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Diagnostic and Prognostic Analysis of Battery Performance & Aging based on Kinetic and Thermodynamic Principles

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Project ID ES124

2012 DOE Vehicle Technologies Program Annual Merit Review

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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, given variable usage in real applications.** **Performance (New Materials):** **— abiding need for property predictions (electrolytes)**

Budget	Partners
Funding Received (ABR; includes testing support): **FY 11: $ 325K** **FY 12: $ 350K**	**<u>Hawaii Natural Energy Institute</u>: misc. Diagnostic Testing and Analysis** **<u>Argonne National Lab</u>: ABR oversight & collaboration** **<u>Project Lead</u>: INL (K. Gering)**

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. A robust framework for life-modeling is needed to keep pace with ever-evolving development of advanced EDV batteries.

Our objectives include:

ES096

- 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.

ES124 ✓

- Develop advanced life-modeling tools that will complement DADT, and provide a robust predictive platform for technology optimization.
- Provide tools that optimize operational protocol to minimize aging. (chemistry and application-specific, but with generalized approach).
- Provide diagnostic and prognostic modeling tools that aid in battery pack design, management, and secondary use.

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

Milestones

Milestone	Status	Date
Develop and validate constituent modules that cover aging diagnostics and predictions for capacity loss, kinetic performance, and cell conductance change.	Completed	By Aug. 2009
Theoretical developments for Aging Path Dependence over arbitrary and variable aging conditions (CellSage)	Completed	Nov. 2011
Demonstrate CellSage for capacity loss predictions	Completed	Nov. 2011
Apply CellSage to additional Li-ion Chemistries and Usage Scenarios	Ongoing	
Integration of CellSage into system-level ES monitoring, diagnostics, management, and control (MDMC)	Ongoing	
Theoretical development of *Ion Skipping* component to Advanced Electrolyte Model (AEM)	Completed	April 2011
Expansion of AEM database to include new solvent and salts	Ongoing	
License of AEM to Private Sector company	License terms in development	

Approach

- A robust modeling method has been developed from thermodynamic, mathematical, and chemical kinetic principles that enables prediction of aging processes over arbitrary and variable aging conditions. This modeling approach is perfectly suited to evaluating *aging path dependence*.
- Capability is envisioned as being integrated or embedded into an application or within onboard device monitoring and control systems to allow adaptive diagnosis and control of batteries to extend service life. Can be applied to numerous non-battery and non-vehicle scenarios.

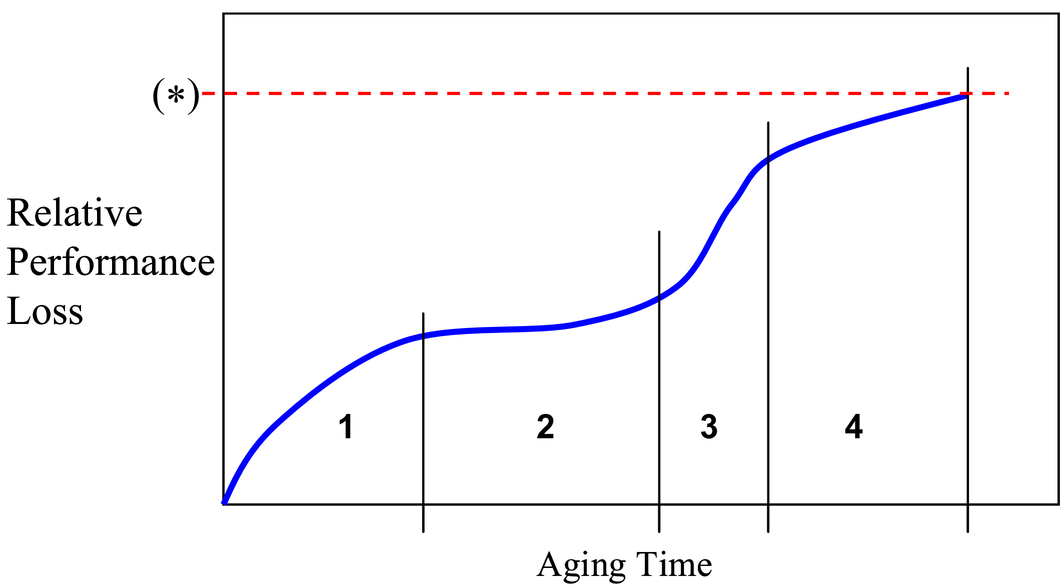
Benefits:

- Predictive tool can substantiate if battery life meets warranty conditions.
- Capability supports optimization of battery pack design and related thermal management systems, making them more economical and the application more efficient (a lighter battery pack gives higher MPG in EDVs).
- Capability supports evaluation of battery secondary-use scenarios.

Knowledge of path dependence enables path optimization to prolong cell lifetimes.

Modeling Path Dependence of Cell Aging

- INL aging models are easily adaptable to Path Dependence scenarios, using a "batch reactor" approach to describing the kinetics of degradation mechanisms.
- Reaction kinetics and thermodynamics are key to understanding the aging process along the path. A change in aging conditions (stress inputs) can accelerate or decelerate degradation mechanisms, and can initiate new ones.
- Cell aging models can simultaneously judge loss of capacity, rise in impedance, loss of power, self discharge, etc., where each have a standardized basis.



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

INL Physics-based models can optimize the path to minimize the outcome of the endpoint (∗) by the end of the last aging period.

Key Model Features

Current (I), heat (Q)

- Cells are modeled under a batch reactor scenario.
- General method is founded on a *Deviation from Baseline Approach,* where the baseline is an operating condition relevant to the chosen application.
- Chemical kinetic parameters for degradation mechanisms are evaluated at each unique aging condition, over several domains of battery conditions (temperature, state of charge, cycling type, etc.).
- Thermodynamic evaluations permit a reliable framework for quantifying extent of reactions and optimizing the aging path.
- Sigmoidal-based mathematics allows for self-consistent and seamless evaluations of each aging mechanism. Given a performance loss metric 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,

