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

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Idaho National Laboratory

Overview

Timeline	Barriers
Project Start: April 2008 **Project End:** Ongoing **Percent Complete:** Extent of project completion depends on meeting key decision points and milestones built into schedule	**Cell/battery Life and related path dependence**

Budget	Partners
Funding Received: **FY 08: $ 80K** **FY 09: $ 220K** **FY 10: $ 460K**	**Hawaii Natural Energy Institute** **University of California at Pomona** **Argonne National Lab**

Objectives / 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.

Our objectives include*:

- Develop a platform of Diagnostic Testing (DT) geared toward specific issues in vehicular applications (e.g., HEV, PHEV).
- Employ DT to examine mechanistic contributions to cell aging.
- Develop advanced modeling tools that will complement DT.
- 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 on 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

Approach

- This work aims to bridge the gap between ideal laboratory test conditions and PHEV field conditions by isolating the predominant aging factors of Li-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 DT, 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 Li-ion cell is viewed as a batch reactor with aging processes modeled by sigmoidal mathematics.

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 performance 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,

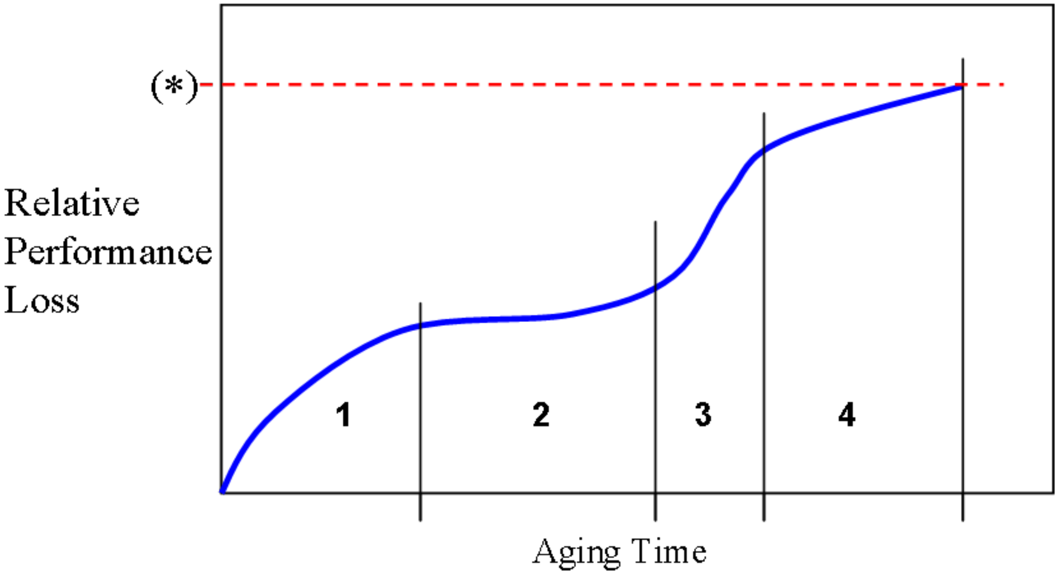
M_j : theoretical maximum limit of capacity loss under mechanism j considering the thermodynamic limit of degradation under j for a batch system.

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.

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.

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.

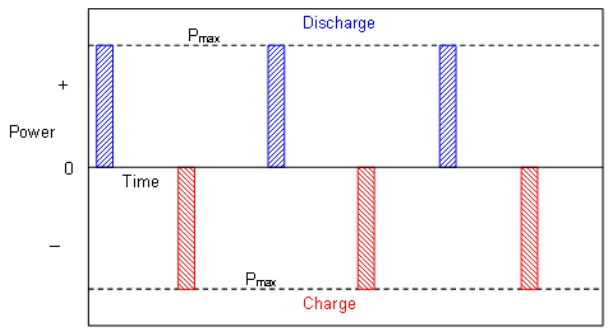
These cells are high quality, showing good stability and low cell-to-cell variability.

Example of Diagnostic Testing:
Aging Path Dependence
(two ongoing studies)

Path Dependence Studies ***(two examples)***

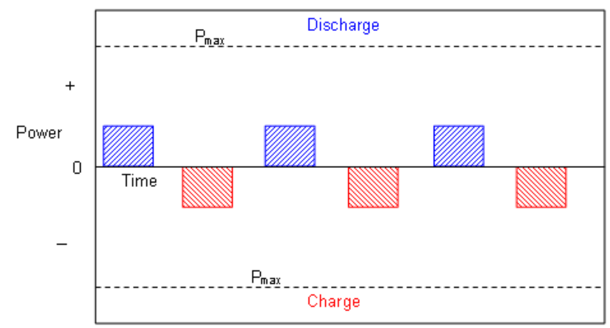
Study 1: Constant-power pulses of various magnitudes, using a time-average cumulative discharge energy that is equal for all scenarios.
Is there an aging path dependence due to severity and randomness of power pulses?

Scenario 1 (Baseline)

