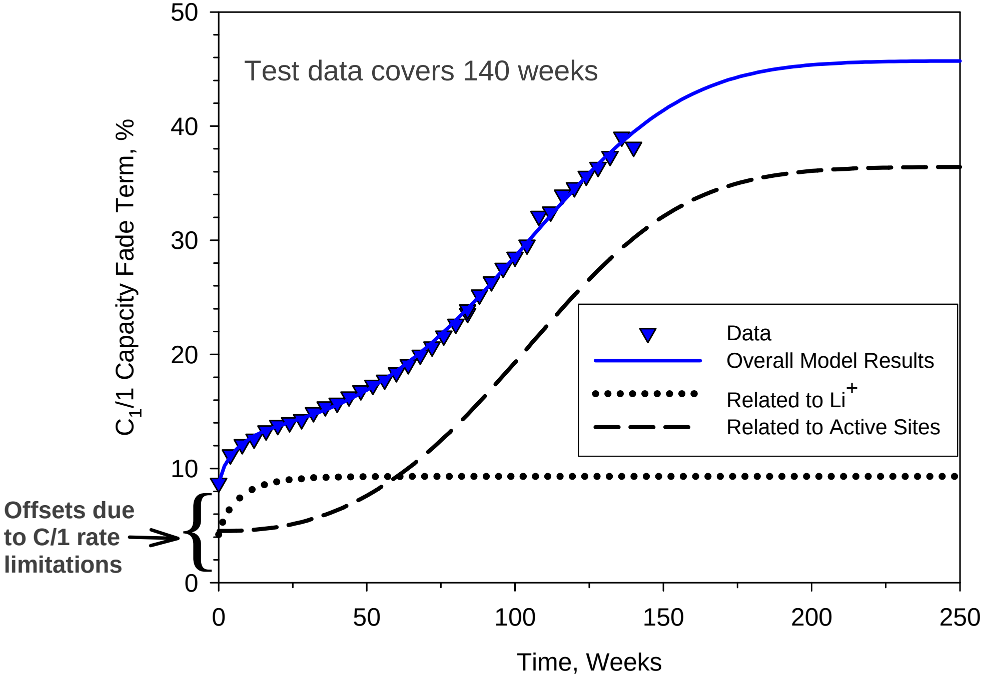


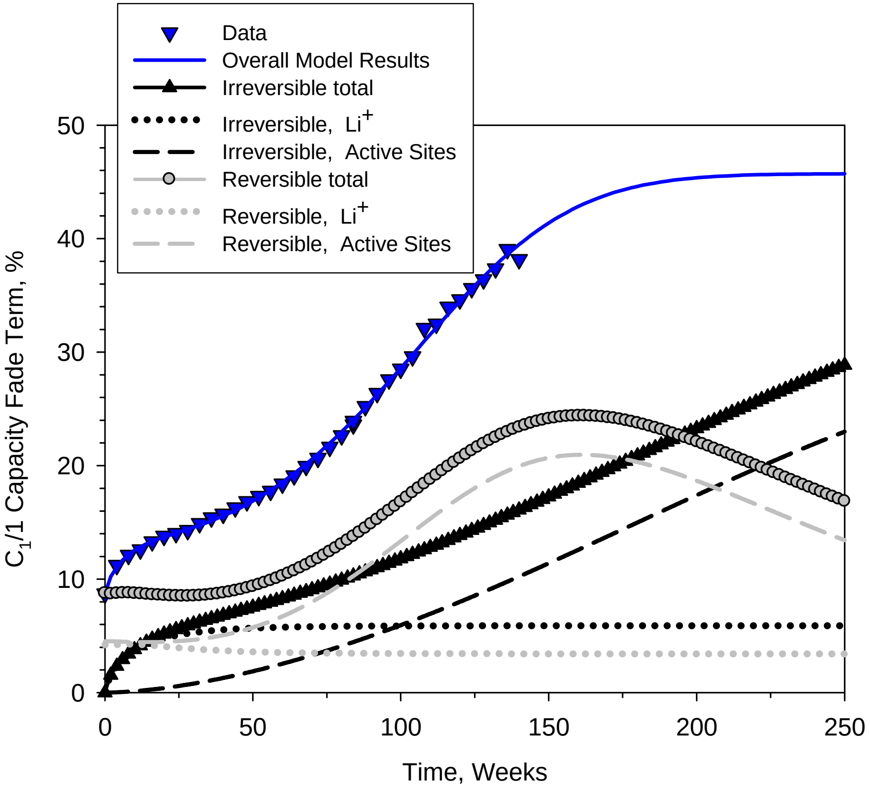
Gen2 Cell 80 at –30 °C



Modeling Capacity Loss Over Life

(Gen2 Li-ion Cells under cycL Testing at 25 °C)





- The rate of lithium consumption is high during initial time (continued SEI formation; side reactions), but tapers off considerably by 30 weeks.
- Reversible contributions to fade dominate at early time, are tied primarily to active sites, and undergo a