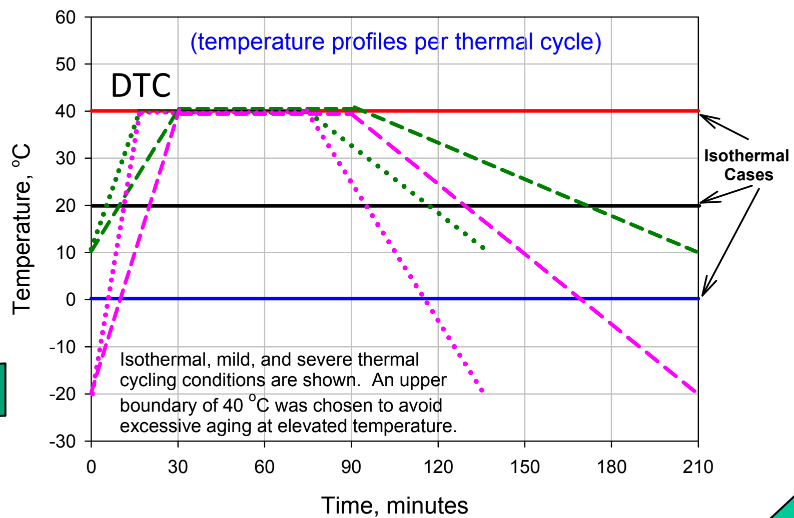
M_j : theoretical maximum limit of capacity loss under mechanism j considering the thermodynamic limit of degradation under j for a batch system.

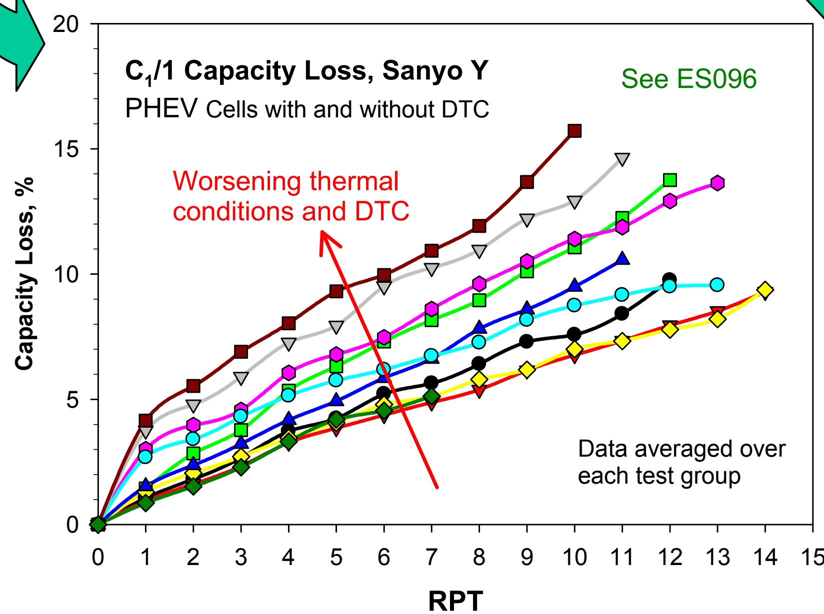
Approach

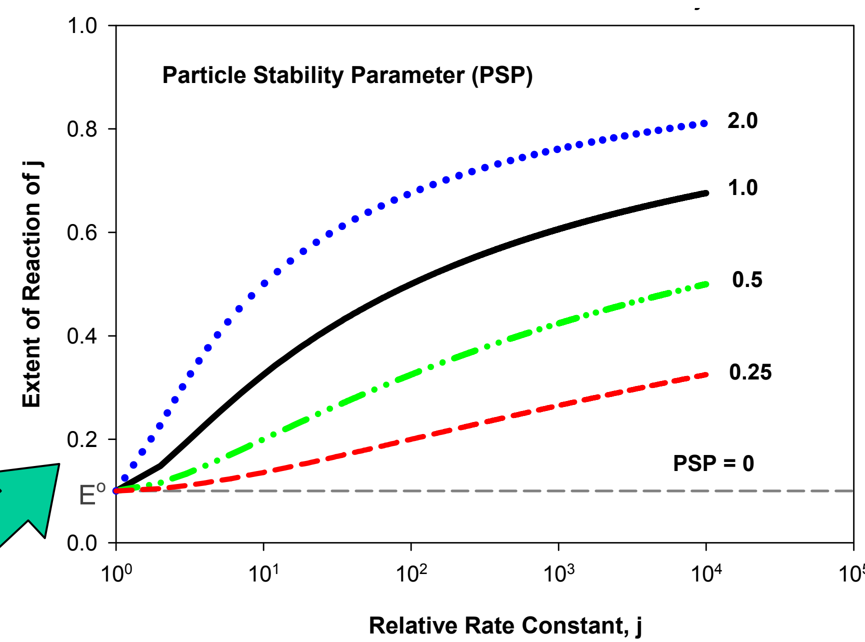
Daily Thermal Cycling (DTC)

From Cold-start to Operating T

Model describes influence of DTC on extent of each j degradation mechanism







- **PSP represents the relative susceptibility of electrode particles to mechanical degradation (fracturing and breakup) under the conditions of combined electrochemical and thermal cycling.**
- **This factor is related to particle sizes and bulk shape factors, in terms of accessible area per unit volume, given a particle shape, as well as to mechanical stress-strain response of the materials.**

The term E^o is the reaction extent without influence from DTC, arbitrarily given a value of 0.1 here for demonstration purposes. A value of unity is assumed for $a_{j,BL}$ for demonstration purposes.

Approach

Method Protocol

1. **Choose Stress Factors** (T, SOC, cycle type, etc.)
2. **Choose Aging Metrics** (Capacity Loss, Power Fade, etc.)
3. **Design & Perform Baseline Experimental Matrix**
4. **Obtain Sensitivity Analysis of Aging to Stress Factors**
5. **Train Model Rate Expressions (REs)**
6. **Apply REs to Arbitrary Aging Conditions; Thermodynamic Analyses**
7. **Predict Aging Over Time, Optimize Service Path, Optimize Thermal Management Scheme, etc.**

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Deviation from Baseline Approach

Given an Aging Response $\Psi_{j,i*}$ (e.g., capacity loss):

$$\Psi_{j,i*} = \Psi_{j,BL} + \left[\begin{array}{l} \left(\frac{\partial \Psi_j}{\partial T} dT\right)_{SOC,cyc} + \left(\frac{\partial \Psi_j}{\partial SOC} dSOC\right)_{T,cyc} + \left(\frac{\partial \Psi_j}{\partial cyc} dcyc\right)_{SOC,T} + \cdots \\ + \left\{ \left(\frac{\partial \Psi_j}{\partial SOC}\frac{\partial SOC}{\partial T} dT\right)_{cyc} + \left(\frac{\partial \Psi_j}{\partial cyc}\frac{\partial cyc}{\partial T} dT\right)_{SOC} + \cdots \right\} \\ + \{\text{higher order terms}\} \end{array} \right]_{i*}$$

