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

May 16, 2012

Project ID ES096

2012 DOE Vehicle Technologies Program Annual Merit Review

Overview

Timeline	Barriers
Project Start: April 2008 **Project End:** Ongoing **Percent Complete:** ≈ 70%. 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** **Abuse Tolerance, Reliability and Ruggedness**

Budget	Partners
Funding Received: **FY 11: $ 750K (All DADT, including subcontracts)** **FY12: $ 700K (All DADT, including subcontracts)**	**Hawaii Natural Energy Institute (HNEI) at University of Hawaii at Manoa** **Argonne National Lab**

Relevance

Long-term usage of lithium-ion batteries in vehicle applications represents a significant warranty commitment and a long-term safety risk. Yet, there is insufficient knowledge regarding prolonged aging processes in such batteries, particularly in cases of strong path dependence of aging.

Our objectives include:

- Establish a platform of Developmental & Applied Diagnostic Testing (DADT) designed for particular issues in EDV batteries:
  - ➲ defined by application-specific performance.
- Employ DADT to examine mechanistic contributions to cell aging.
- Utilize DADT results to support advanced prognostic modeling tools (ES124).
- Utilize DADT knowledge to support improvement of materials.
- Apply DADT to series strings of cells to understand string aging dynamics.
- Develop/optimize an operational protocol to minimize the aging process (chemistry-specific, but with generalized approach).

Our overarching goal is to understand the mechanistic progression of aging for batteries in their intended applications, and provide a foundation for improving cell materials and minimizing aging rates.

Milestones

Milestone	Status	Date
INL Path Dependence Studies 1 and 2: • Power Pulse Performance Hysteresis • Daily Thermal Cycling superimposed onto PHEV cell cycling	Ongoing	
Validation of Path Dependence Response regarding T and SOC	Completed Phase 1	Feb. 2012
Pouch Cell Pressure Optimization & Aging Study	Started	March 2012
Supplemental DADT (INL): • Self-discharging mechanisms • Current conditioning as aging parameter • Low-temperature EIS hysteresis	Completed, with follow-on work in progress	Phase 1's completed Jan.-Feb. 2012
Start/completion of HNEI Aging Study 2 (isothermal matrix)	Completed	Nov. 2011
HNEI Supporting DADT: • Thermal excursion and related degradation and path dependence • Over-charge and over-discharge experiments	Completed	Aug.-Sept. 2011
Diagnostic Modeling Tool to Synthesize Aging Scenarios (HNEI)	Completed	Sept. 2011
String-level studies (degradation tied to cell-to-cell interactions and variations), using Sanyo Y cells or others (HNEI and INL)	Ongoing	Phase 1 completed March 2012

Approach

- This work bridges 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, frequency and severity of thermal cycles, and multi-cell string dynamics.

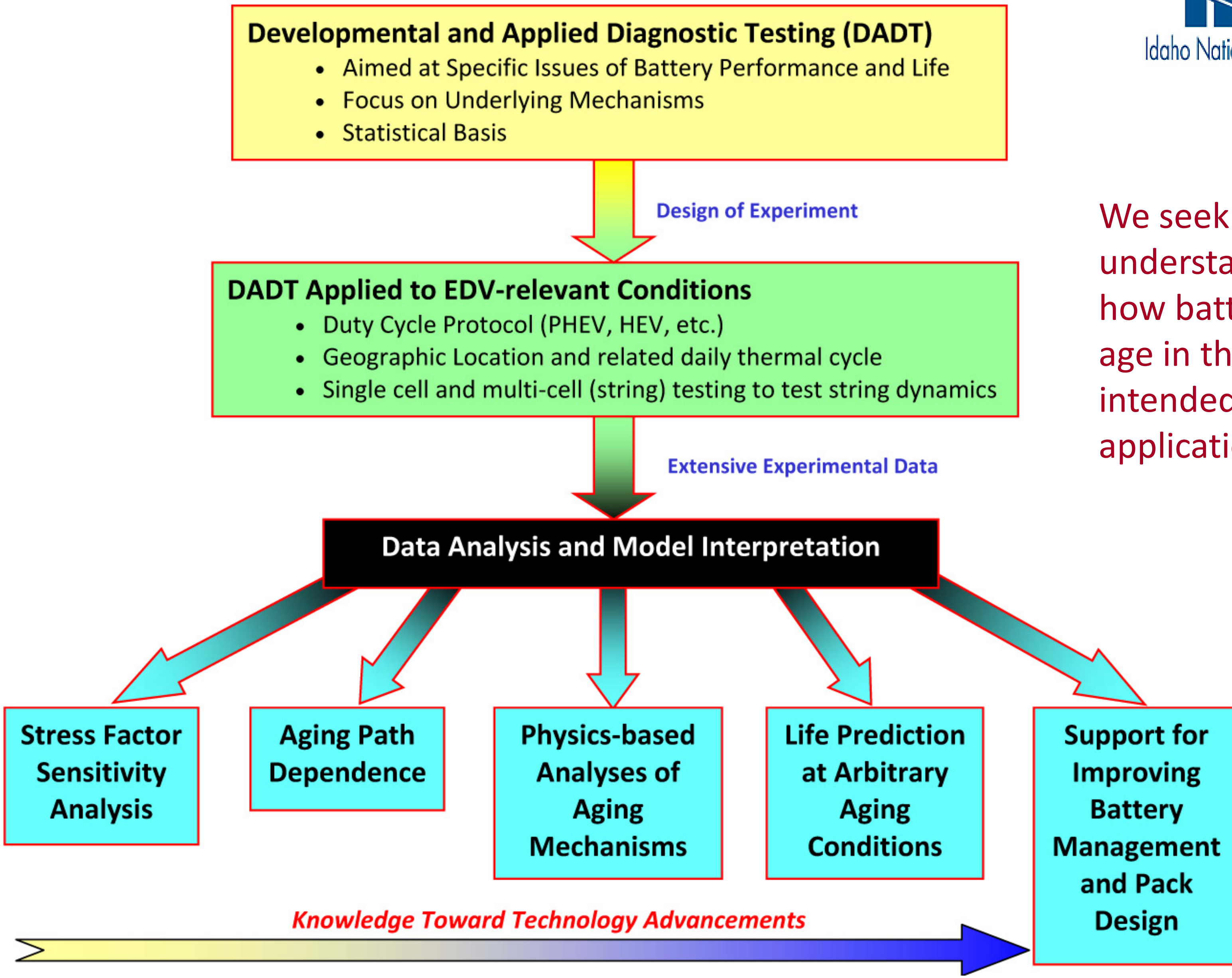
- Through DADT, these factors are then studied in controlled and repeatable laboratory conditions to facilitate mechanistic evaluation of aging processes and path dependence thereof. We employ a diagnostic-based RPT that targets optimal metrics for isolating aging mechanisms.

- Knowledge gained from DADT supports Prognostic Modeling Tools that enable diagnostic and predictive analyses over multiple domains, looking at aging mechanisms and key performance issues (ES 124).

- 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.

We seek to understand how batteries will age in their **intended** application.

Approach

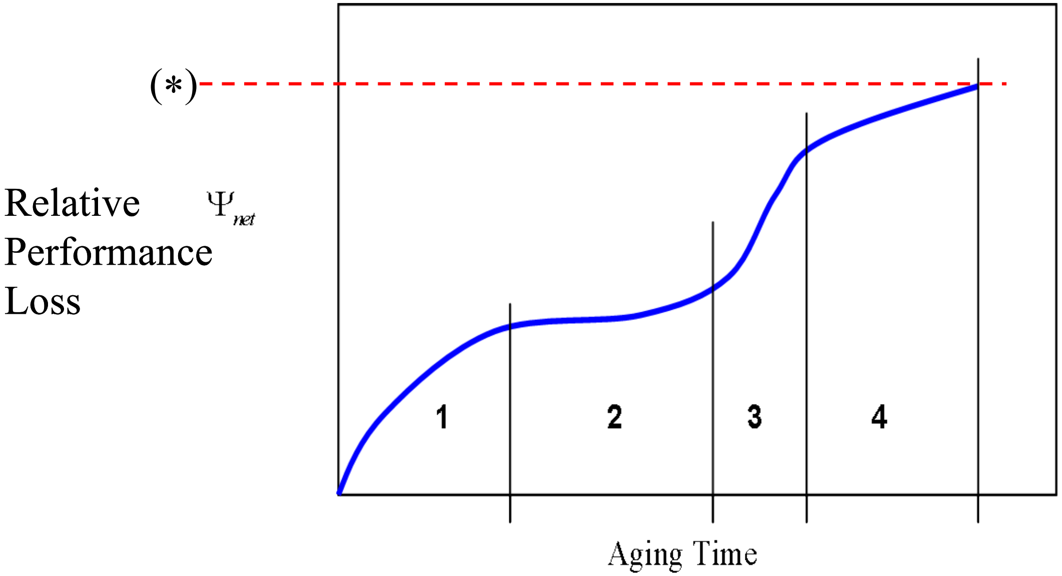


We seek to understand how batteries age in their intended application.

Path Dependence of Cell Aging

INL aging models are easily adaptable to Path Dependence scenarios (ES124)

- 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 progression of irreversible aging processes 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.

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, due to how irreversibilities in degradation occur between states.