maximum at around 150 weeks. In comparison, irreversible losses grow steadily over the time period.
- Capacity fade is dominated by mechanisms that impact active sites, initially by reversible mechanisms through about 180 weeks, then by irreversible mechanisms thereafter.
- Under these test conditions the theoretical limit of capacity loss is effectively met by about 200 weeks.

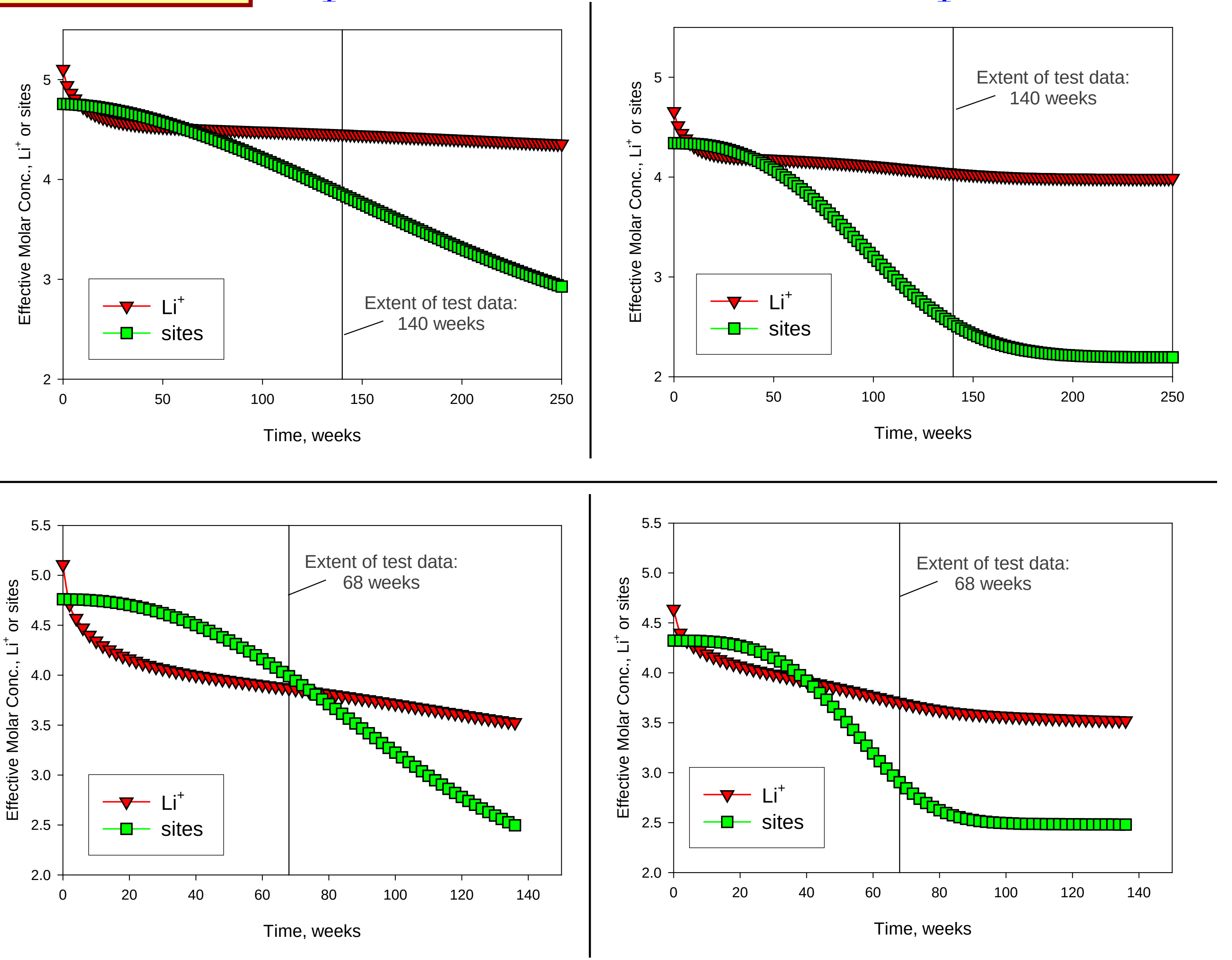
Concentration Terms (capacity loss)