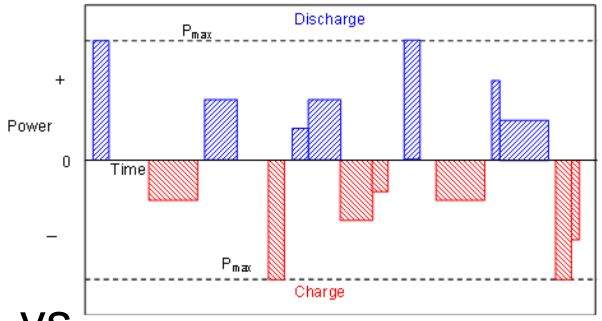


VS

Scenario 2

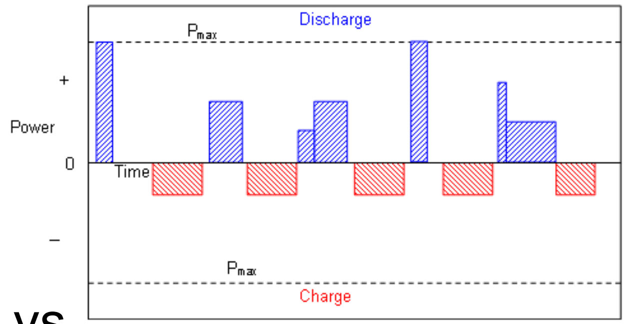


Scenario 3



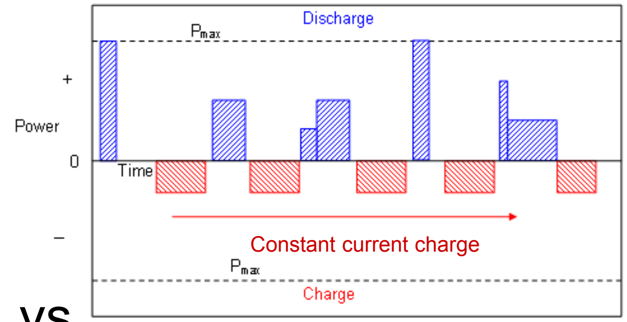
VS

Scenario 4



VS

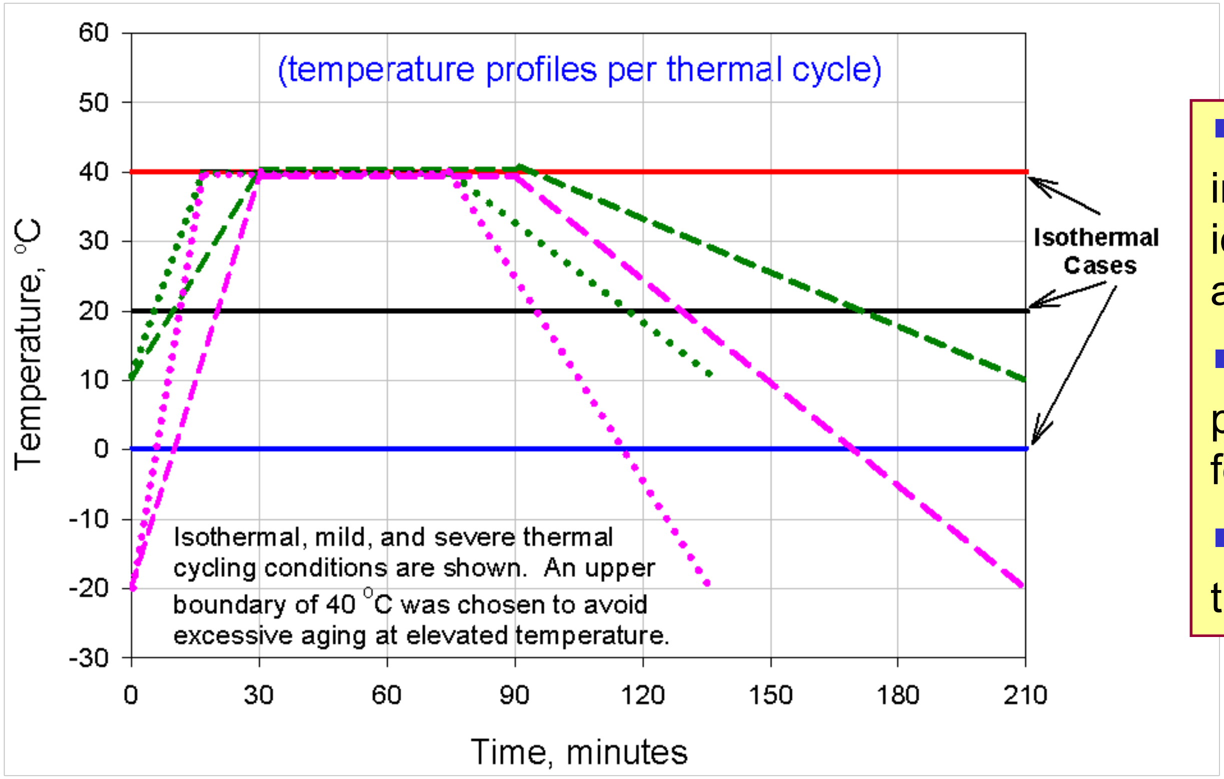
Scenario 5



VS

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.

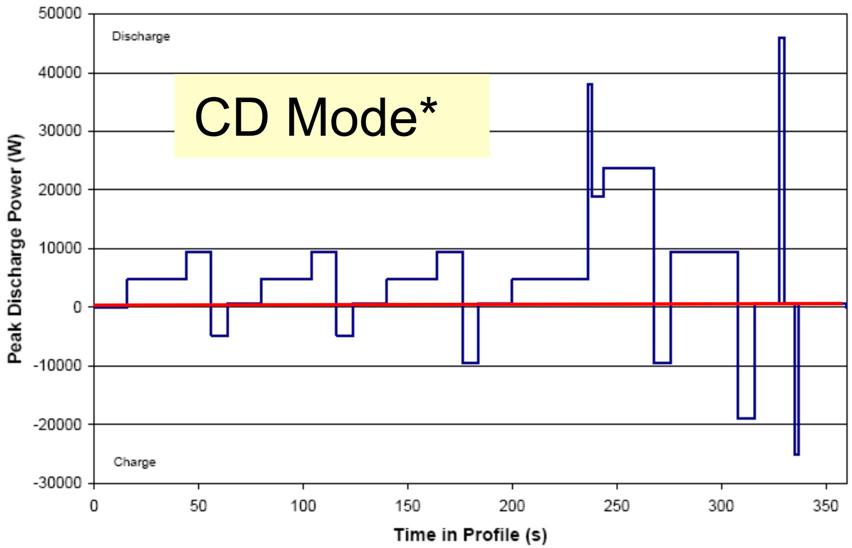
Path Dependence Studies

Study 2 cont.: 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 net profile represents a one-hour one-way commute.

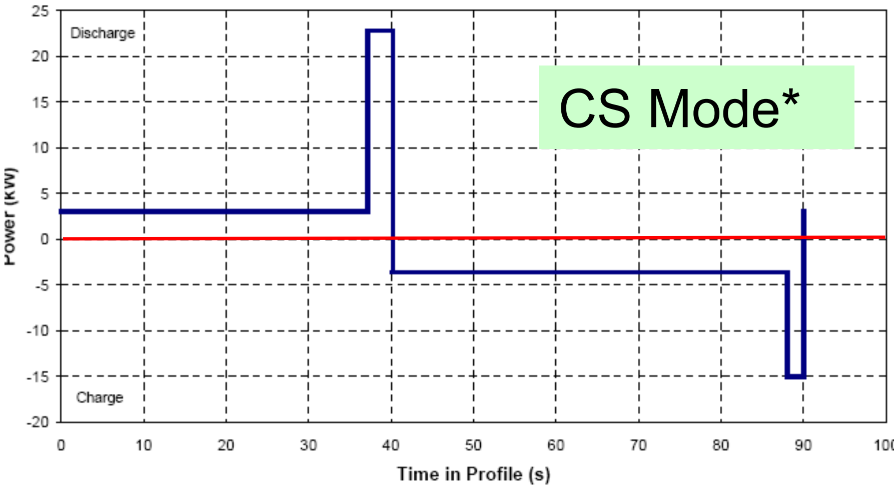
Duty Cycle $\left\{ \begin{array}{l} CD_1\ (SOC_0 \text{ to } SOC_1), \text{ then ten CS at } SOC_1 \\ + \quad CD_2\ (SOC_1 \text{ to } SOC_2), \text{ then ten CS at } SOC_2 \\ + \quad CD_3\ (SOC_2 \text{ to } SOC_3), \text{ then ten CS at } SOC_3,^{*} \end{array} \right\}$ **Cycle-life Profiles**

where

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



Charge-Depleting Cycle Life Test Profile for Maximum PHEV Battery



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

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

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).