Li-ion Chemistry Used for Studies: Sanyo 'Y'

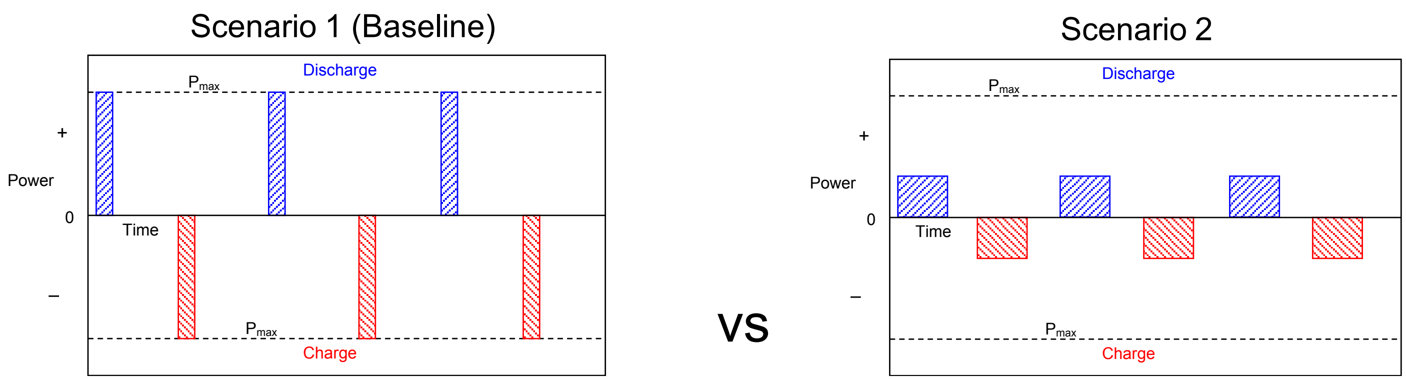
Configuration: 18650
Cathode: $\{LiMn_2O_4 + LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2\}$
Anode: graphitic
V_{max} = 4.2 V (100% SOC)
V_{min} = 2.7 V (0% SOC)
90% SOC = 4.07 V
70% SOC = 3.94 V
35% SOC = 3.65 V
Electrode Area: 800 cm^2 (estimated)
$C_1/2$ discharge capacity: 1.9 Ah,
$C_1/1$ discharge capacity: 1.86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

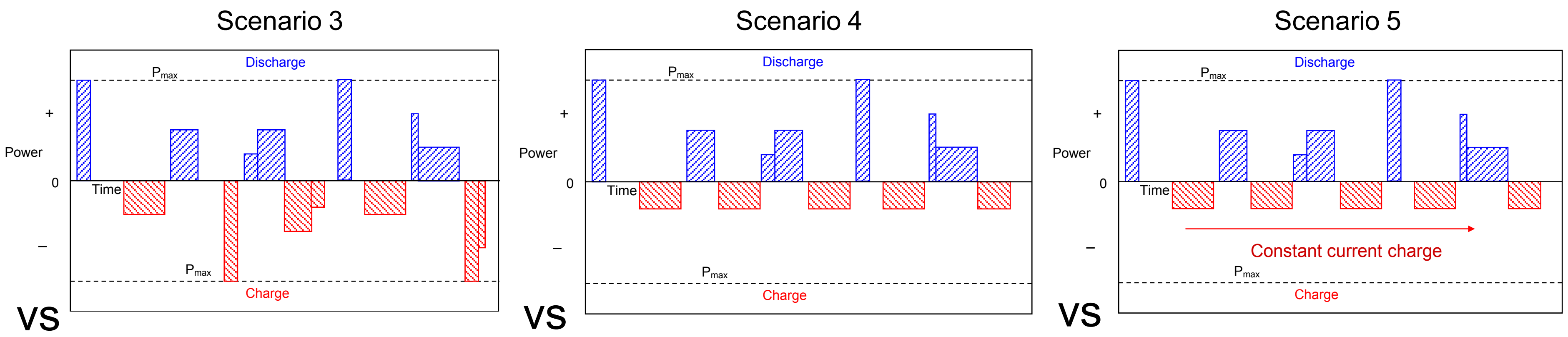
These cells are high quality, economical, and show good stability and low cell-to-cell variability.

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?

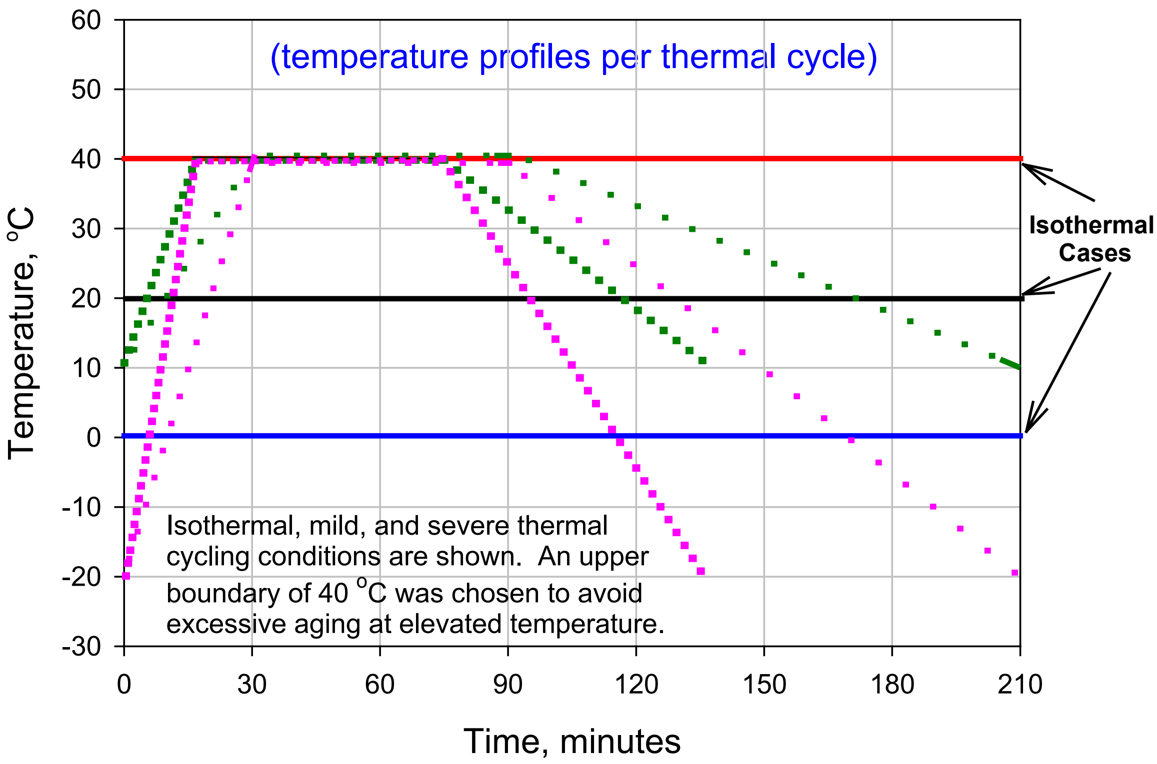




Approach

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.

Approach

Path Dependence Studies

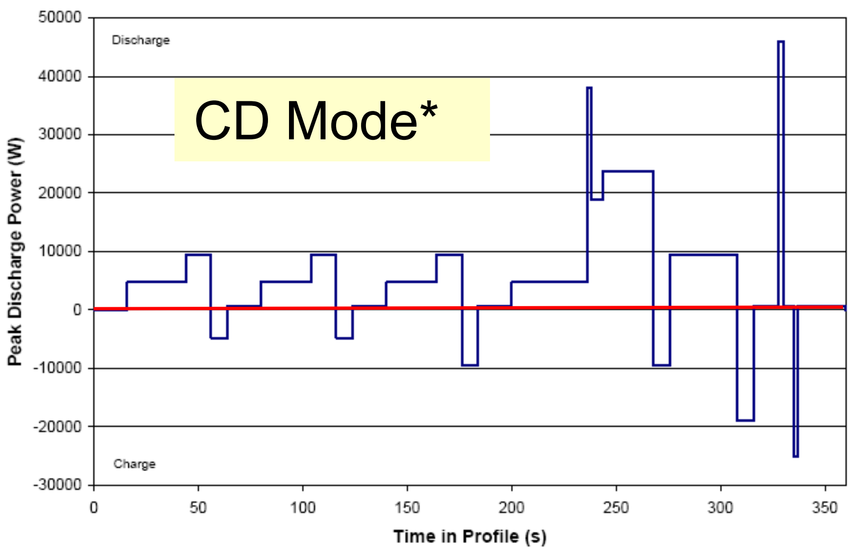
<u>Study 2 cont.:</u> Duty Cycle: a *standard cycle-life profile* is defined here as consisting of one CD profile (360 s each) followed by ten CS profiles (90 s each), giving an overall profile duration of 21 minutes. Herein we define a *duty cycle* as three standard cycle-life profiles in sequence,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

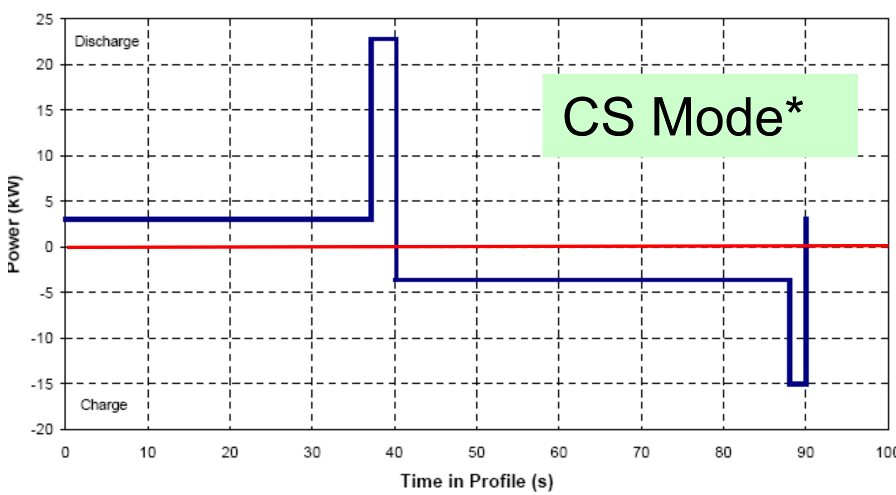
} **Cycle-life Profiles**

where

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



Charge-Depleting Cycle Life Test Profile for Maximum PHEV Battery

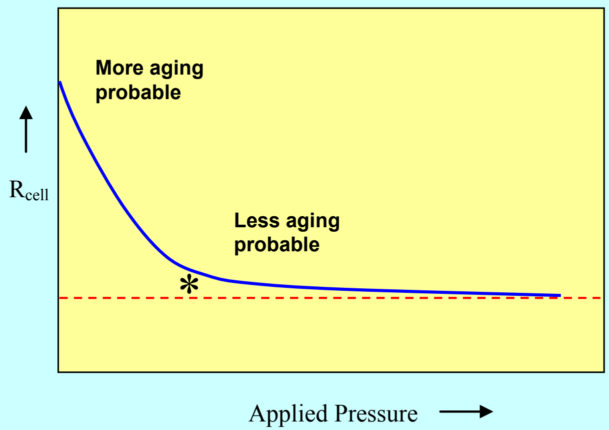


Charge-Sustaining Cycle Life Test Profile (50 Wh) for Maximum PHEV Battery

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

Approach

Understanding Pressure Effects on Pouch Cell Performance and Aging



Shown here is the general principle of adding pressure to pouch cells to reduce cell impedance and to standardize the pressure at which cells should be tested and utilized. The inflection point (*) is the point at which adding more pressure does not produce further significant decrease in impedance. Having pressure close to (*) will help inhibit gas formation while pressure far past the inflection may cause physical damage to the cell.