Gen2 Data, cyc-L conditions

$C_1/25$ **$C_1/1$**

25 °C

45 °C



Collaborations

- **Hawaii Natural Energy Institute.** Involved in diagnostic analysis of cell performance data to determine path dependence effects related to aging conditions tied to PHEV test protocol. HNEI work is coordinated by Prof. Bor Yann Liaw.
- **University of California at Pomona.** This work has been suspended due to recent health considerations of Prof. Lloyd Lee at UC-Pomona. When resumed, we will apply density functional theory (DFT) and rigorous treatment of electrolyte properties to determine how the SEI structure and chemistry affects local electrochemical behavior and efficiency and local thermodynamic behavior of electrolyte species. Findings of this work will allow greater diagnostic analysis of interfacial limitations in lithium-ion cells.
- **Argonne National Lab**. Provides oversight and coordination on key issues regarding the ABRT program. Battery testing and modeling tasks are complementary between INL and ANL.

Future Work

- We will continue to monitor aging trends for our path dependence studies over the next several months, and will quantify the impact of thermal cycling on Sanyo Y cell aging.
- Mechanistic analyses and modeling of mature data sets will be performed at the completion of this work to determine the extent of path dependence of cell aging, wherein existing INL and HNEI modeling tools will be applied.
- Demonstrate INL diagnostic/predictive modeling capabilities through software that integrates key modules regarding performance over life (CellSage).
- Future path dependence studies could involve other duty cycles (e.g., FUDS, DST), or temperature parameters defined for a particular city or region.
- Pending cell availability, we will perform DADT on other viable commercial cells to elucidate path dependence of aging for alternate cell chemistries (e.g., LTO or silicon anodes, phosphate-based cathodes).

Summary

- Using Sanyo Y cells as a test platform, we have detected path dependent aging in both capacity and impedance data.
- Early trends in capacity fade data show there is accelerated aging when cells experience significant thermal cycling while performing duty cycles. Conversely, cells under calendar-life conditions are more immune to thermal cycling aging effects. Thus, combined thermal and chemical gradients act to compound the stress experienced at the material level.
- Impedance rise is a strong function of test condition, and in many cases the amount of conductance loss far outweighs capacity loss. EIS data shows a noteworthy rise in R_{ohmic}. Continuation of this trend implies that these cells will be more power limited, rather than energy limited, later in life.
- In general, aging effects related to thermal cycling will have a sobering impact on warranty commitments for HEV, PHEV, and EV scenarios, and calls for better thermal management. *Thus, thermal cycling should be considered as a standard aging condition for batteries intended for vehicle applications (HEV, PHEV, EV), and could be useful as an accelerated aging condition.*
- INL and HNEI have developed complementary computational tools used to model, diagnose, and predict performance and aging of electrochemical cells. These tools are being applied to issues of aging path dependence to elucidate mechanisms of cell degradation, and will come to full implementation on the mature datasets.