Or,

$$\Psi_{j,i*} = \Psi_{j,BL} + \left[\begin{array}{l} \Delta\Psi_{j,T} + \Delta\Psi_{j,SOC} + \Delta\Psi_{j,cyc} + \cdots \\ + \left\{ \Delta\Psi_{j,SOC\bullet T} + \Delta\Psi_{j,cyc\bullet T} + \cdots \right\} \\ + \{\text{higher order terms}\} \end{array} \right]_{i*}$$

And then, $\Psi_{i*} = \sum_{j}^{n_j} \Psi_{j,i*}$ for n_j contributing mechanisms

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Other Meaningful Terms

Regarding Maximum Extent of Reaction terms M_j , and K_{eq}

$$\left[\left(1 - M_{i*}\right) \xrightarrow{\textit{pseudo-equilibrium}} M_{i*}\right]_j$$

$$M_{j,i*} = \lim_{t\to\infty} \Psi_{j,i*} \quad \text{as a single independent response}$$

$$M_{i*} = \sum_{j}^{n} M_{j,i*} \quad \text{for n contributing mechanisms}$$

$$K_{j,i*} = \frac{M_{j,i*}}{1 - M_{j,i*}} = \frac{M_{j,BL} + \sum_{k=1}^{n_k} \Delta M_{j,i*,k}}{1 - \left(M_{j,BL} + \sum_{k=1}^{n_k} \Delta M_{j,i*,k}\right)}$$

$$K_{i*,net} = \frac{M_{i*}}{1 - M_{i*}} = \frac{\sum_{j}^{n_j} M_{j,i*}}{1 - \sum_{j}^{n_j} M_{j,i*}} = \frac{\sum_{j}^{n_j}\left(M_{j,BL} + \sum_{k=1}^{n_k} \Delta M_{j,k}\right)}{1 - \sum_{j}^{n_j}\left(M_{j,BL} + \sum_{k=1}^{n_k} \Delta M_{j,k}\right)}$$

$$K_{i*} = \exp\left(\frac{-\Delta G_{i*}}{RT}\right) \quad ; \quad K_{j,i*} = \exp\left(\frac{-\Delta G_{j,i*}}{RT}\right)$$

Technical Accomplishments & Progress

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).**

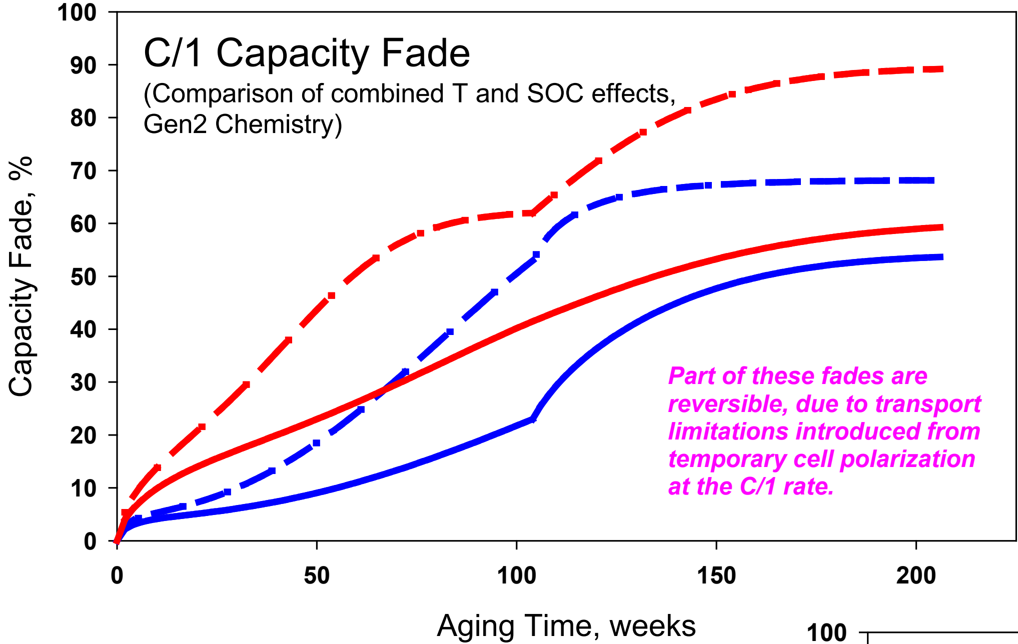
Method has been applied to multiple use scenarios, including city-wise evaluation of cell aging.

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**

Tech. Accomplishments

Examples of PD Studies



Scenario 1: **100% SOC for 104 weeks,
then 60% SOC for 104 weeks**
Scenario 2: **60% for 104 weeks,
then 100% for 104 weeks**

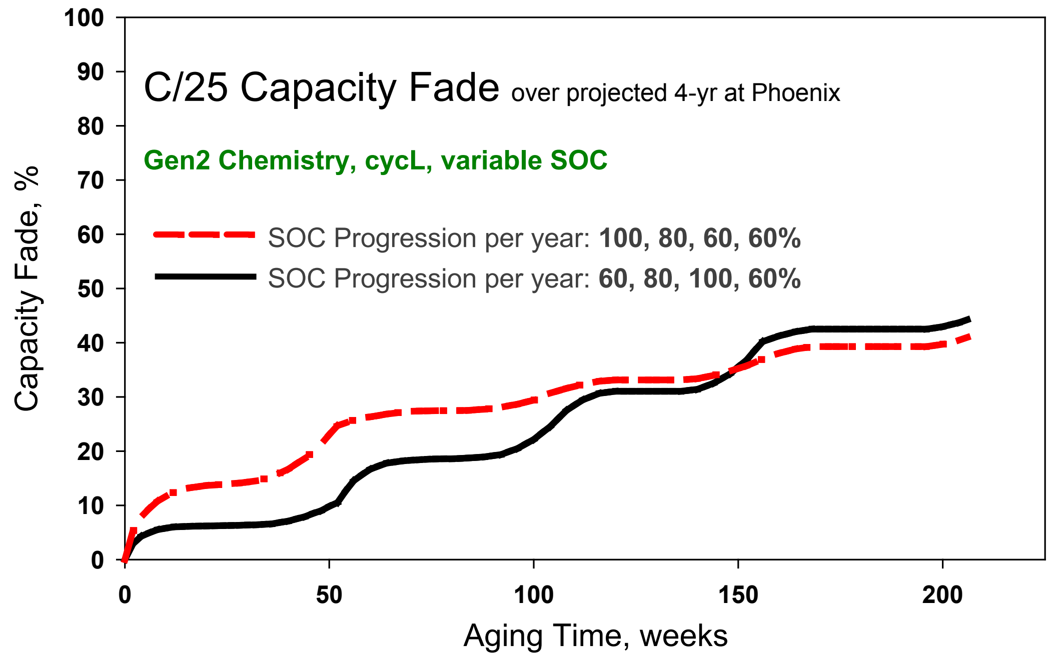
Aging at 25 °C: solid curves
Aging at 45 °C: dashed curves

Cycle-life conditions, Gen2 chemistry

Total Fade shown for each case.