Candidate Cells, Tier 1

Li-ion 15 Ah (C/1)

Mn-Spinel/Carbon

2.5-4.2 V

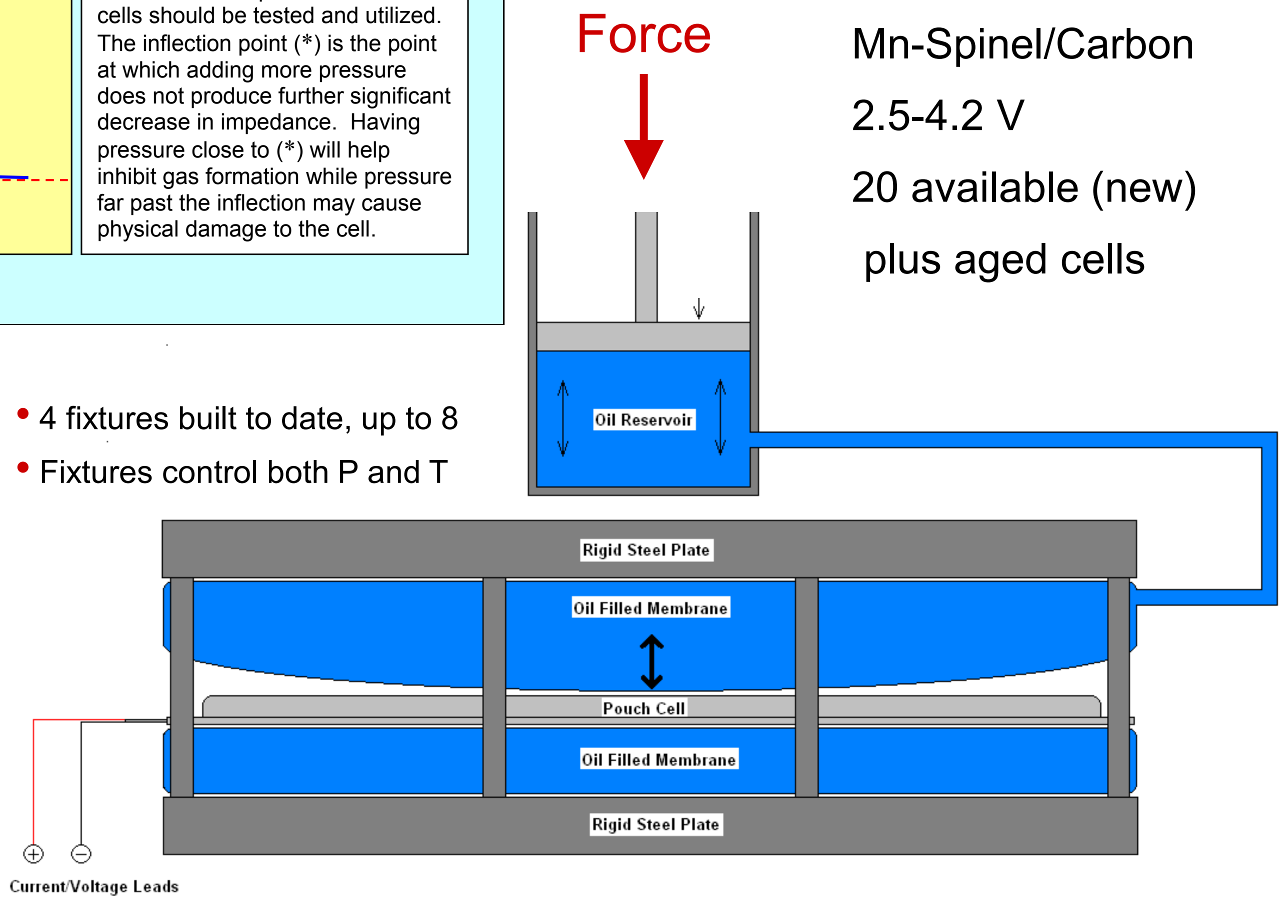
20 available (new)

plus aged cells

Fixture

- Liquid filled membranes apply even pressure on pouch cell, and enable heat transfer to achieve consistent temperatures.
- System will allow for determination of volume gassed by the cell as it undergoes testing.

- 4 fixtures built to date, up to 8
- Fixtures control both P and T



The lack of applied pressure can be a stress factor for pouch cell aging.

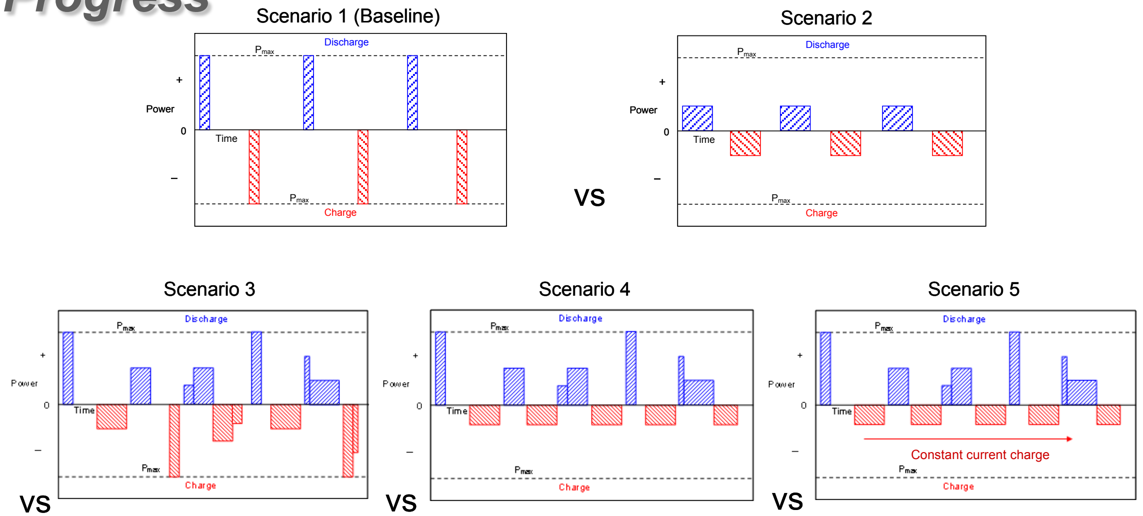
Technical Accomplishments & Progress

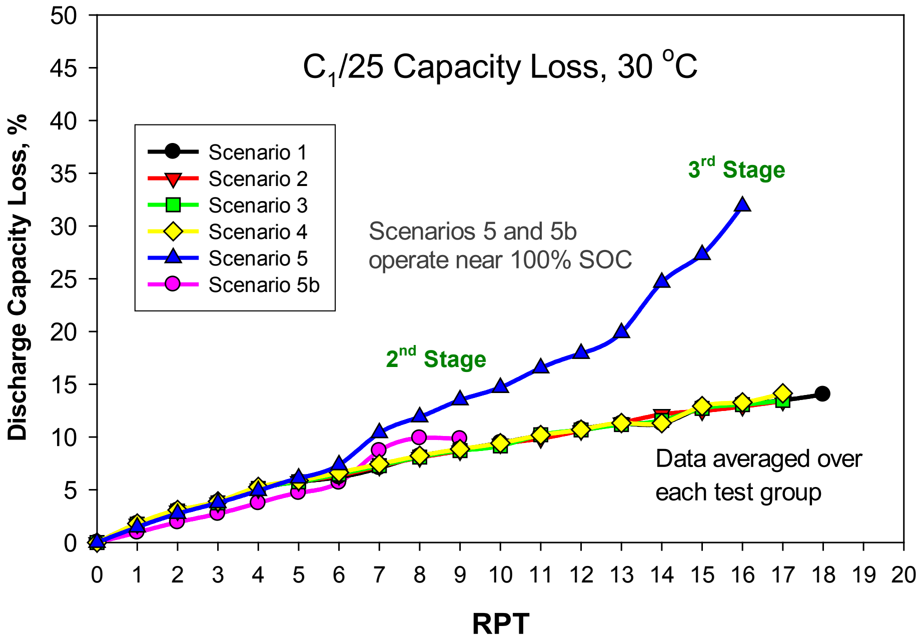
- Parallel studies at INL and HNEI are ongoing that involve over 100 commercial lithium-ion cells, with some Phase 1 sub-elements completed. These studies will continue to the extent they achieve mature trends for diagnostic (mechanistic) analyses.
- INL and HNEI DADT studies are isolating the effects of foremost operational parameters on the aging path. Through DADT we develop strategic testing to determine many aspects of how cells will age in their intended application (here, PHEV). In 2011 DADT progressed within the following areas (started, ongoing, or completed):*
    - Power Pulse Performance Hysteresis
    - Daily Thermal Cycling (DTC) coupled with PHEV cell cycling
    - Validation Testing of Path Dependence Response regarding T and SOC
    - Pouch Cell Pressure Optimization & Aging Study
    - Supplemental & Supporting Studies
        - Self-discharging mechanisms, quantitative analysis
        - Current conditioning as aging parameter
        - Low-temperature EIS hysteresis
    - Aging study involving isothermal matrix (HNEI)
    - Thermal excursion and related degradation and path dependence (HNEI)
    - Over-charge and over-discharge experiments (HNEI)
    - Diagnostic Modeling Tool to Synthesize Aging Scenarios (HNEI)
    - String-level studies (degradation tied to cell-to-cell interactions and variations), using Sanyo Y cells or others (HNEI and INL)