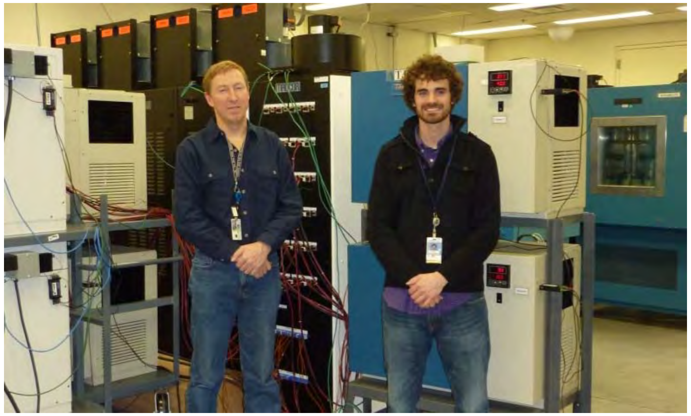
The immediate benefits of this work are (1) to provide more realistic and accurate life predictions by accounting for the influence of thermal cycling effects and related path dependence on aging mechanisms, and (2) provide a basis for improving battery development, diagnosis, and management. Knowledge of aging path dependence lends itself to optimizing usage conditions for particular cell chemistries so as to prolong the lifetime of batteries in service.

Acknowledgements

- DOE Vehicle Technologies Program
- Brian Cunningham, DOE-EERE, VTP
- Peter Faguy, DOE-EERE, VTP
- David Howell, DOE-EERE, VTP
- Jeff Belt, INL
- Tim Murphy, INL

U.S. Department of Energy
Energy Efficiency
and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

HNEI



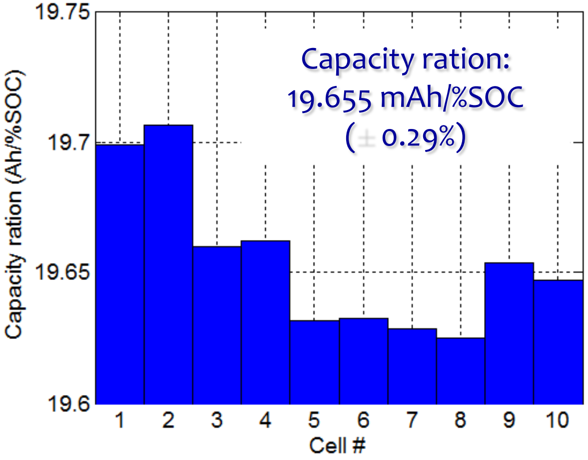
This work was performed for the United States Department of Energy under contract DE-AC07-05ID14517.

Technical Back-Up Slides

Cell-to-cell Variation Analysis

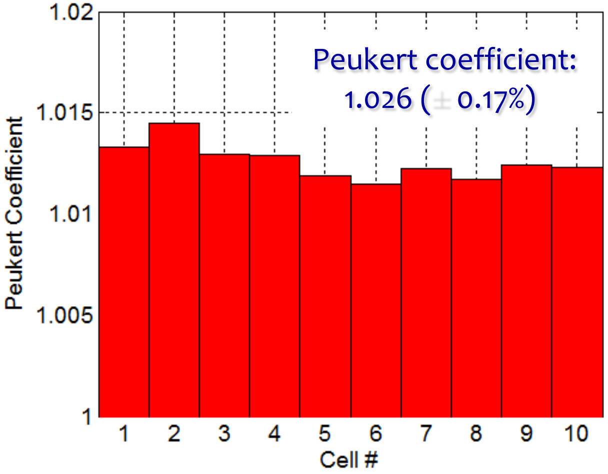
- Assess cell-to-cell variations to establish confidence level for comparison of test results among different protocols and labs.
  - Three attributes can be used to characterize cell variations:

Amount of active material



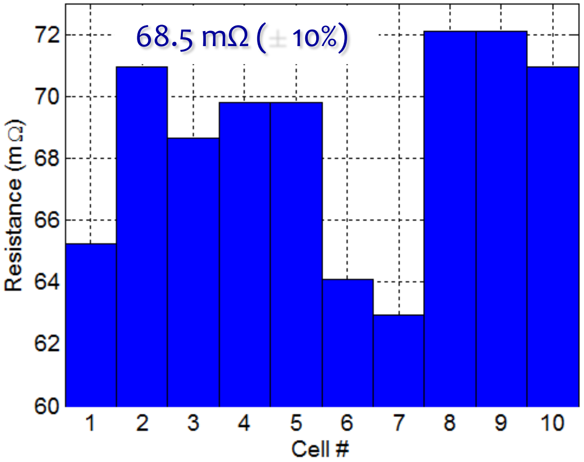
- **Max capacity**

Rate capability



- **Usable fraction of capacity**

Polarization resistance



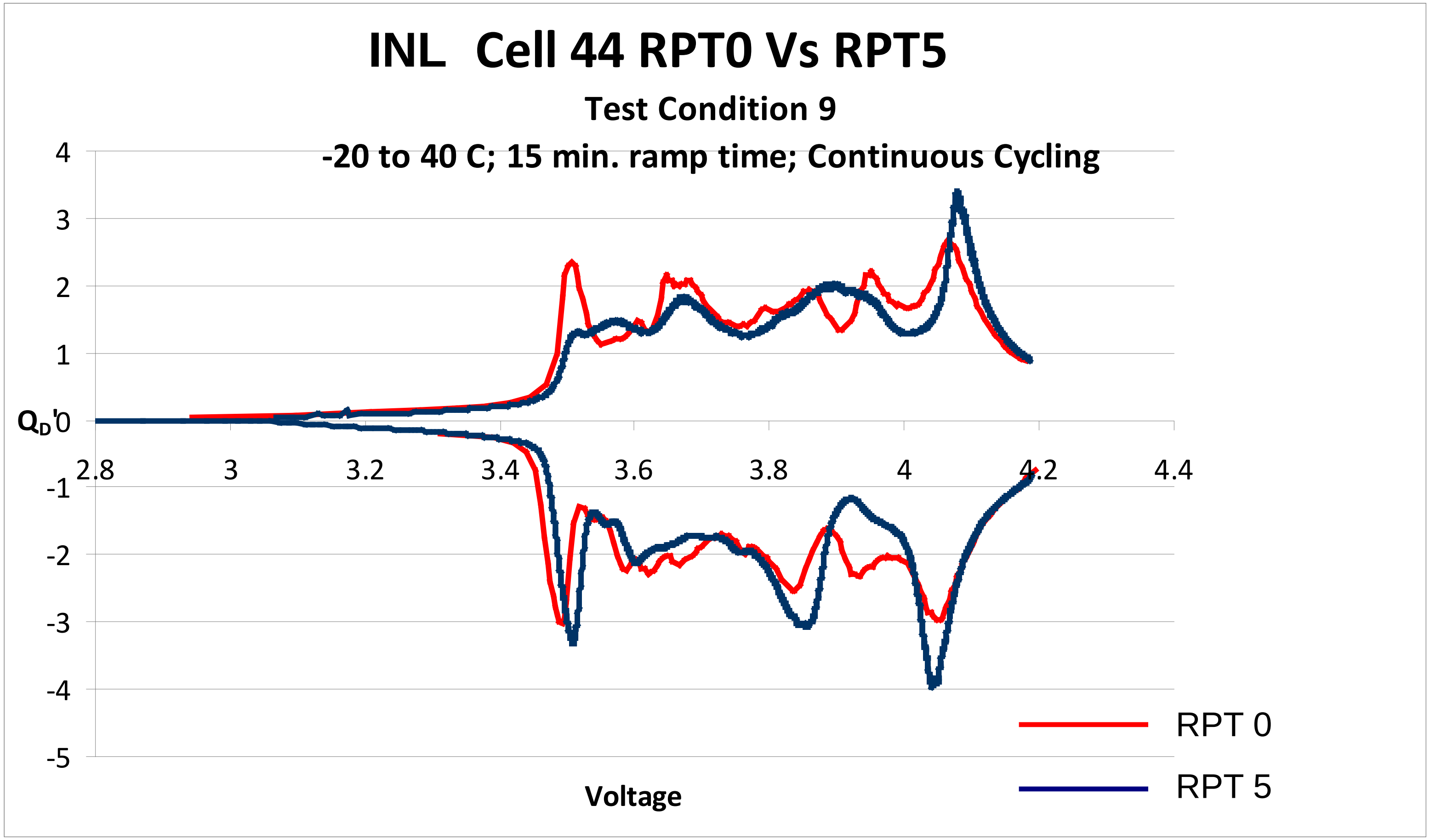
- **Cutoff points**