Technical Accomplishments & Progress

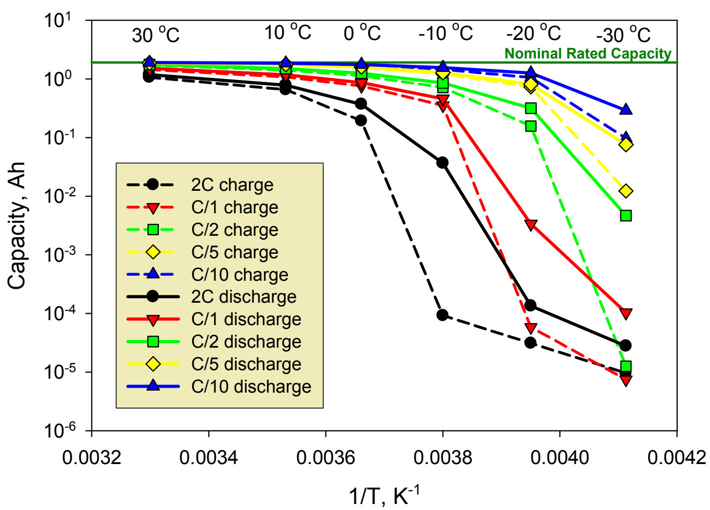
- Initial characterization of Sanyo Y 18650 cells was accomplished, which allowed us to set more precise conditions for the path dependent studies. Collectively, these studies comprised 16 cells.
- Path Dependent Studies 1 and 2 recently commenced (Sept/Dec 2009), so only early trends are available to date. Collectively, these studies comprise 45 cells. These studies will continue for at least 12 months or until adequate performance loss is seen to elucidate mature trends.
- Key computational methods have been developed and benchmarked on Gen2 and other Li-ion cell performance and aging data. These include methods that cover:
    - Capacity loss over aging,
    - Cell conductance loss over aging,
    - Cell Kinetic performance over multiple domains,
    - Incremental Capacity Analysis,
    - Equivalent Circuit Analysis

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

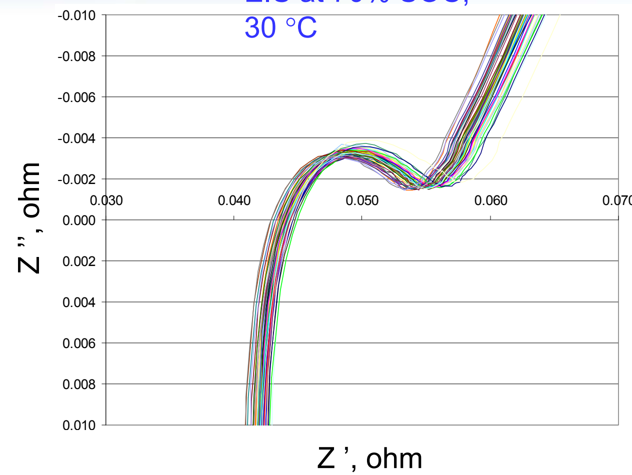
Sampling of Data

useful toward aging characterization

Polarization Study Results for Sanyo Y Cell 19

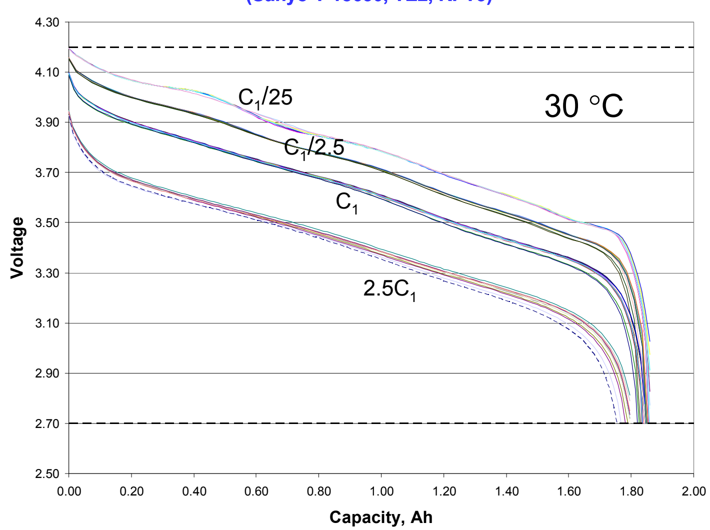


EIS at 70% SOC, 30 °C

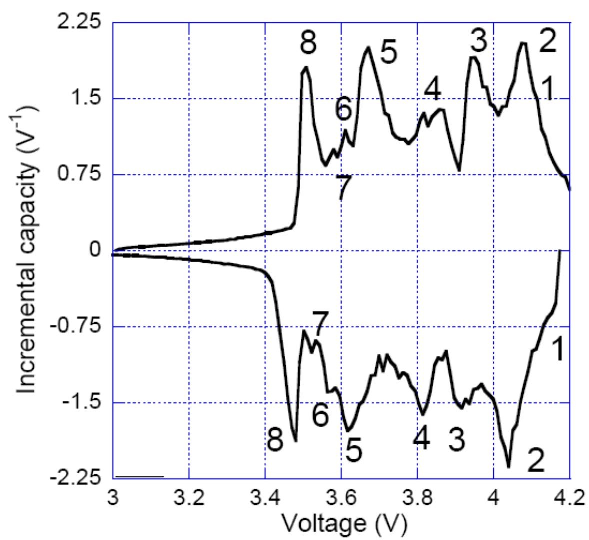


Discharge Capacity Curves

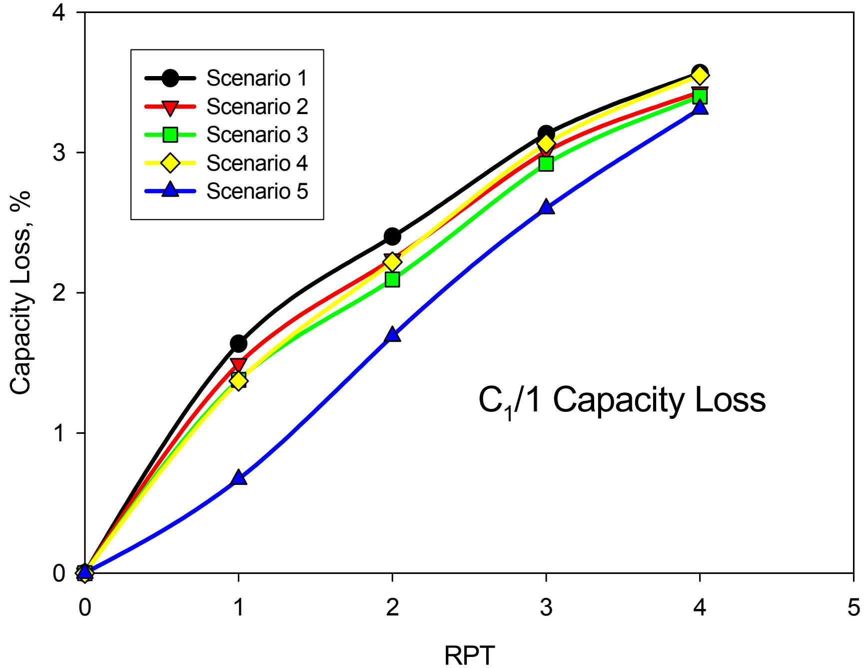
(Sanyo Y 18650, TE2, RPT5)