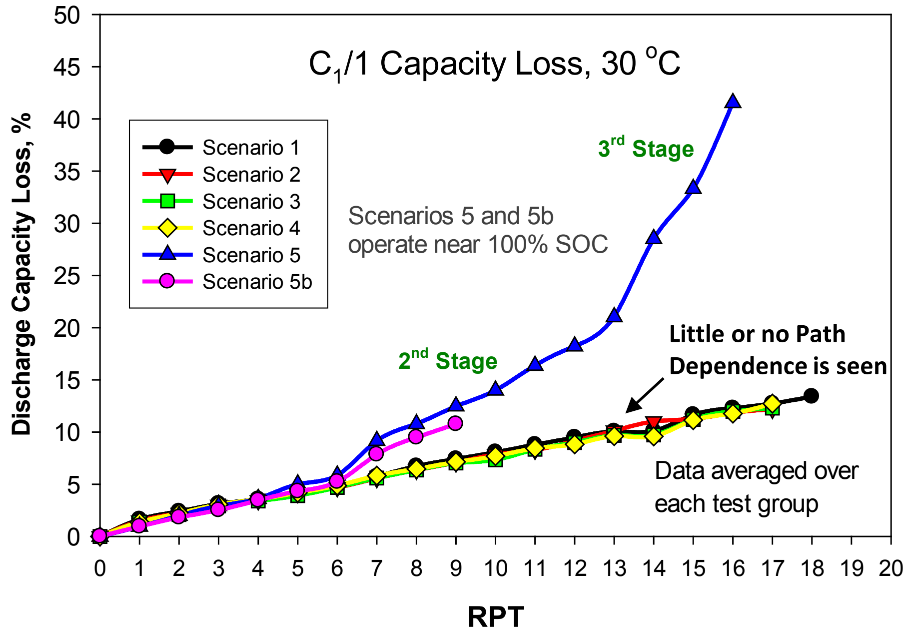
****Numerous papers were either published, submitted or drafted in this period.***

Tech. Accomp. & Progress

PD-1







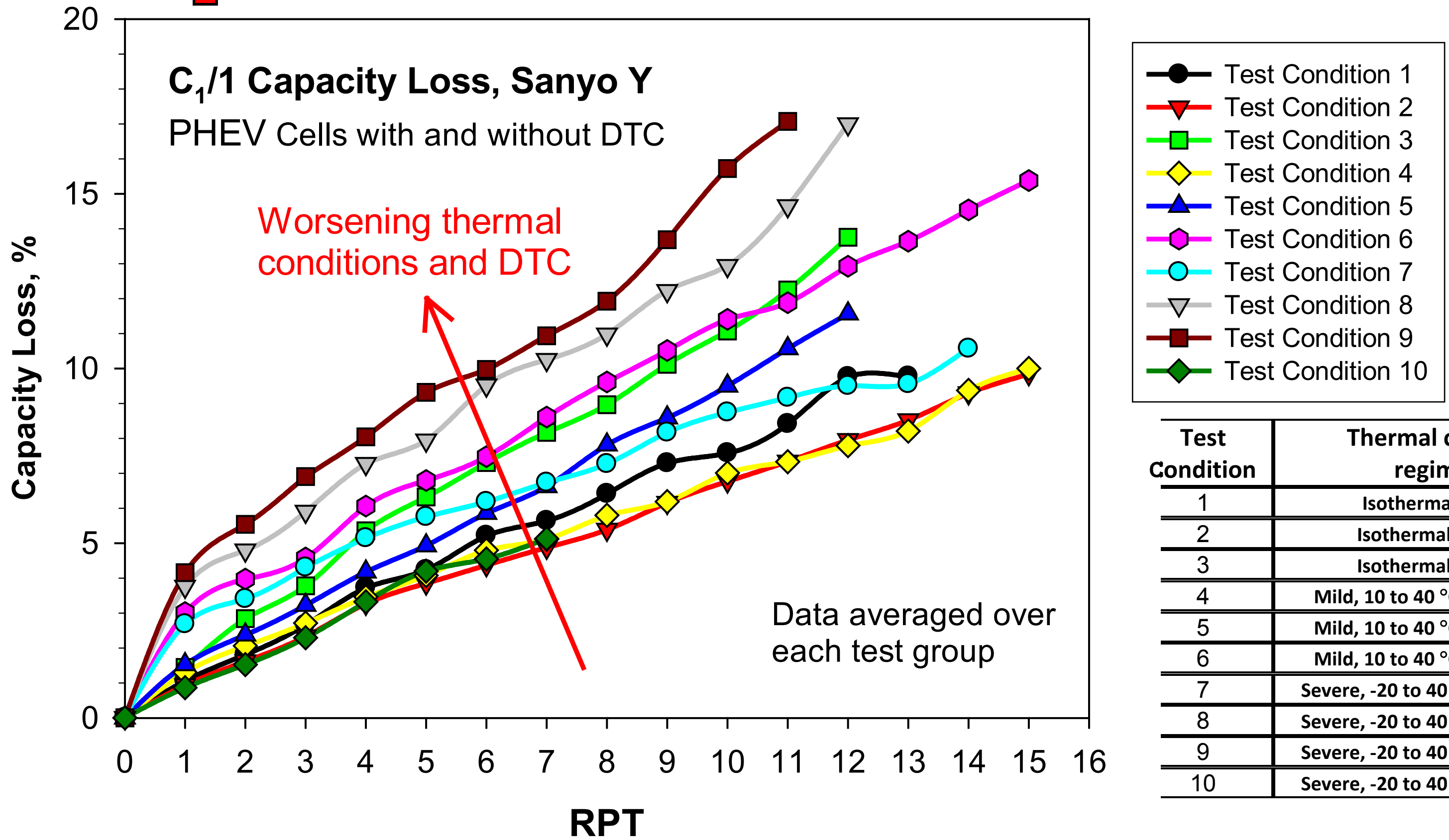
The data shows how these cells are charge sensitive when operated near 100% SOC. Testing past 12 months is crucial for detecting later stages of degradation.

Idaho National Laboratory

Tech. Accomp. & Progress

PD-2

These results suggest that EDV batteries operated at colder climates will undergo additional degradation possibly due to particle fracturing from excessive stress, and should have more sophisticated thermal management (see also ES124).



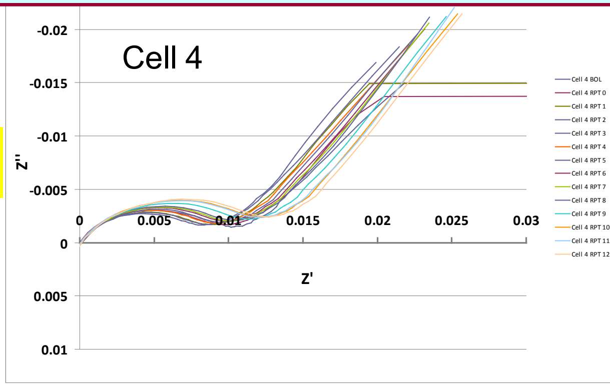
Test Condition	Thermal cycling regime	Duty cycle frequency
1	Isothermal, 0 °C	Continuous
2	Isothermal, 20 °C	Continuous
3	Isothermal, 40 °C	Continuous
4	Mild, 10 to 40 °C in 30 min.	1 Round trip/day
5	Mild, 10 to 40 °C in 30 min.	Continuous
6	Mild, 10 to 40 °C in 15 min.	Continuous
7	Severe, -20 to 40 °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)

There is Aging Path Dependence in the Thermal Regime. Thermal cycling effects on capacity are more evident for cells actively undergoing duty cycles. In contrast, cells under calendar-life conditions and thermal cycling experience slower aging (Condition 10).

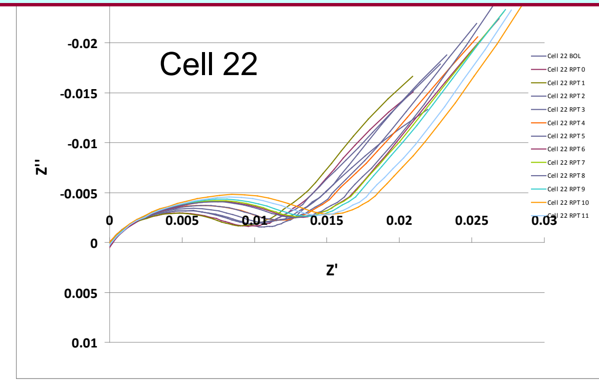
Tech. Accomp. & Progress

PD-2, Normalized EIS Data over RPTs at 30 °C, Sanyo Y (selected conditions)