Little cell-to-cell variations → anticipate consistency in test results

Validate good confidence level

Expect less imbalance issue for battery pack applications

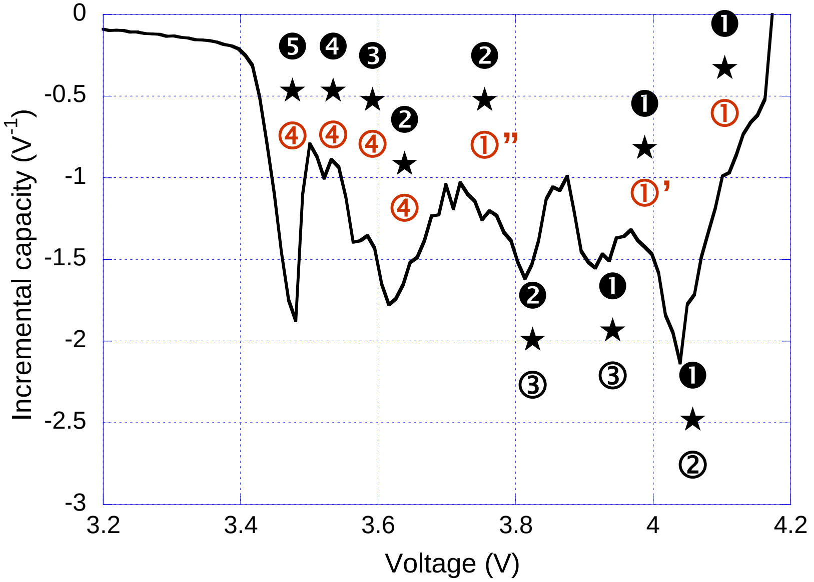
Incremental (differential) Capacity Analysis (ICA)