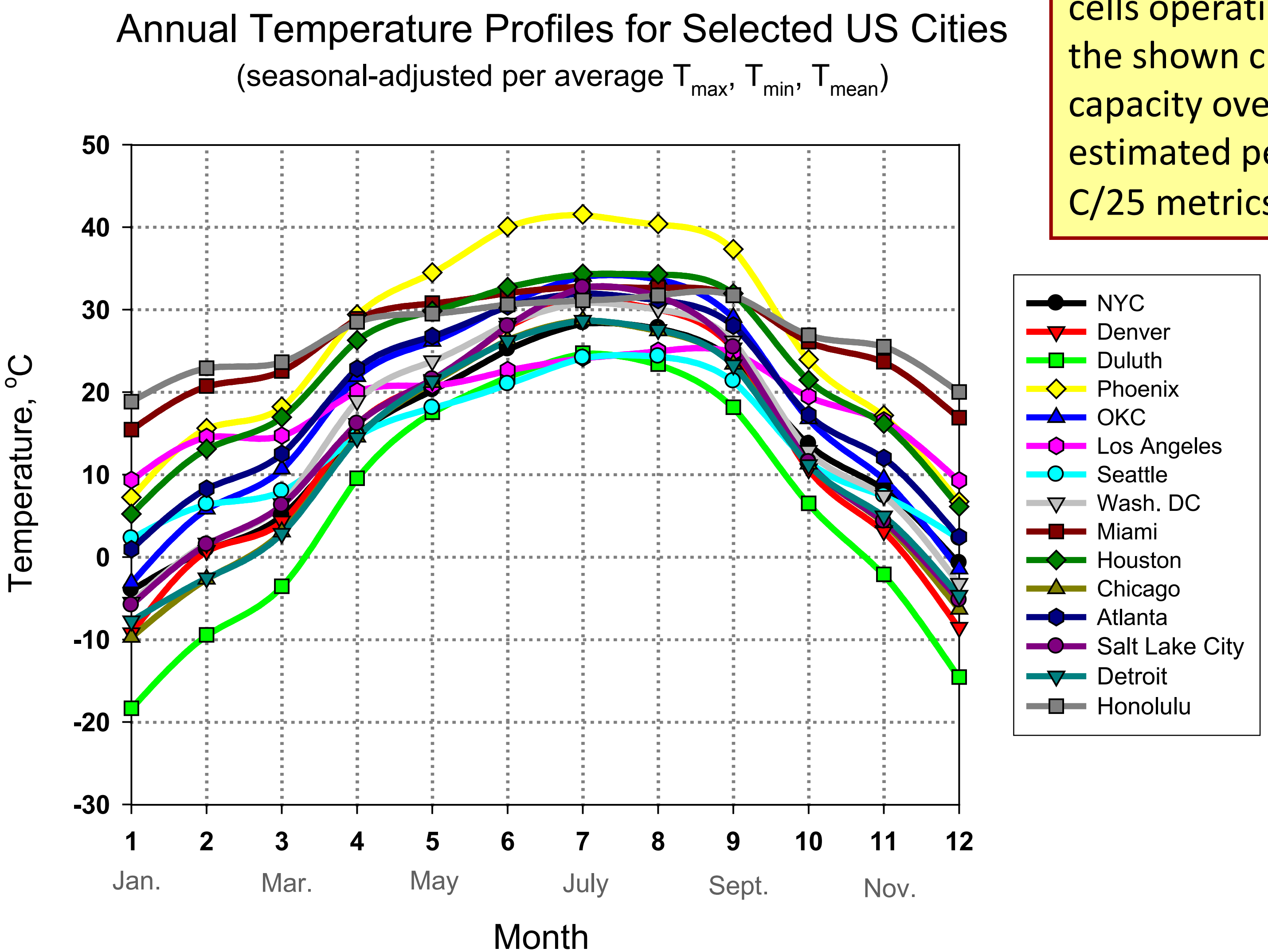
By the end of four years all cells had experienced the same net conditions within each study.

The greatest path dependence of aging is seen as SOC is varied over time at the higher temperature.



Tech. Accomplishments

Battery Aging simulations were performed for Gen2 cells operating at each of the shown cities. Loss of capacity over time was estimated per C/1 and C/25 metrics.



Source: NOAA National Data Centers
(http://ols.nndc.noaa.gov/plolstore/plsql/olstore.prodspecific?prodnum=C00095-PUB-A0001#TABLES)