62.5%

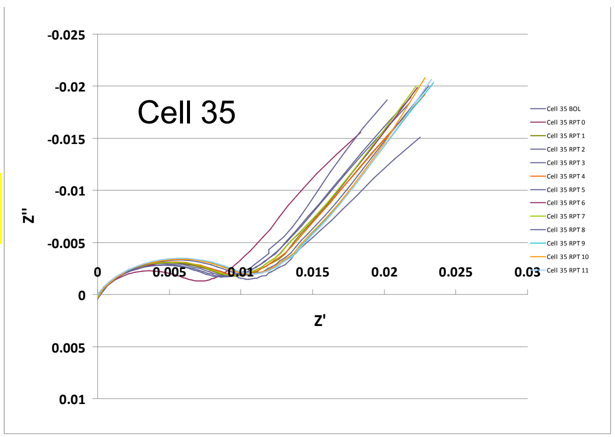


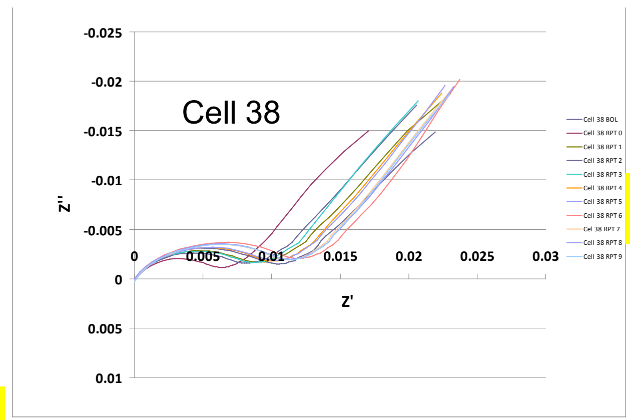
Worsening Thermal Cycling Conditions



77.8%

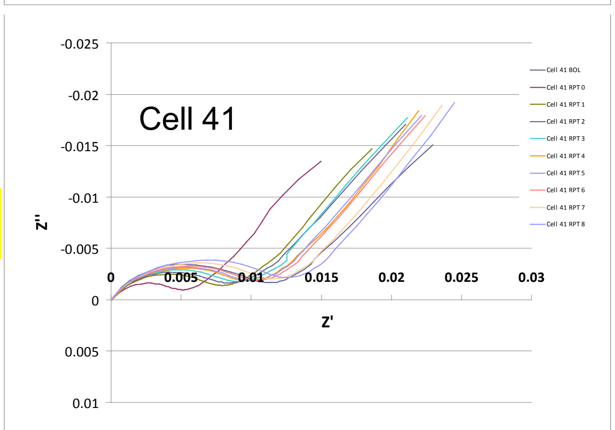
71.4%



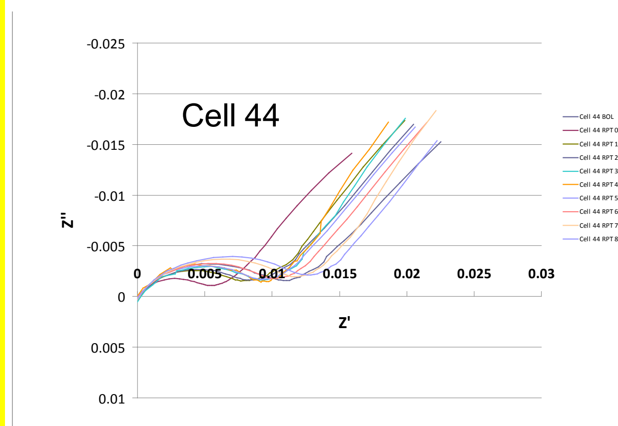


92.3%

136%



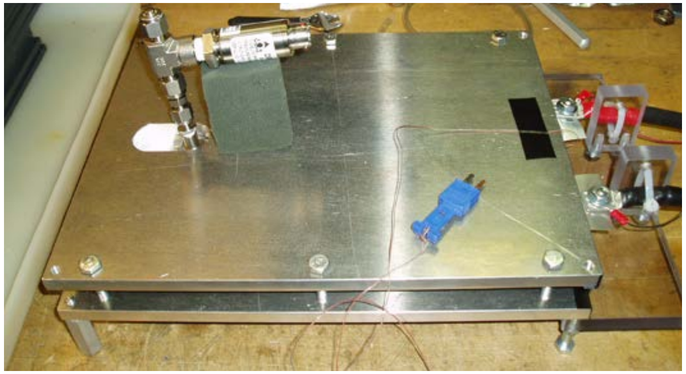
Numbers in Blue are net percent increases in Arc widths. The trends track with capacity loss data.



125%

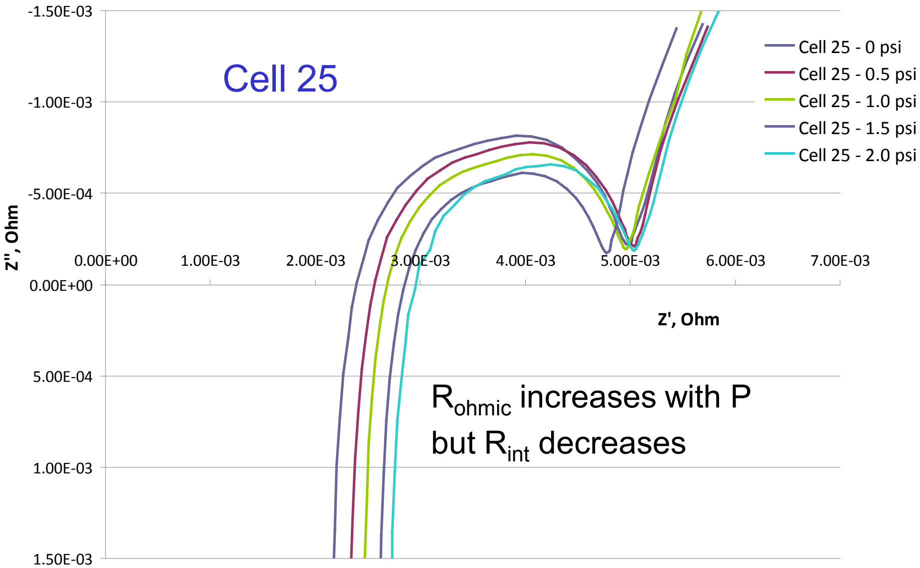
Understanding Pressure Effects on Pouch Cells…

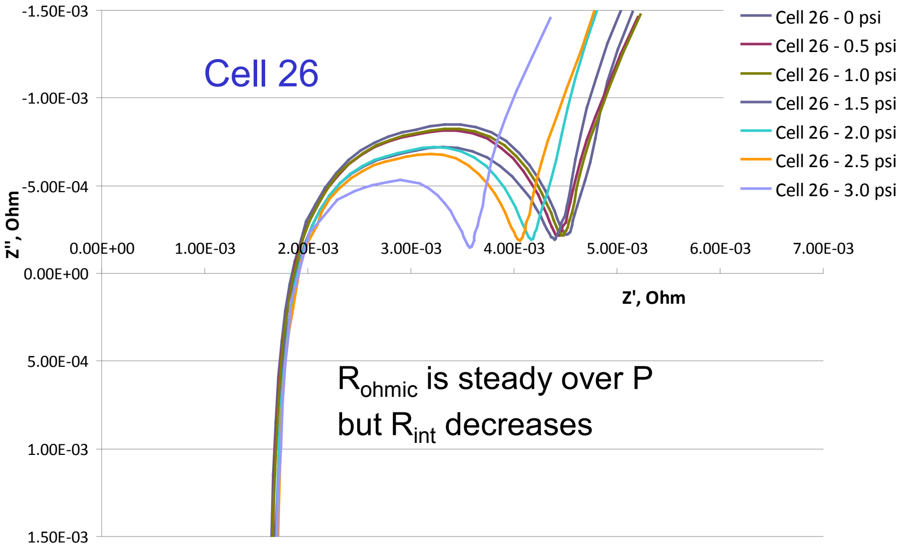
Phase 1



There has been little or no concerted effort to <u>standardize</u> and <u>manage</u> the application of pressure to pouch cells during testing……until now.

EIS measurements show that cell impedance does indeed drop as pressure is applied, but that two "identical cells" (both unaged) respond differently.





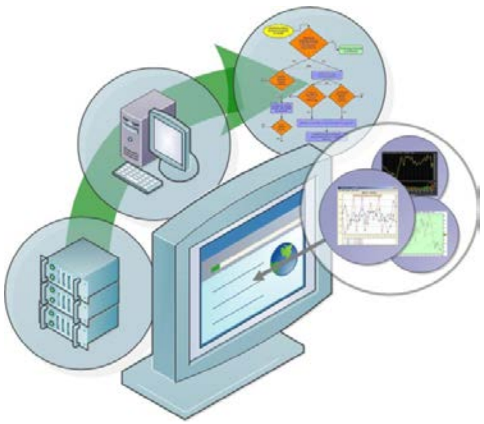
Battery Database Management System (BDMS)

(in collaboration with HNEI)

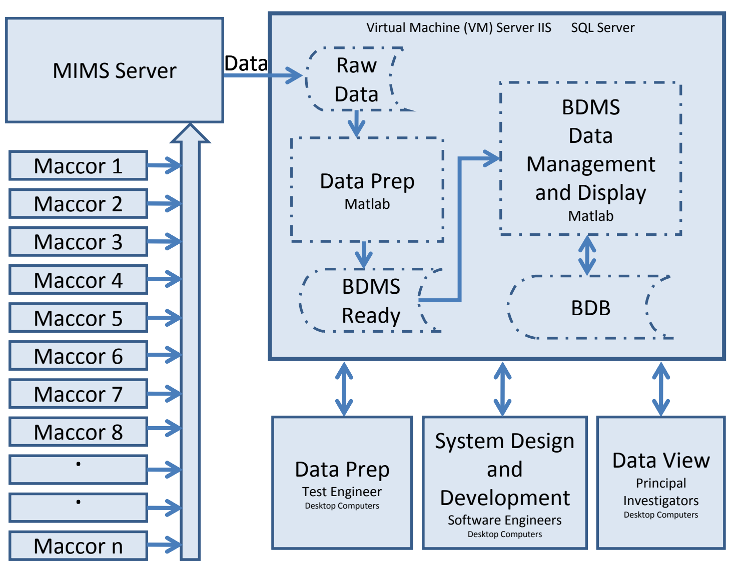
Purpose

To facilitate the efficient and timely extraction of large and numerous datasets needed for diagnostic analysis by INL and collaborators. Platform resides within a virtual environment. ***This will accelerate bringing DADT knowledge to DOE and the battery R&D community.***

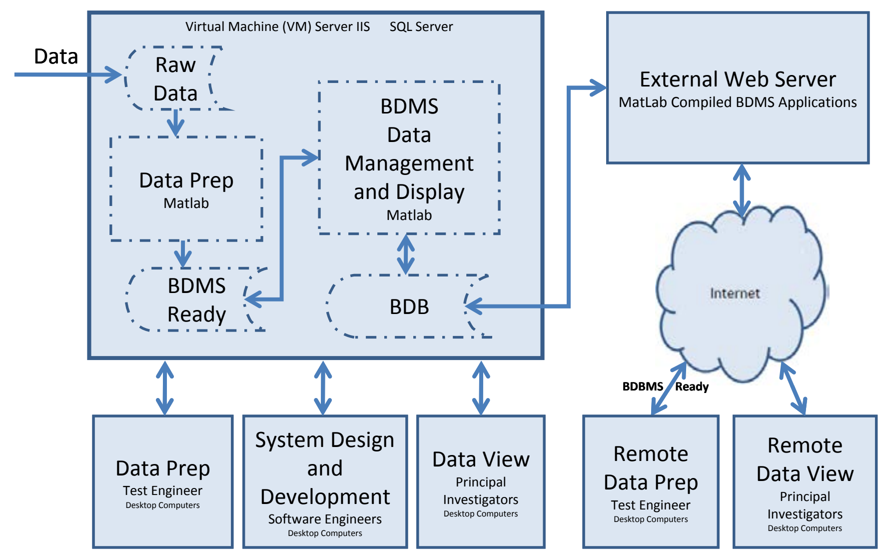
Significant progress has been made to build infrastructure for a dynamic database that is adaptable, expandable, trainable, and highly interactive.