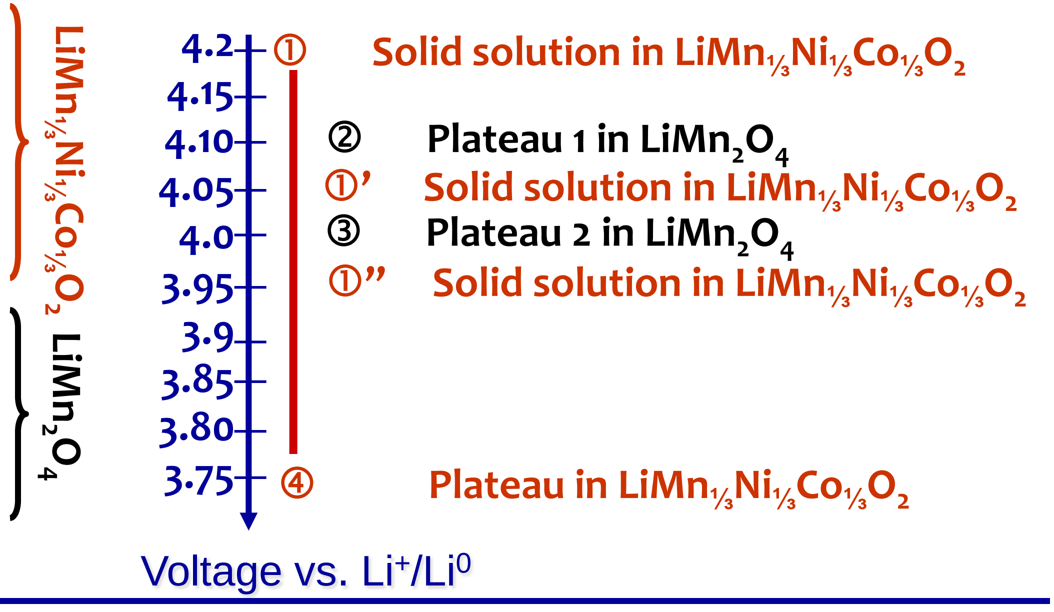


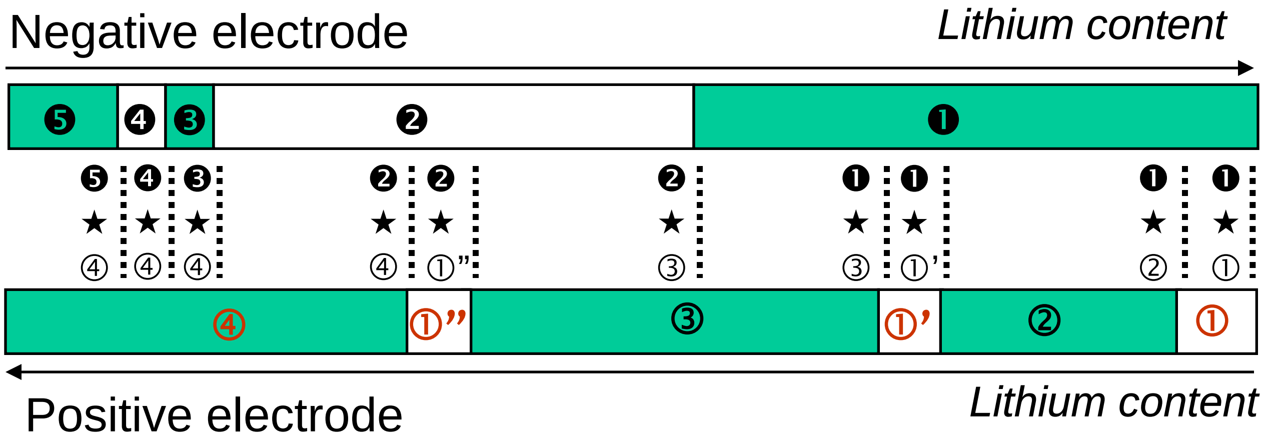
ICA provides an accurate, quantitative method to look at capacity attributes and related aging mechanisms (Dubarry, Liaw).

Incremental Capacity Analysis

- Incremental capacity peak indexing







IC curves and indexed peaks allow us to derive temporal changes on cell or electrode components for aging mechanism identification

Reference Performance Test (RPT)

The RPT is designed to facilitate Diagnostic Analysis of cell data. There are three primary components to the RPT, all assessed at 30 °C :

(A) static and residual capacity (SRC) over a matrix of current,

(B) kinetics and pulse performance testing over current for SOCs of interest,

(C) EIS for SOCs of interest (90, 70, 35%).

The RPT is performed on cells every 28-day test interval.

A “pulse-per-day” (PPD) is also performed to provide a quick diagnostic snapshot (20-s discharge and charge pulses at 90% SOC, 30 °C).