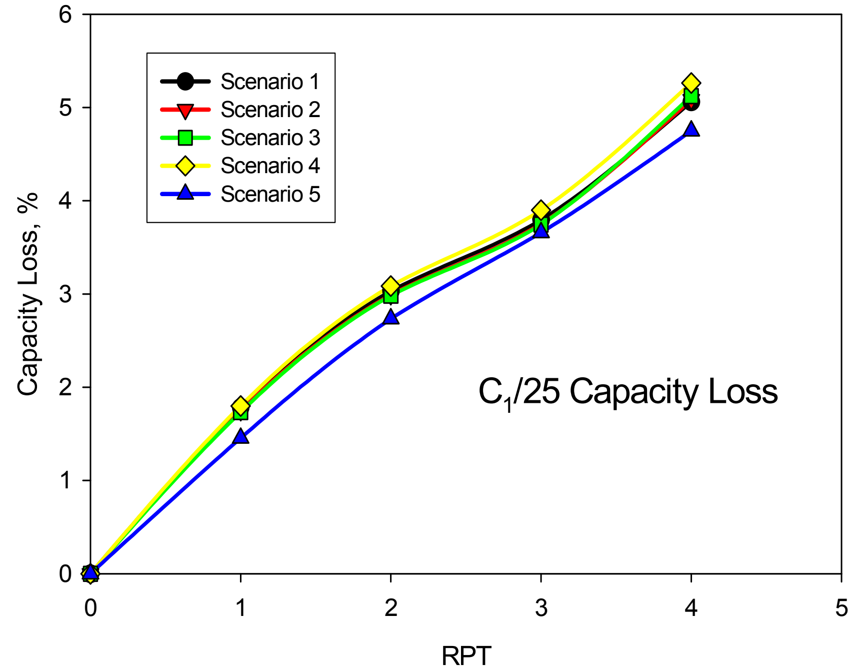


Incremental Capacity Analysis, ICA (HNEI)



From Path Dependent Study 1
Capacity Loss over Aging

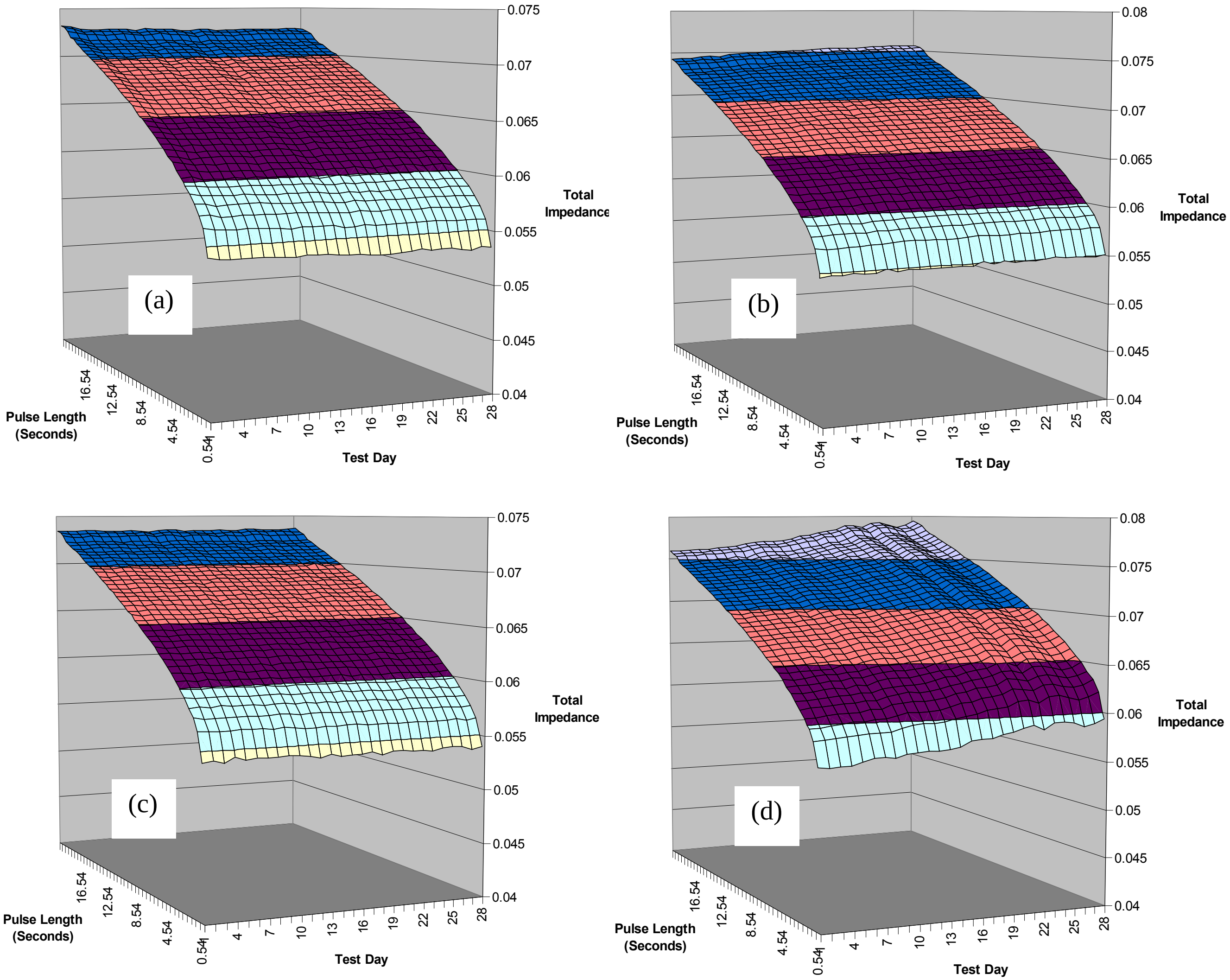




Pulsing at P_{max} generally results in the most capacity fade, while having constant current charge pulses attenuates the rate of loss. These are very early trends that need more maturity to provide detailed information about the possible number and type of degradation mechanisms.

From Path Dependent Study 2

Pulse-per-Day Discharge Impedance (selected conditions)



Early PPD impedance data covering one month for selected cells at

(a) 20 °C isothermal,
(b) 40 °C isothermal,
(c) mild thermal cycling,
(d) severe thermal cycling.

Impedance growth is greater for cases of elevated temperature and for more severe thermal cycling.

We will continue to monitor PPDs over the next several months.