Stage 1 Development



Stage 2 Development and Deployment

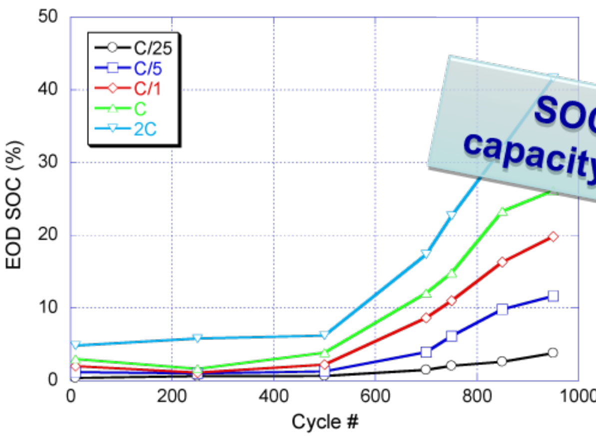


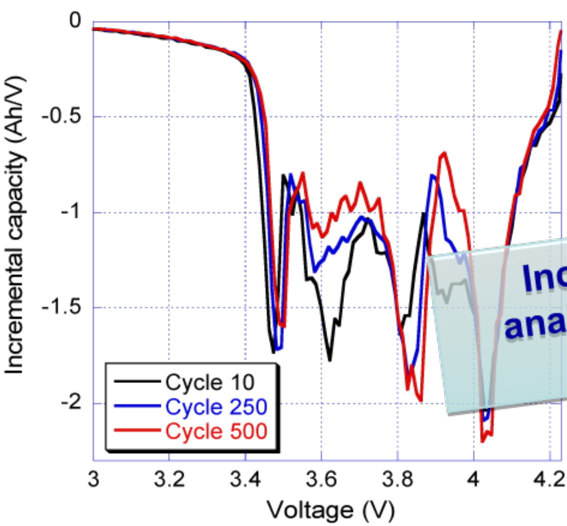
Diagnostic Studies by HNEI

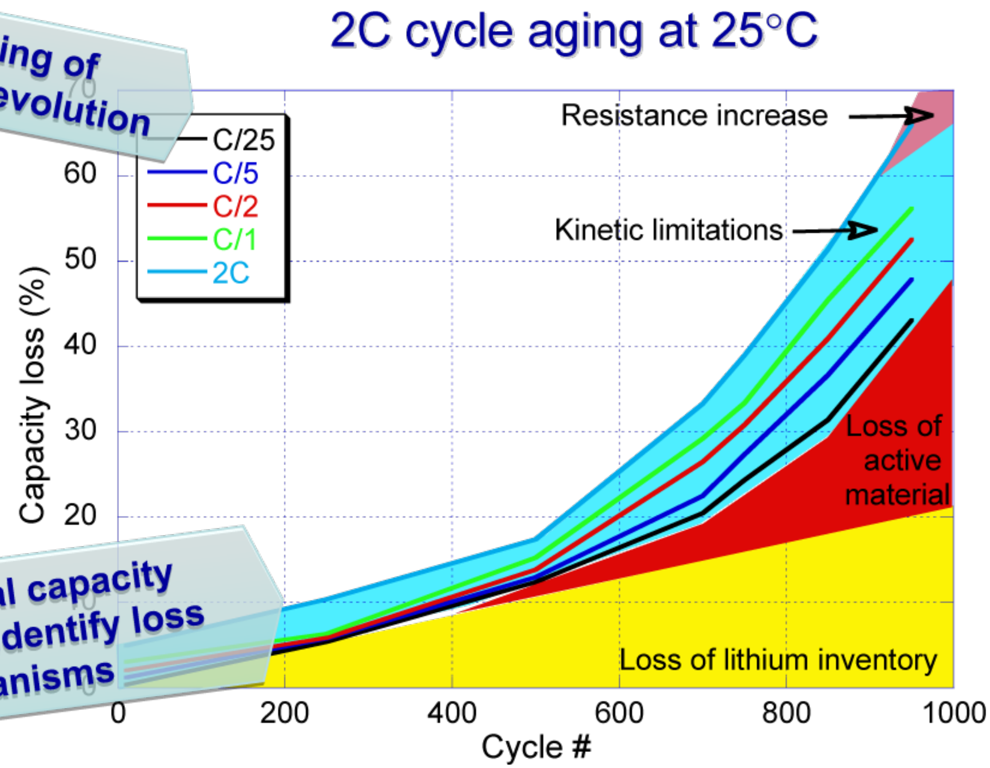
- Diagnostic Analysis of two-stage degradation of Sanyo Y cells operated under 2C cycling at RT. Aging regimes: **Stage 1** (1-500 cycles); **Stage 2** (500-950 cycles).
- Effect of Thermal Excursions on aging path dependence (complements INL DTC studies).
- Development of a backward-looking simulation tool of degradation scenarios to infer aging mechanisms.

Diagnosis of Cell Degradation

- Diagnostic tools:
  - Equilibrium cell voltage to infer SOC → temporal SOC tracking of capacity loss
  - Incremental capacity analysis → identify loss mechanisms



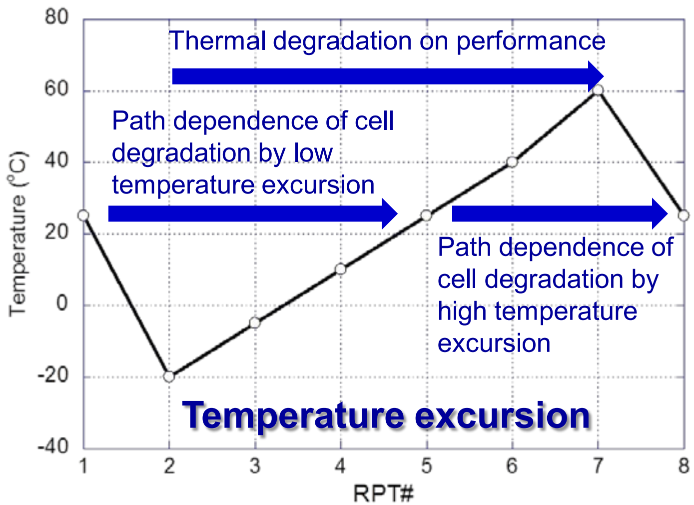


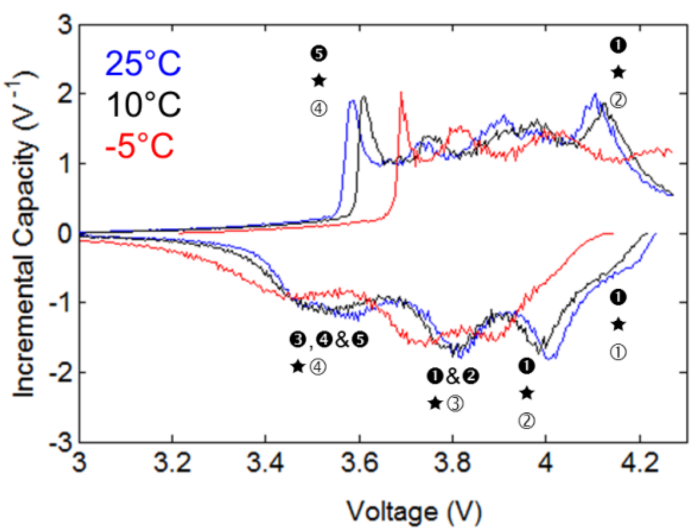


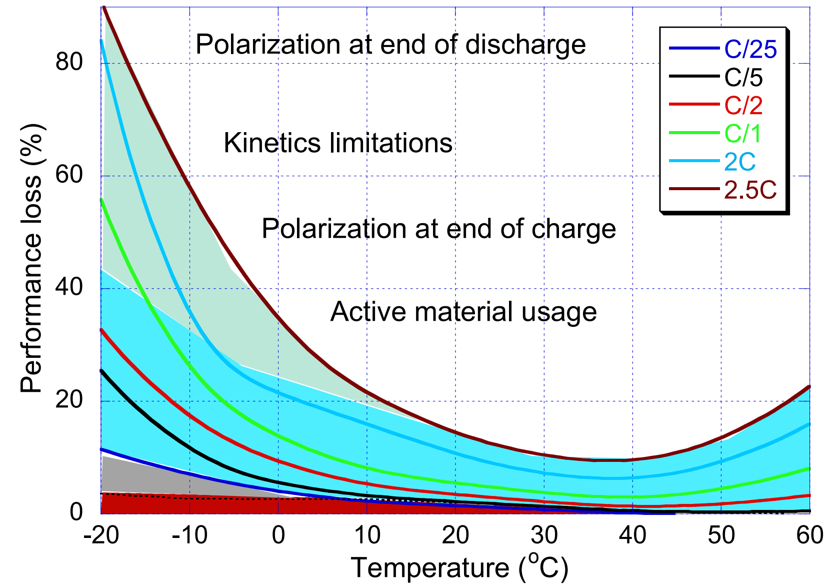
Dubarry et al. *J. Power Sources* 196 (2011) 10336.