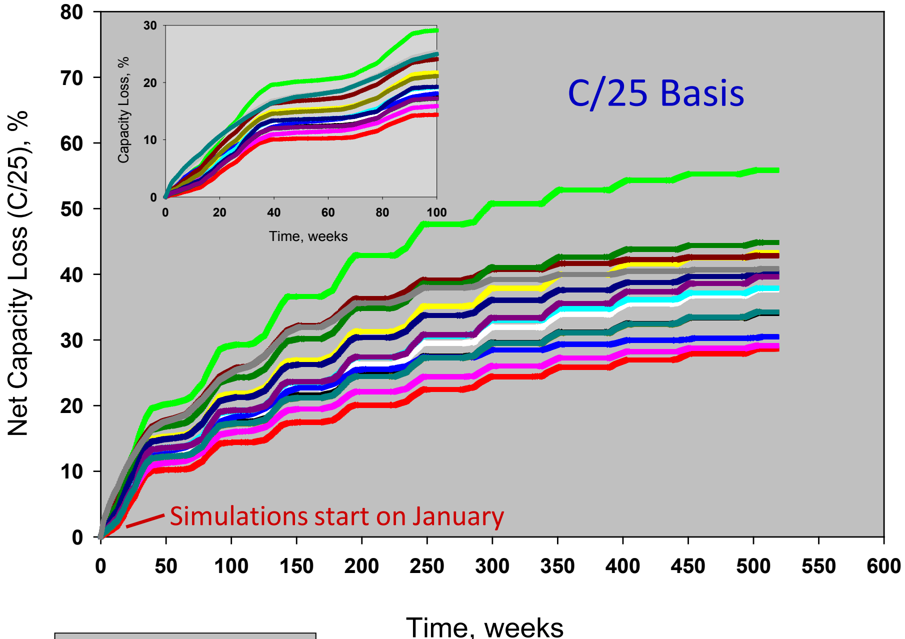
Tech. Accomplishments

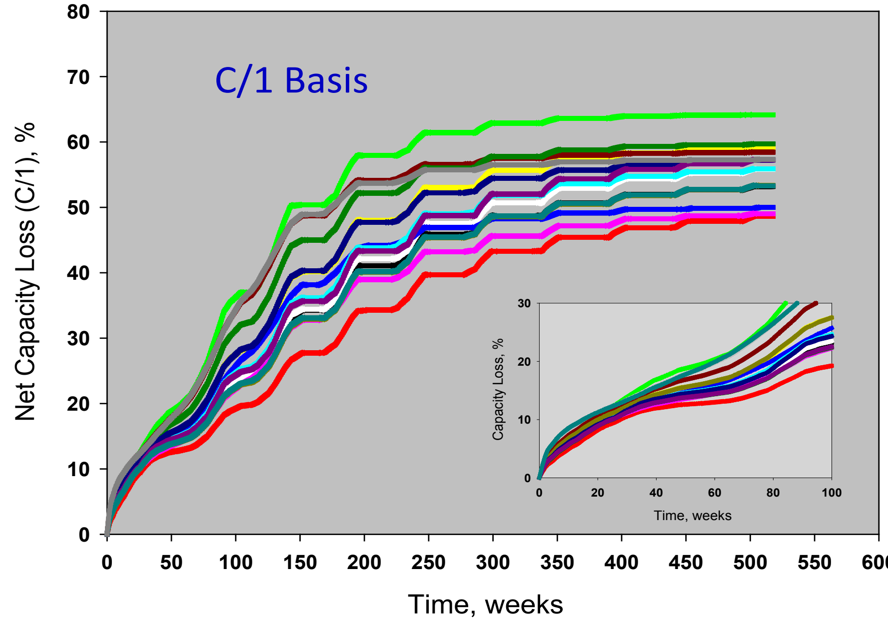
Estimated Capacity Losses for Cells Operating in Selected US Cities: No DTC Included in Model

Predictions provided by INL CellSage

Conditions of Simulation:
Gen2 cell chemistry (NCA/Graphite)
HEV cycle-life protocol (scaled power pulses)

80% SOC nominal
Average Monthly T used for each City
10-year simulation





Seasonal temperature variance generates a stair-step effect.
Capacity Loss shown is comprised of two mechanisms:
(1) loss of lithium inventory, and
(2) loss of active intercalation sites.
A portion of the C/1 loss is reversible due to cell polarization at the higher rate.

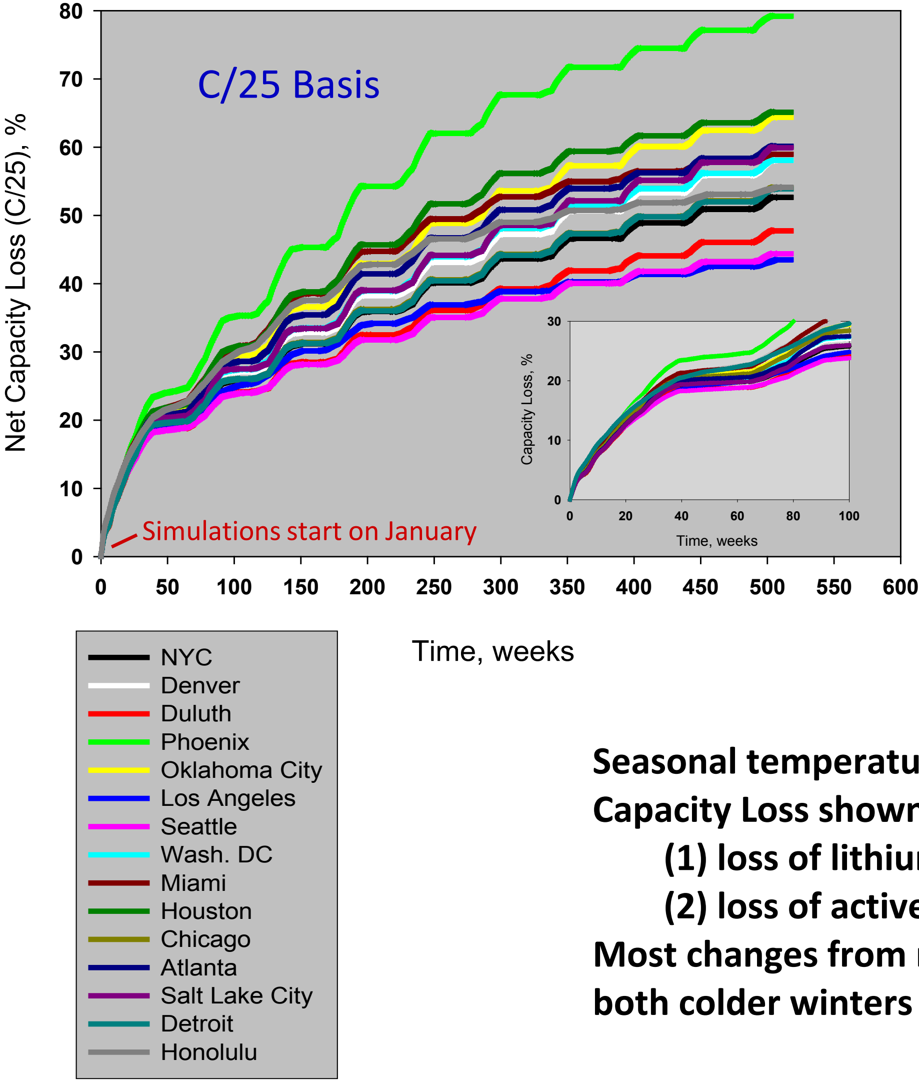
….and yet the effects from DTC are needed to reflect the reality of EDV applications….