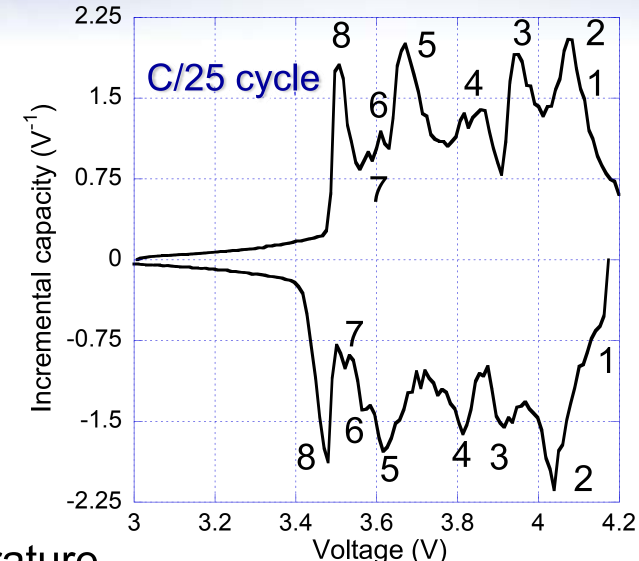
INL/HNEI Technology Snapshots for Electrochemical Systems Modeling

Tools accomplish robust analysis over multiple domains

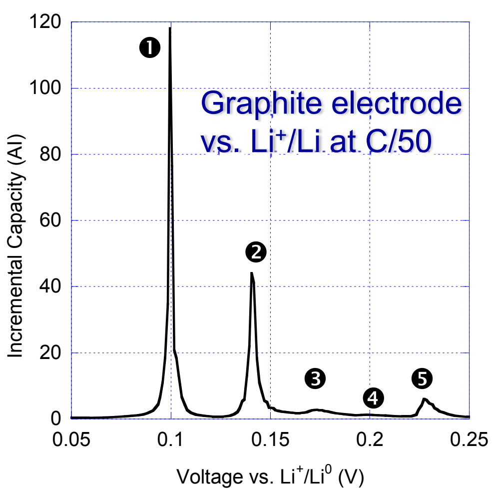
Model parameters represent physical, chemical, electrochemical, or molecular quantities.

Incremental Capacity Analysis (ICA)

Initial conditioning and characterization tests



- Incremental capacity curves
  - Very complex signature
    - Composite positive electrode materials
    - Convolution with graphite negative electrode
    - At least eight (8) identifiable peaks
  - Indexing the peaks by convolution
    - Graphite negative electrode is known in the literature
      - Five (5) identifiable peaks representing staging phenomena



J. Electrochem. Soc. 148 (2001) A1159-A1163

Electrochem. Solid State Lett. 9 (2006) A454-A457.

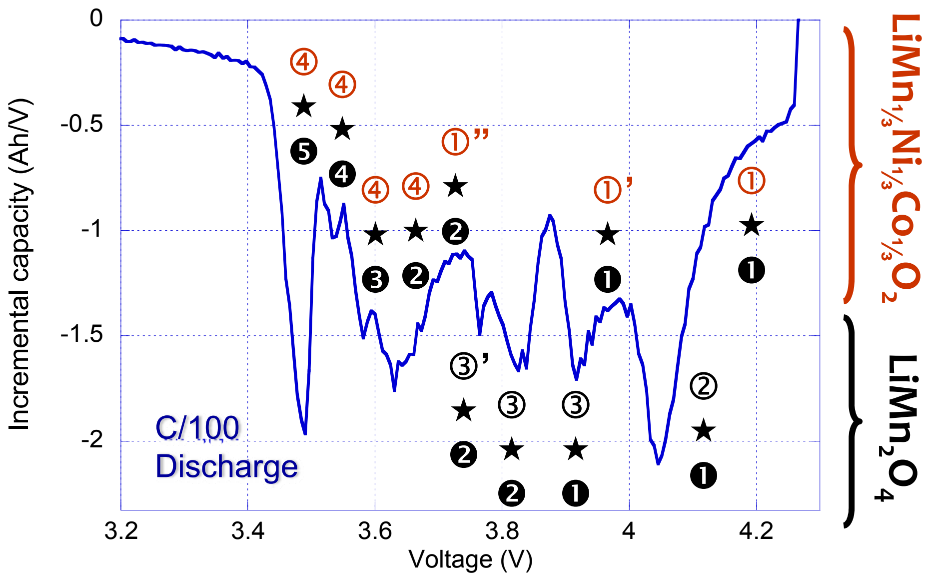
Electrochim. Acta 41 (1996) 2639-.