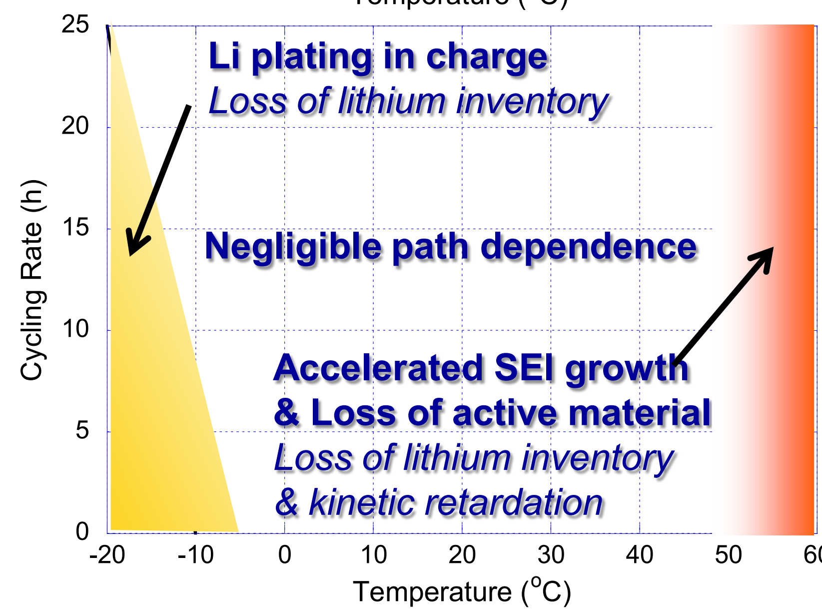
Degradation in Thermal Excursions

- Path dependence on thermal aging





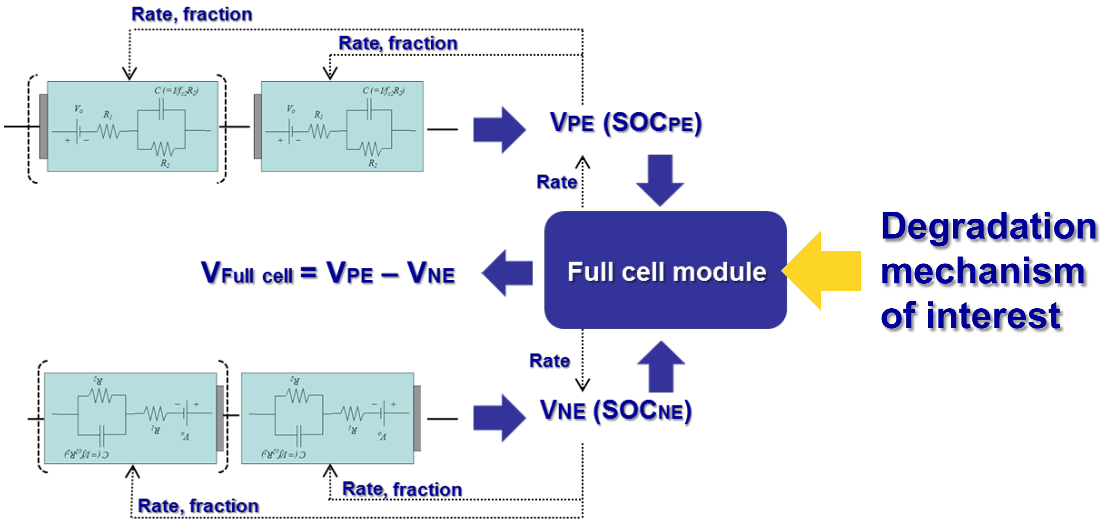




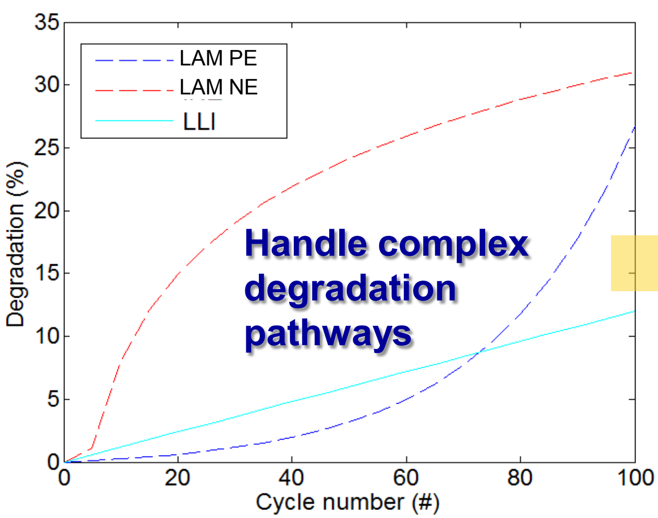
Dubarry et al. *J. Power Sources, to be published*

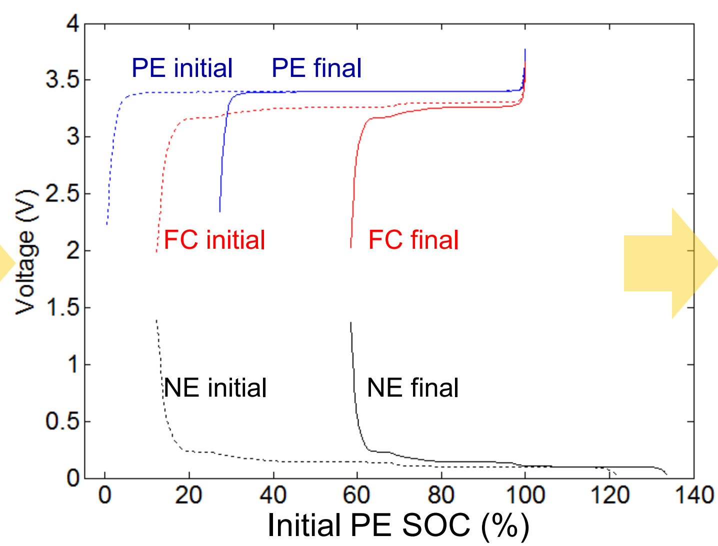
Diagnostic Modeling Tool to Synthesize Aging Scenarios

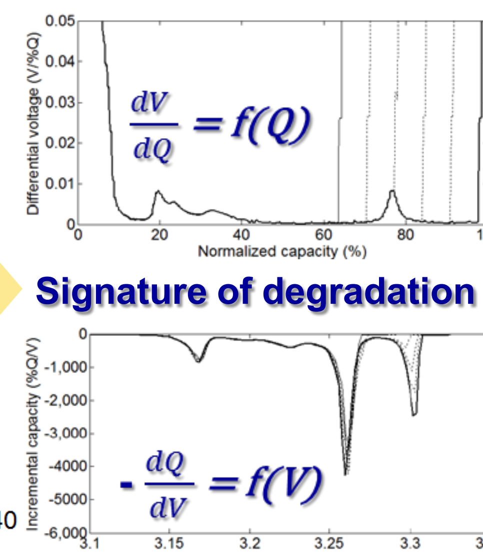
- Backward looking simulation of degradation scenarios to infer aging mechanism



- Use experimental half-cell data: easy to use; high fidelity
- Versatile; inclusive
- Handle electrode-specific degradation
- Simulate multiple processes in degradation
- Apply to composite electrodes







Dubarry et al. *J. Electrochem. SOC., submitted*

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.
- **USDRIVE Program.** Initiated dialogue in 2011 regarding DADT activities as they pertain to PHEV-type cycling coupled to thermal cycling.
- **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

- **Aging diagnostic analyses:** we will continue to monitor aging trends for our path dependence studies to achieve mature datasets that will serve multiple diagnoses.
- **Integrate DADT findings into cell life prognostic models** per ES124 (CellSage).
- **Pouch Cell Pressure Management & Optimization**: determine if there is a common or universal range of pressure that boosts performance and prolongs longevity of pouch cells.
- **DADT with other duty cycles** (e.g., FUDS, DST), or temperature parameters defined for a particular city or region.
- **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). We have signed a NDA with A123 for new testing.
- **SOC Sensitivity:** We want batteries to operate at high SOC to benefit from higher capacity and power, but at what elevated SOC threshold do we start to see multi-stage degradation and excessive self-discharge? This is chemistry dependent, but DADT protocol is standardized.
- **String Testing**: continue this crucial test component to understand aging dynamics within a series population. Will involve typically 3-9 cells per string.
- **Positron Analysis of Materials**: PAS and PALS can be used to provide post-mortem of materials to determine before/after changes in surface and internal properties due to DTC.

Idaho National Laboratory

Summary

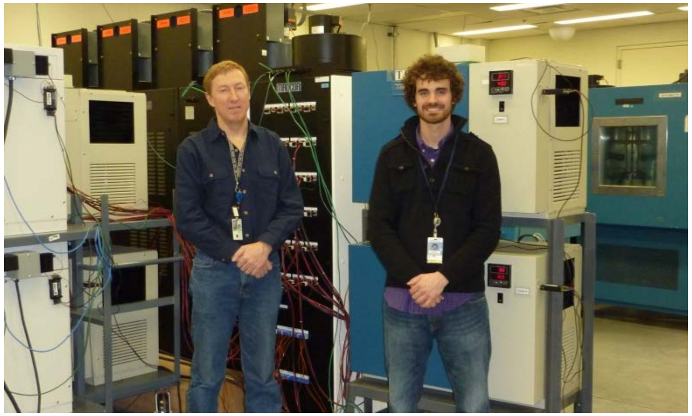
- Parallel DADT studies at INL and HNEI have involved over 100 commercial lithium-ion cells, where we are isolating the effects of foremost operational parameters on the aging path, such as magnitude of power pulses, the effects of high SOC, temperature excursions, and magnitude of daily thermal cycling during duty cycles. These studies will continue so as to achieve mature trends for diagnostic (mechanistic) analyses.
- Knowledge gained through DADT involving (NMC + Spinel)/carbon cells shows
  - Aging path is unique to operational and environmental conditions that promote various irreversibilities to degradation processes.
  - Daily Thermal Cycling can double the rate and extent of capacity loss, making more important the need for advanced, adaptive thermal management. This accelerated loss is believed to be due to high material stress under combined thermal and electrochemical cycling. *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.*
  - Distinct aging stages appear under more prolonged aging, e.g., operating at high SOC can produce as many as three (3) distinct stages of degradation. Long-term testing is vital!
  - Operating at low temperature vs high temperature both produce irreversible capacity losses but through different mechanisms. This can result in path-dependent aging behavior.
  - Cell impedance rise generally tracks with capacity loss, suggesting that a common set of mechanisms affects both metrics. Yet, increases in ohmic resistance over aging could make these cells more power-limited than energy limited later in life.
  - Cells under calendar-life conditions are more immune to thermal cycling aging effects.
- *Knowledge of Path Dependence enables Path Optimization.*
- (DADT + Advanced Physical Models) = Robust and accurate diagnostics and life predictions

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

Approach: ES096 feeds directly into ES124

Cell's Age

Cell Sage

Battery Performance Diagnostics and Prediction

Novel INL computational tools useful toward ♦cell design ♦performance characterization ♦evaluation of aging trends.