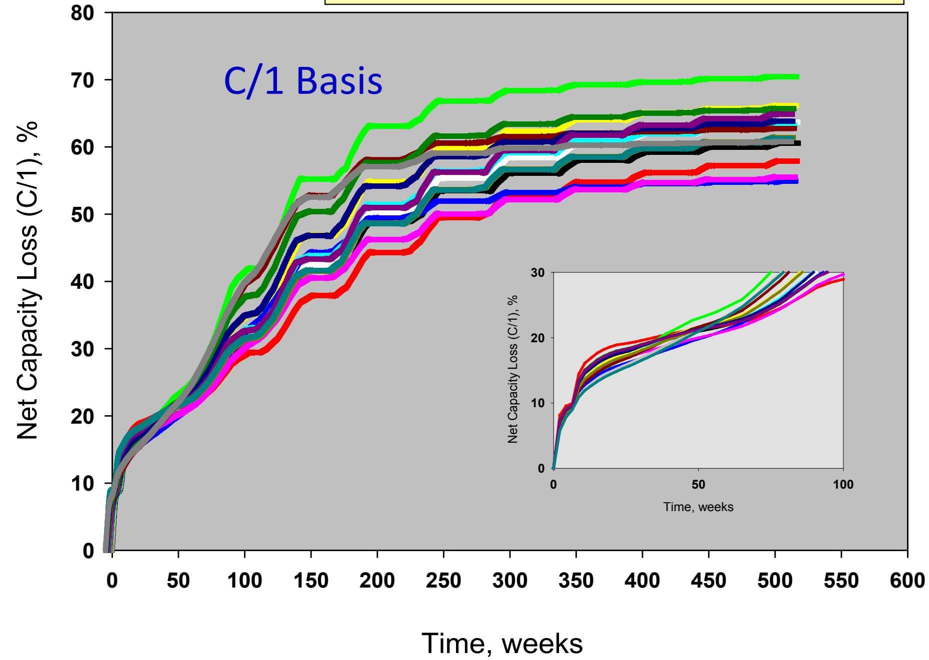
Tech. Accomplishments

Estimated Capacity Losses for Cells Operating in Selected US Cities: DTC Included in Model

T_{max} = 40 C, T_{min} = $T_{monthly,ave}$

Conditions of Simulation:
- Gen2 cell chemistry (NCA/Graphite)
- HEV cycle-life protocol (scaled power pulses)
- 1 Round-trip per day (2-hr)
- 80% SOC nominal
- T_{max} (DTC) = 40 °C per Thermal Management
- T_{min} (DTC) = Average Monthly T per City
- 15-minute temperature ramp after cold start
- 10-year simulation





Seasonal temperature variance generates a stair-step effect.
Capacity Loss shown is comprised of two mechanisms:
(1) loss of lithium inventory, and
(2) loss of active intercalation sites.
Most changes from non-DTC scenario occur for cities having both colder winters and warmer summers.

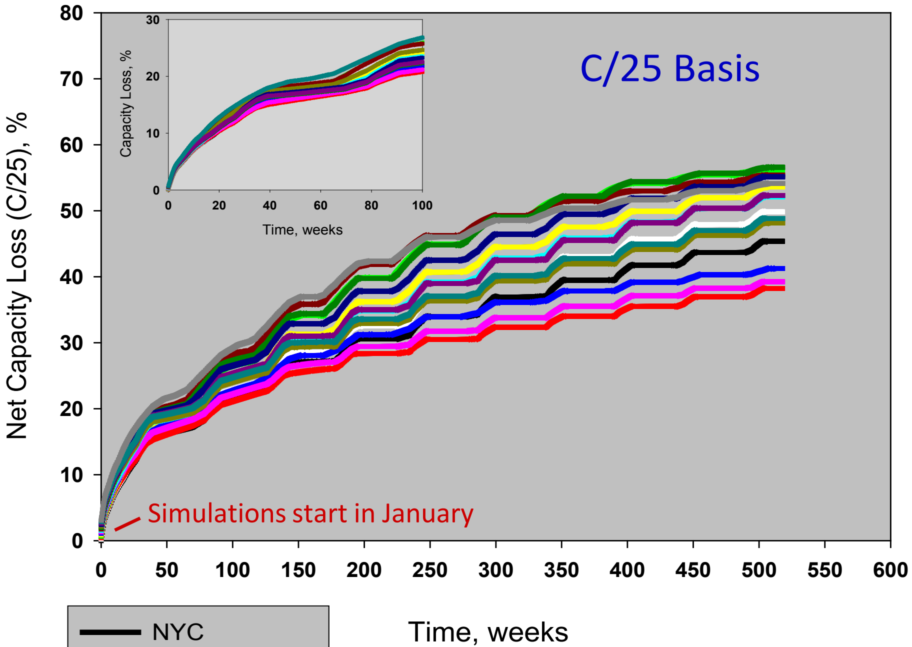
Tech. Accomplishments

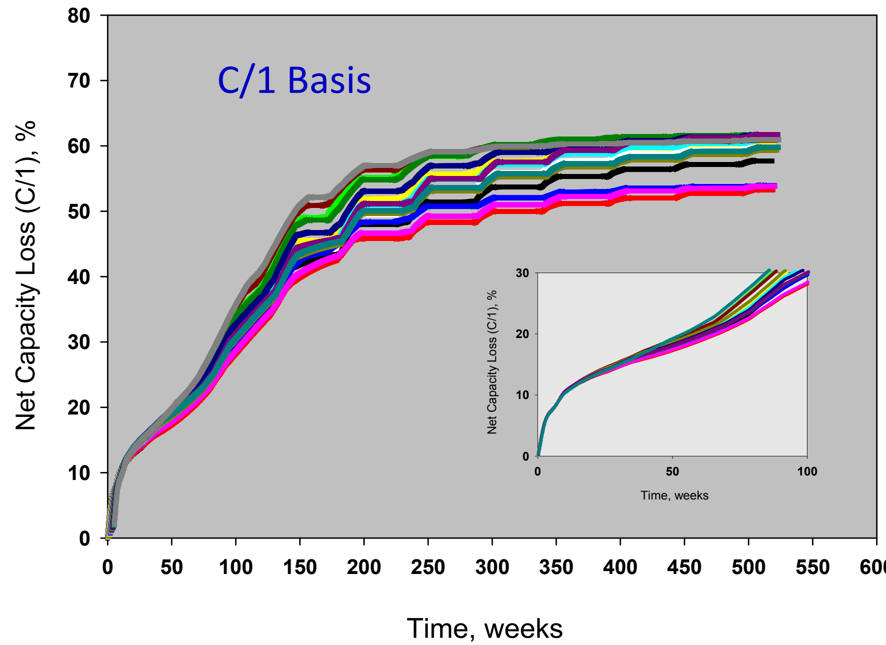
Capacity Losses for Cells Operating in US Cities:

DTC Included in Model, with Thermal Management

(T_{max} = 30 °C, T_{min} = 15 °C)

Conditions of Simulation:
- Gen2 cell chemistry (NCA/Graphite)
- HEV cycle-life protocol (scaled power pulses)
- 1 Round-trip per day (2-hr)
- 80% SOC nominal
- T_{max} (DTC) = 30 °C per Thermal Management
- T_{min} (DTC) = 15 °C per Thermal Management
- 15-minute temperature ramp after cold start
- 10-year simulation





Cities group more closely due to common Thermal Management parameters. Thermal management for both Tmax and Tmin under DTC is critical for prolonging cell life.

Capacity Loss shown is comprised of two mechanisms:

(1) loss of lithium inventory, and

(2) loss of active intercalation sites.

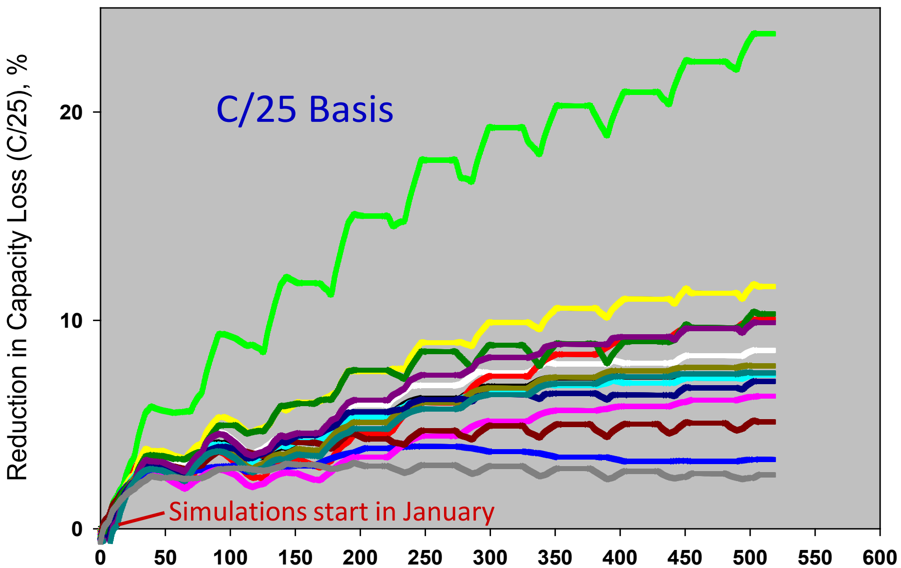
Tech. Accomplishments

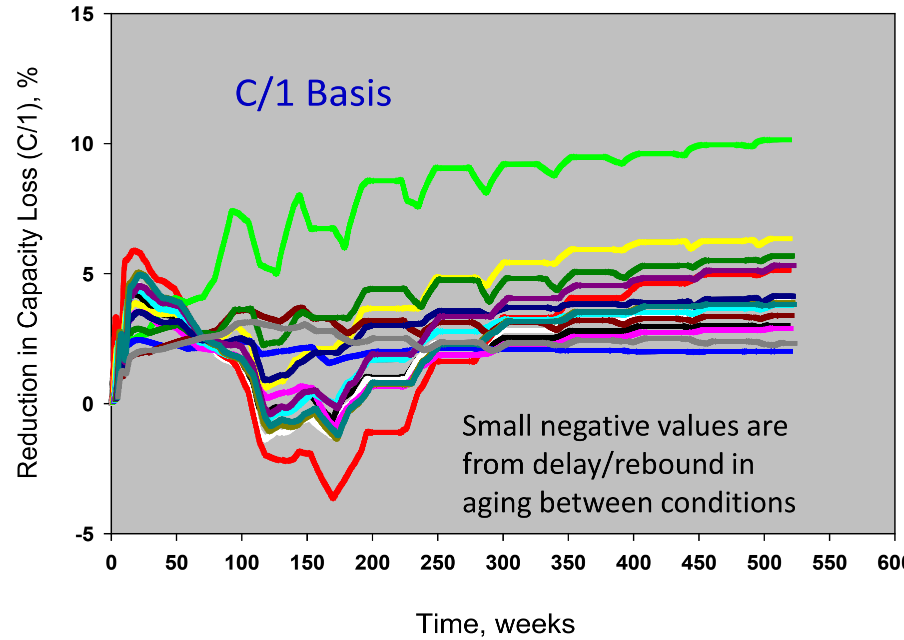
Reduction in Capacity Losses for Cells Operating in US Cities:

DTC Included in Model, with Thermal Management

(T_{max} = 30 °C, T_{min} = 15 °C)

Conditions of Simulation:
- Gen2 cell chemistry (NCA/Graphite)
- HEV cycle-life protocol (scaled power pulses)
- 1 Round-trip per day (2-hr)
- 80% SOC nominal
- T_{max} (DTC) = 30 °C per Thermal Management
- T_{min} (DTC) = 15 °C per Thermal Management
- 15-minute temperature ramp after cold start
- 10-year simulation





Reduction in Capacity Loss is assessed relative to the condition of T_{max} = 40 °C and T_{min} = Average Monthly Temperature per City

Thermal management (TM) shows most benefit for cities having both colder winters and warmer summers. Operation in mild climate cities shows the least benefit from the chosen TM parameters.

Reduction in Capacity Loss is more profound for the C/25 metric.