J. Power Sources 123 (2003) 247–252

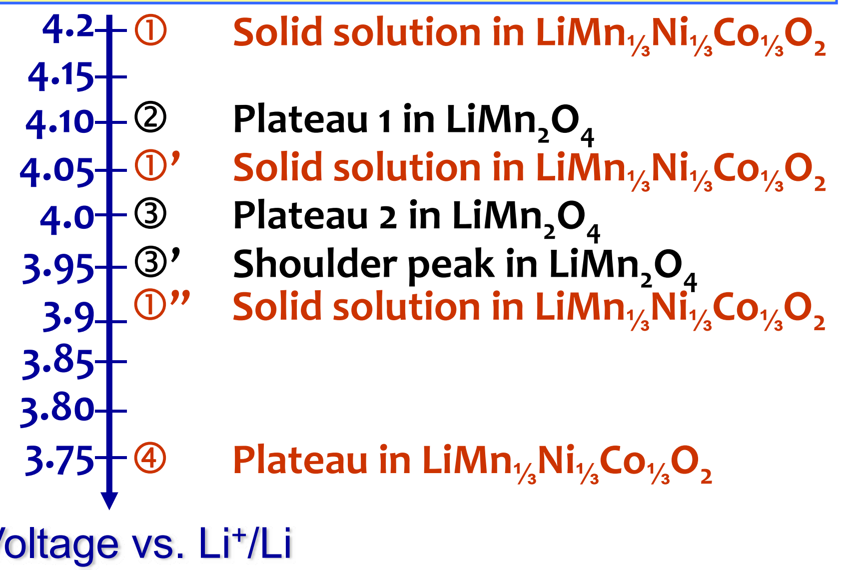
Synthetic Metals 159 (2009) 1255–1260

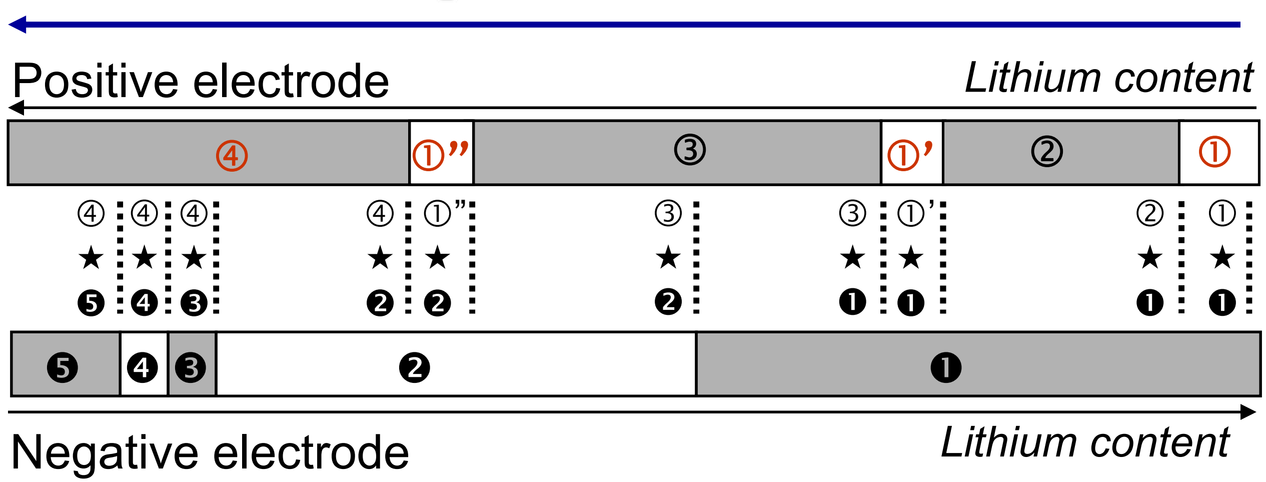
Complete IC Peaks Indexing

Initial conditioning and characterization tests



Incremental capacity peak indexing of Sanyo Y cell





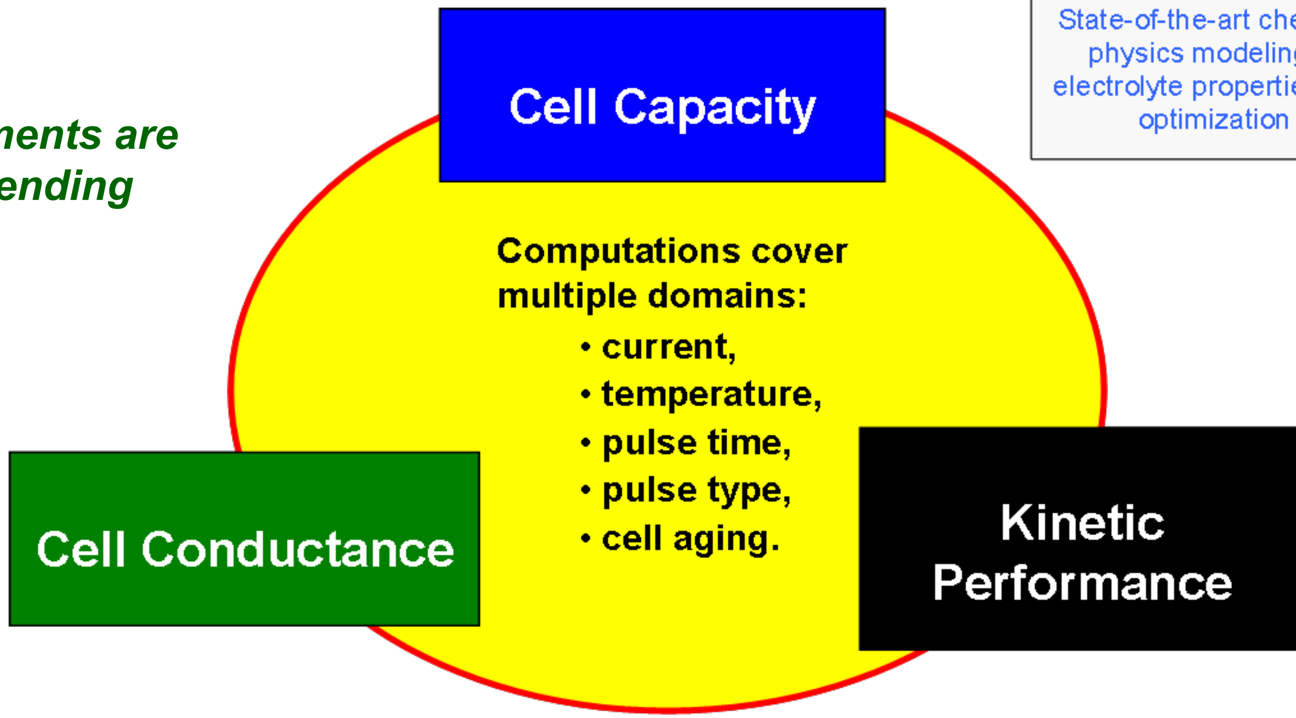
- After indexing, the two constituents in the PE can be assessed independently
- Electrode composition can be estimated —
  x $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ + *y* $LiMn_2O_4$

INL Essential Modeling Tools

Advanced Electrolyte Model (AEM)

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

Key Elements are Patent Pending

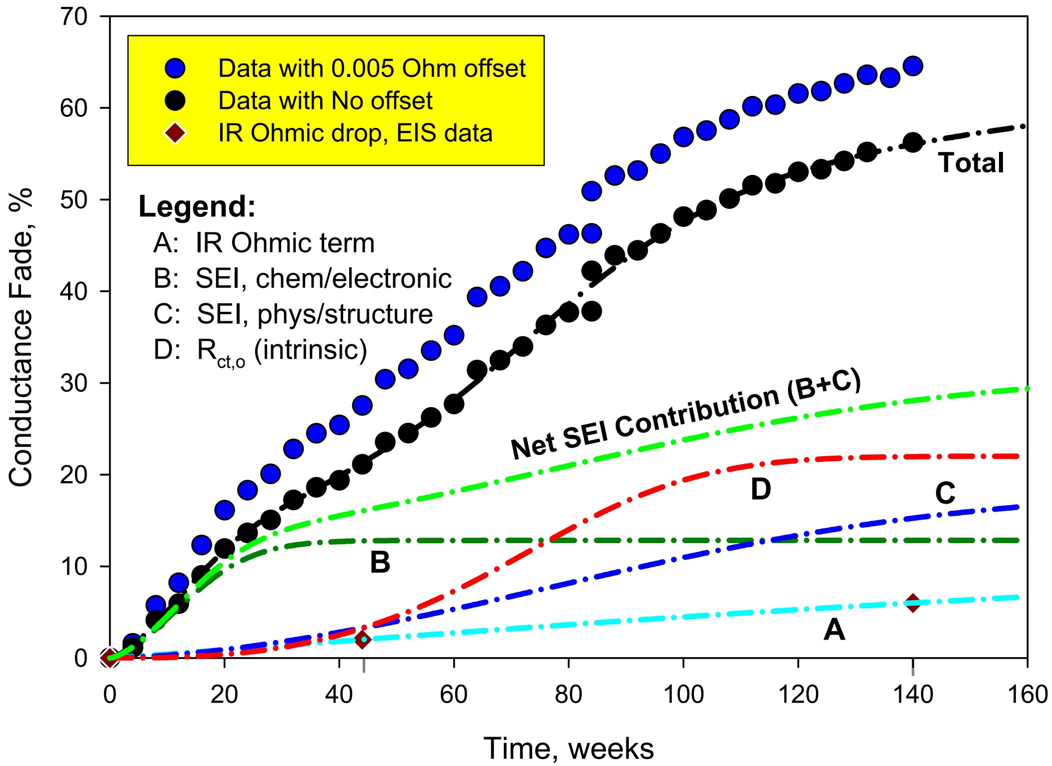


These capabilities lend themselves to mechanistic analyses, cell design, and are amenable to <u>aging path dependence modeling</u> per INL protocol; complemented by Equivalent Circuit Models (ECMs).

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

Modeling Cell Conductance

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.