Can be integrated or embedded into numerous applications or within onboard device monitoring and control systems.

Aging trends can be predicted at arbitrary field conditions that are variable over service life, permitting direct analysis of aging path dependence, life optimization, and thermal management design.

Essential battery health metrics are covered:

- ♦ **Contributions to Capacity Loss,**
- ♦ **Contributions to Cell Conductance Loss (pulse R, EIS, IMB),**
- ♦ **Cell Kinetic performance over multiple domains,**
- ♦ **Degradation of Materials due to Daily Thermal Cycling (DTC).**

Method has been applied to multiple use scenarios, including city-wise evaluation of cell aging.

Important Model Parameters: ***singly and in combination, can be variable over time.***

- **Temperature**
- **SOC**
- **Cycling Regime (cal- vs cyc-Life)**
- **Cycling Magnitude/Freq.**
- **DTC range**
- **T-ramping under DTC**
- **City of interest**
- **Cell Chemistry**

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).

Idaho National Laboratory

Validation Testing for T-dependence of Aging PD

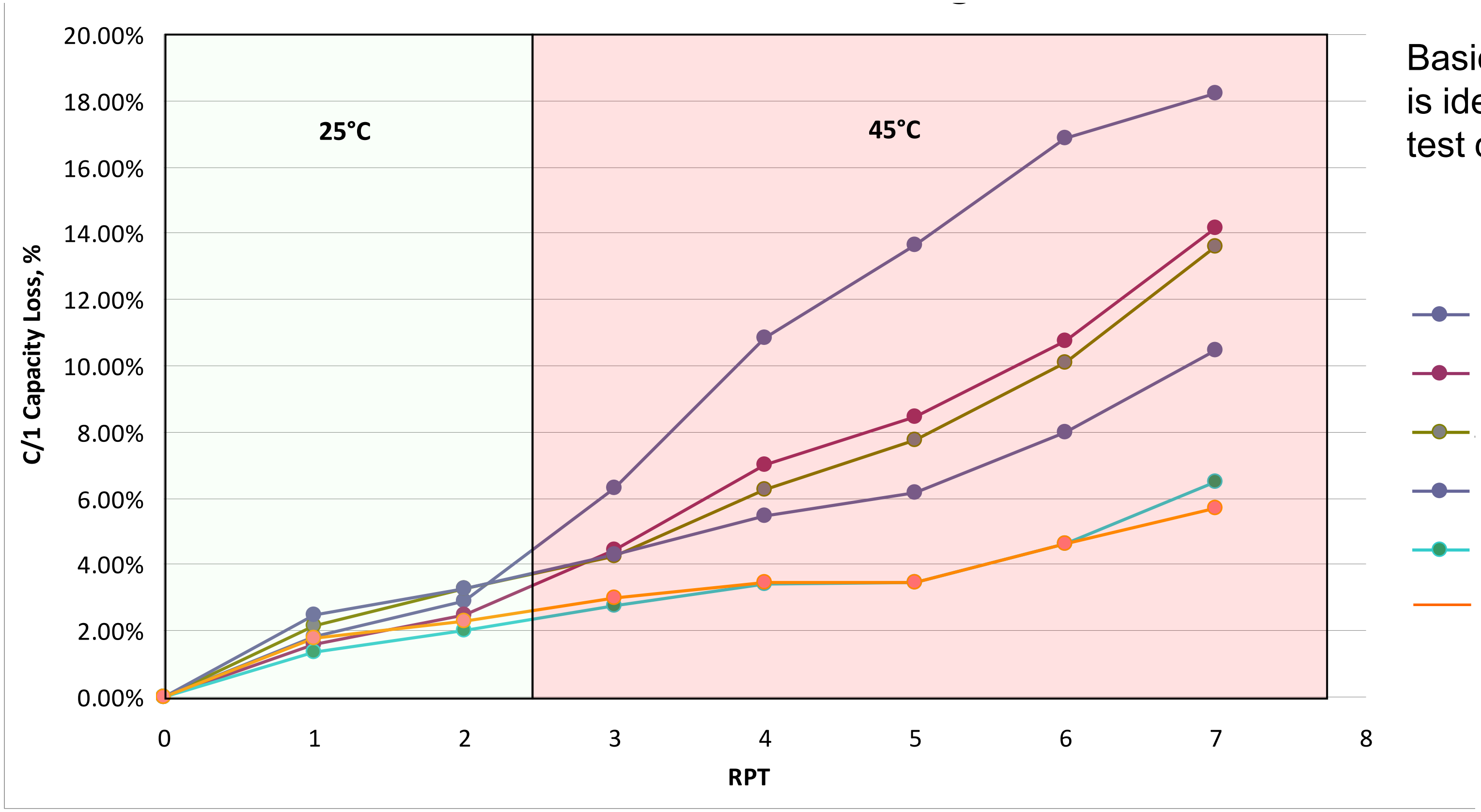
Sanyo Y Cells (NMC+Spinel/Carbon)

Study 1 will identify the Aging PD behavior due to the sequence of **temperature** over cycle-life conditions: • 10 C followed by 50 C • 50 C followed by 10 C • Baseline of 30 C
Study 2 will identify the Aging PD behavior due to the sequence of **SOC** over calendar-life conditions: • 90% SOC followed by 50% SOC • 50% SOC followed by 90% SOC • Baseline of 70% SOC

  – Which provides the greatest aging over a standard test period?

- **Testing is in progress** to establish path dependence behavior.
  - ➲ *Results to date have shown the emergence of path dependence over both T and SOC study groups*.

Prolonging cell life through current conditioning



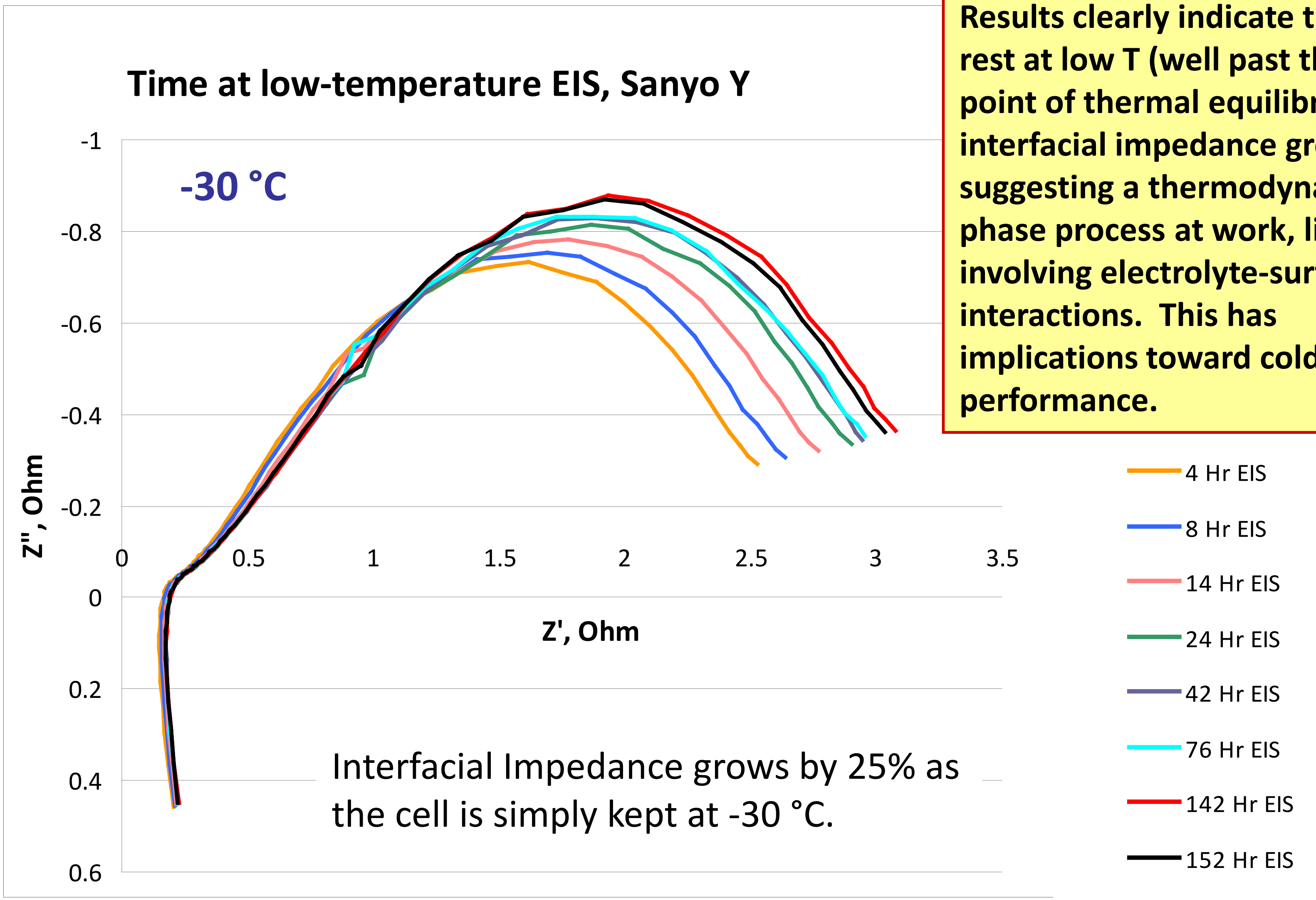
Basic "duty cycle" is identical for all test conditions.

INL test results indicate that current conditioning can profoundly diminish the rate of aging (Sanyo Y). Patent position is being sought.

Idaho National Laboratory

Low-temperature Characterizations

With Implications Toward Cold Start and Low-T Cycling



Results clearly indicate that at rest at low T (well past the point of thermal equilibration), interfacial impedance grows, suggesting a thermodynamic phase process at work, likely involving electrolyte-surface interactions. This has implications toward cold start performance.