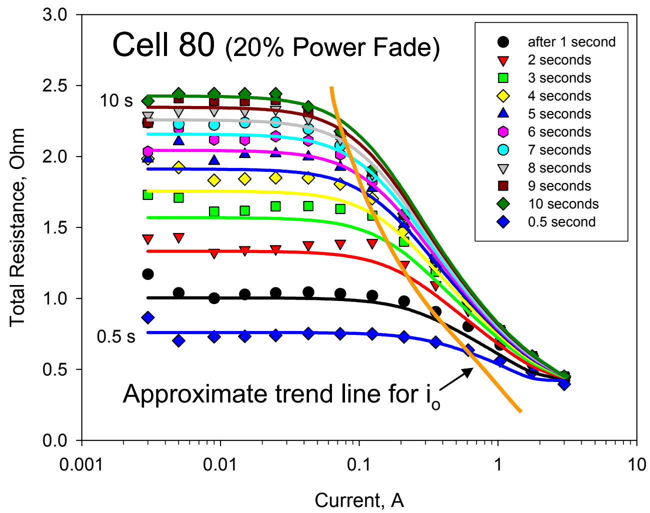
Cell conductance has a principal influence on attainable power, decreasing over the life of a cell.

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

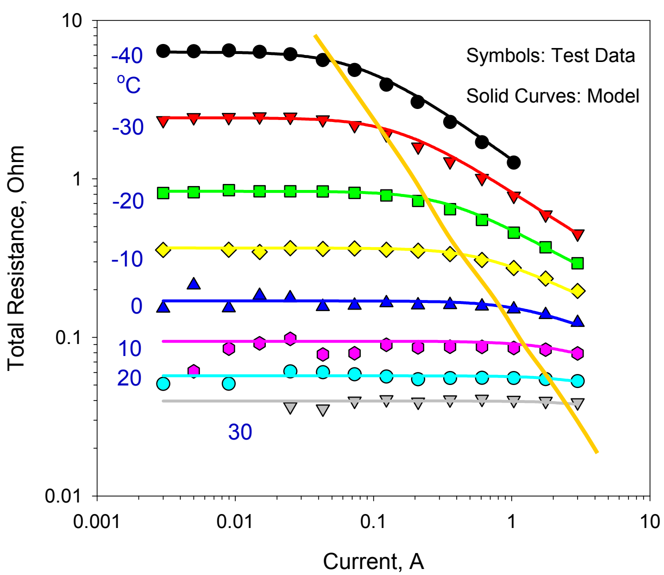
INL Kinetics Modeling

Idaho National Laboratory

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

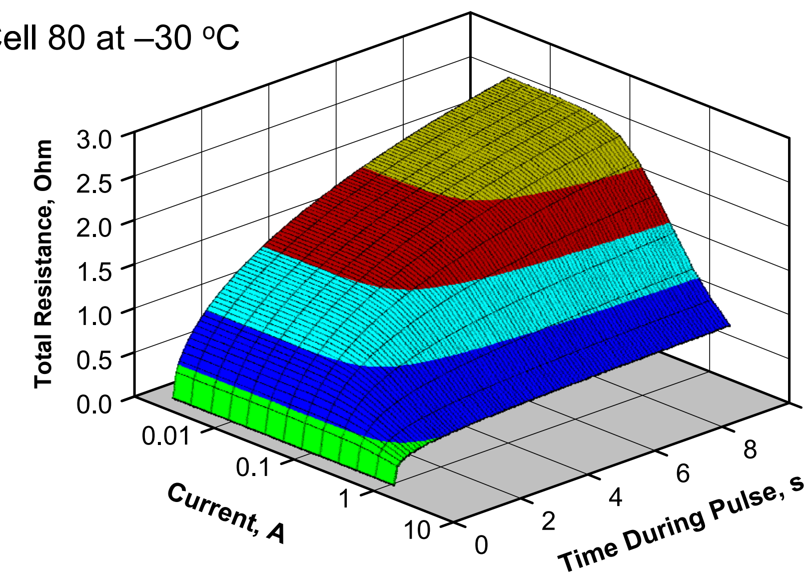


R_{total} at 10 s over temperature



- **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 of rate expressions.**

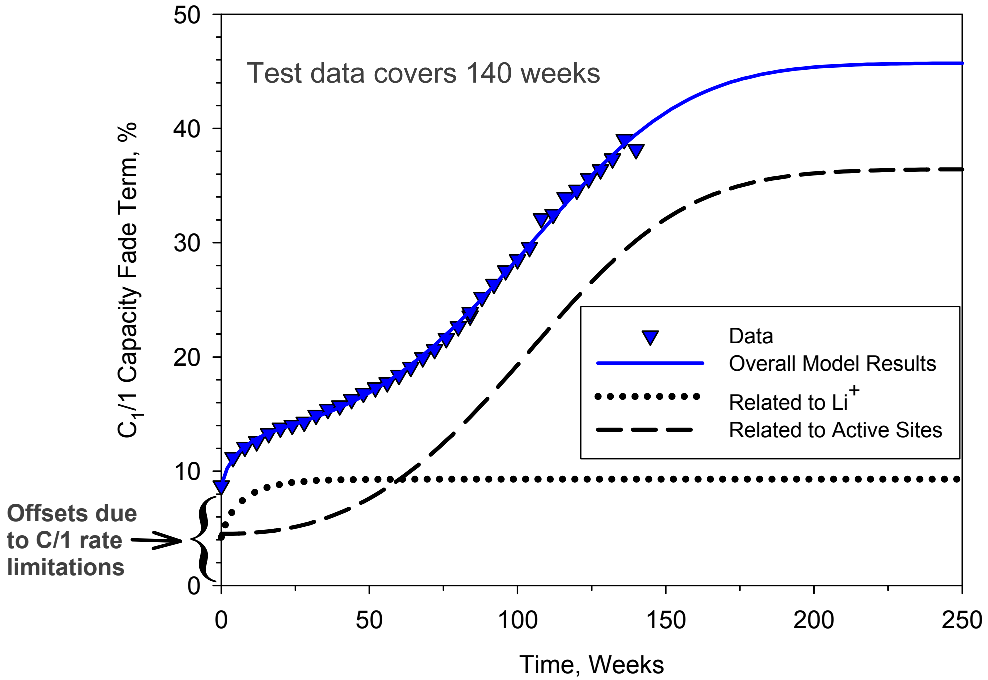
Cell 80 at –30 °C

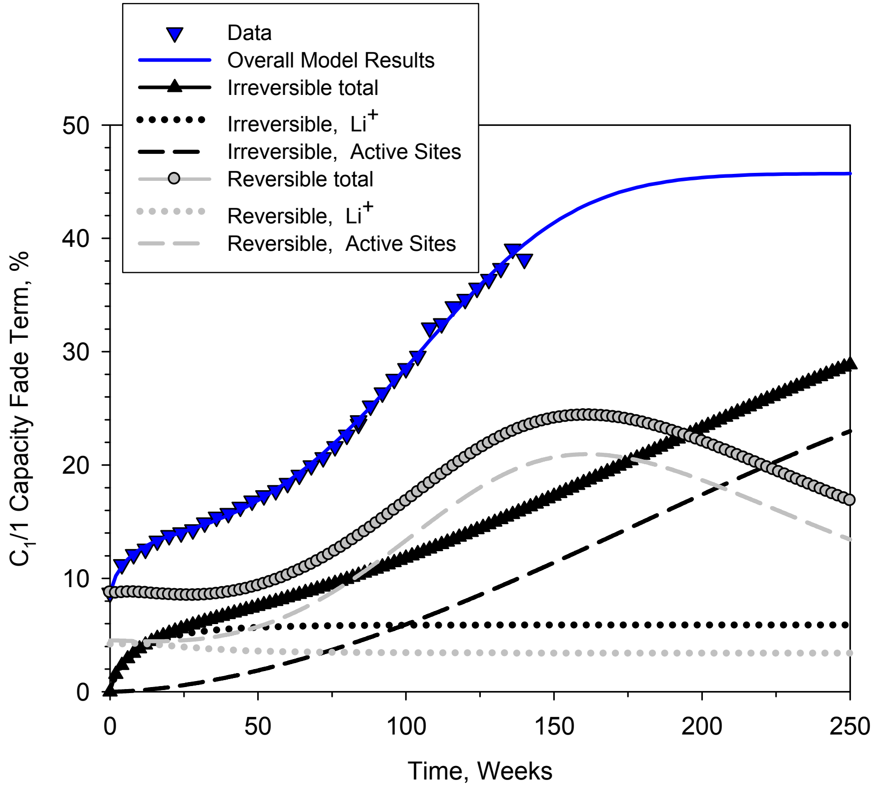


…..and many other performance quantities.

Modeling Capacity Loss Over Life

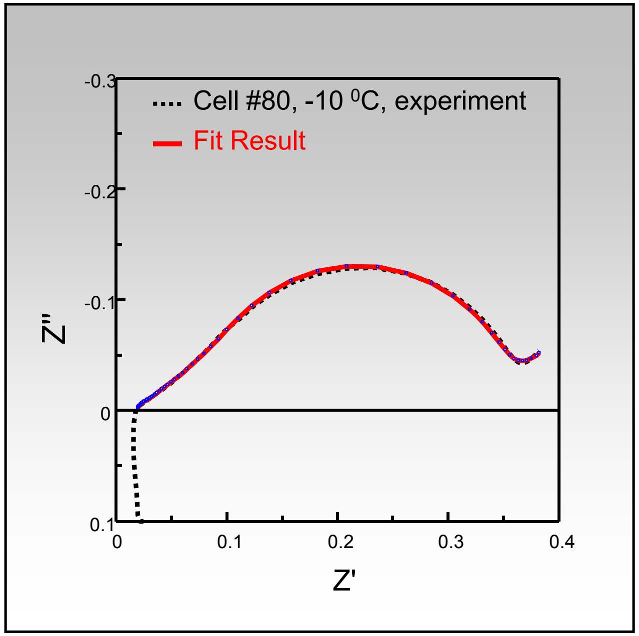
(Gen2 Li-ion Cells under cycL Testing at 25 °C)



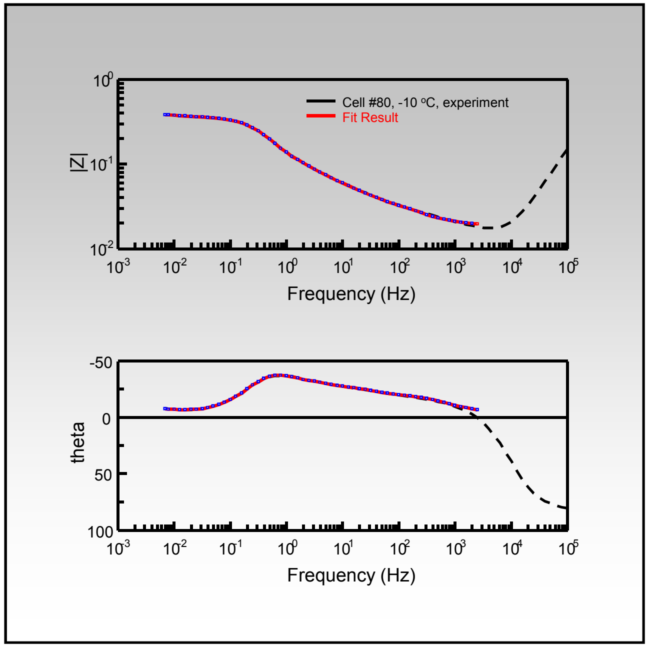


- The rate of lithium consumption is high during initial time (continued SEI formation; side reactions), but tapers off considerably by 30 weeks.
- Reversible contributions to fade dominate at early time, are tied primarily to active sites, and undergo a maximum at around 150 weeks. In comparison, irreversible 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.

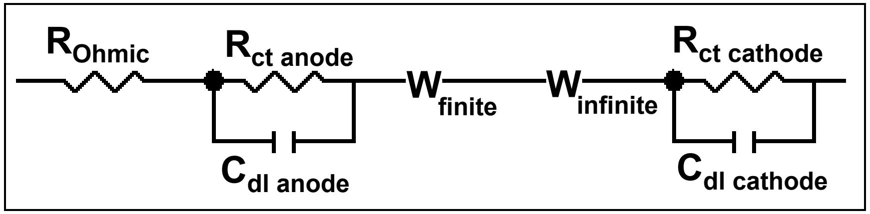
Equivalent Circuit Modeling



Nyquist Plot



Bode Plot



Excellent fit with W_{finite}, which captures interfacial transport

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 applies an advanced form of 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 Li-ion cells. UC-Pomona work is coordinated by an acknowledged expert in statistical thermodynamics, Prof. Lloyd Lee.
- **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.

Summary / Conclusions

- DT is progressing with Sanyo Y cells, looking at various issues of cell performance and path dependence of aging. FY 2010 will be a pivotal year in continuing/completing PHEV-relevant cell testing and diagnostic analysis.
- Early results are useful for assessing BOL trends and initial estimates of parameters for aging models. More extensive data over time is needed to surmise probable degradation mechanisms regarding capacity, impedance, etc.
- INL and HNEI have developed key computational tools used to model, diagnose, and predict performance and aging of electrochemical cells. These tools are targeting mechanisms of cell degradation, related path dependence, and chief causes and conditions of performance loss.
- 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.

The immediate benefits of this work will be (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 and management.

Future Work

- We will continue to monitor aging trends for our path dependence studies over the next several months.
- 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.
- We will quantify the impact of thermal cycling on Sanyo Y cell aging.
- Future path dependence studies could involve other duty-cycles (e.g., FUDS, DST), other temperature parameters defined for a particular city or region, and other Li-ion cell chemistries.
- Pending cell availability, we will perform DT on ABRT Gen4 cells to elucidate path dependence of aging for that cell chemistry.

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- Matthieu Dubarry, HNEI
- Bor Yann Liaw, HNEI
- Lloyd L. Lee, UC-Pomona

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