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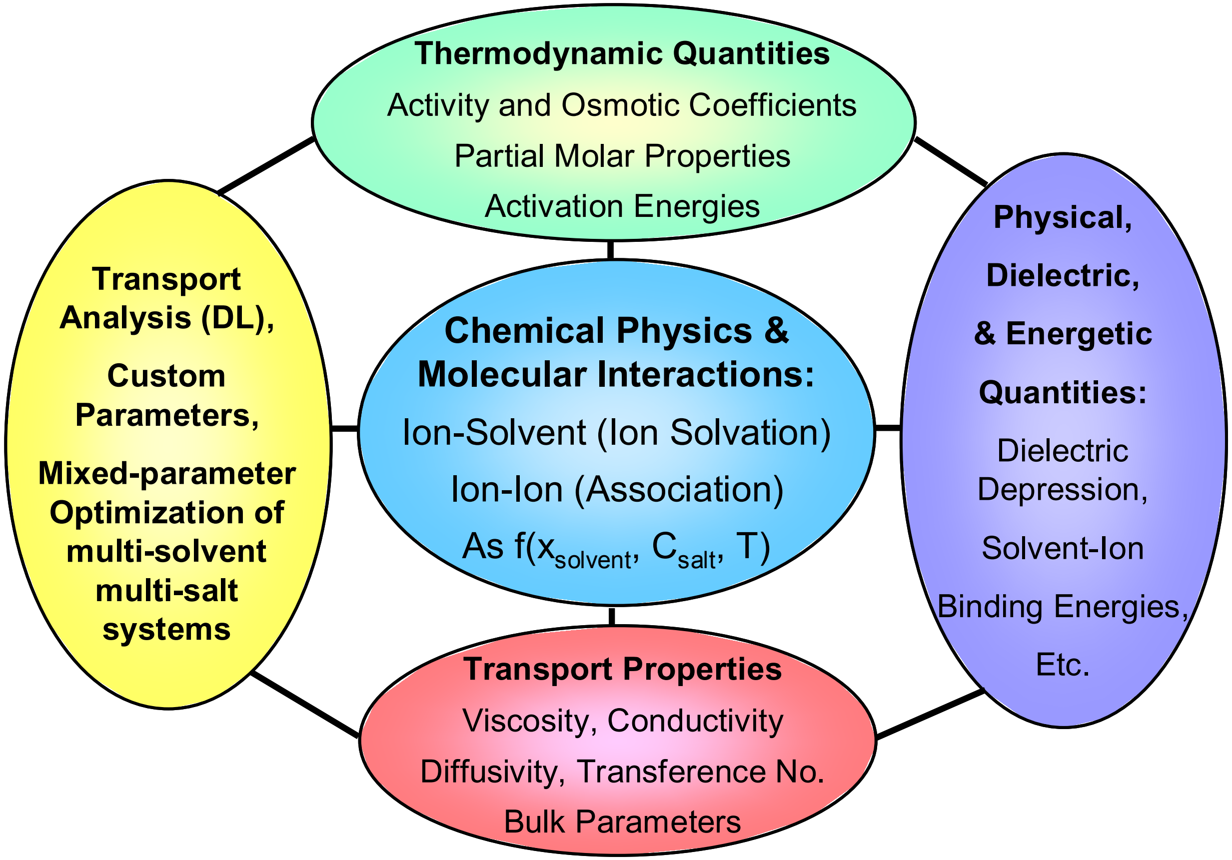
Advanced Electrolyte Model (AEM)



The AEM is routinely used for extensive evaluation of battery electrolyte systems in DOE-EERE and the Private Sector.

AEM drastically reduces the time required for electrolyte development, characterization, and optimization.

AEM is being used within the CAEBAT Program (CD-Adapco team).

AEM is targeting ABR-relevant compounds (siloxanes, phosphazenes).

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.
- **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. ANL contacts: Dennis Dees, Daniel Abraham, Larry Curtiss.
- **Dow Chemical**. Supported electrolyte development work that utilized the INL Advanced Electrolyte Model. Contact: Doug Brune.

Future Work

- Expand database that cross-lists city annual temperature profiles against battery life projections for representative cities and lithium-ion chemistries.
- Create similar database that includes TM scenarios covering both upper and lower temperature boundaries.
- Provide similar evaluations for other duty cycles and lithium-ion chemistries.
- Map out battery life expectancy over a grid of the USA, given cell chemistry, TM boundaries, and usage scenarios.
- Make projections of PD life trends for anticipated secondary and tertiary usage of target chemistries.
- Integration of CellSage into system-level ES monitoring, diagnostics, management, and control (MDMC). One avenue toward integration resides between ES124 and ES122.

Summary

- Battery aging trends in EDVs will vary over diverse usage conditions, affecting whether warranties are met. Two foremost parameters are geographic location and the extent of thermal management.
- Significant progress has been made at INL to establish standardized metrics for battery aging and to employ advanced physical models to understand aging mechanisms and path dependence in diverse usage conditions.
- Complex usage conditions can be simulated, including effects from annual temperature cycles, SOC, cycling type/magnitude, and DTC. Model parameters are physically linked to cell materials and design, “chemistry specific”.
- In general, aging effects related to DTC will have a sobering impact on warranty commitments for HEV, PHEV, and EV scenarios, and calls for better thermal management. *Thus, DTC should be considered as a standard aging condition for battery research intended for vehicle applications (HEV, PHEV, EV), and TM systems should cover both cooling and warming of batteries to mitigate DTC.*
- The immediate benefit of this work is to provide a basis for predicting battery life over arbitrary aging conditions, improving battery diagnosis, design, 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, and to predict if warranties are met.

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- DOE Vehicle Technologies Program
- Tim Murphy, INL

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Technical Back-Up Slides

Aging Parameters,

i.e. “Stress Factors”

A comprehensive test matrix requires a considerable dedication of resources.

Discharge Context:

T, SOC, ΔSOC(t_{pulse}), calL vs cycL, pulse magnitude, pulse mode (constant I, P, or V?)

Charge Context:

Similar to above, but more risky. Most use MRP for charging to avoid undue and unpredictable aging consequences.

Others:

Pressure, Mech. Shock, Thermal Cycling, etc.

Choosing a Basis for Each Aging Metric

Capacity:

- Slow rate analysis needed to determine polarization-free capacity (≤ C/25).
- One or more faster rates to establish an application-relevant value (e.g., C/1).

Conductance:

- Requires an impedance metric that is most meaningful to the application; options include HPPC impedance, EIS data (Z real), or other CC, CP, CV pulse data.
- Power fade data can often be used to mirror conductance fade trends.

Kinetics:

- A logical basis is the exchange current density and the related Intrinsic Charge Transfer Resistance

$$R_{ct,o} = \left(\frac{RT}{i_o F \left(\alpha_{a,o} + \alpha_{c,o} \right) A_e} \right) = \left(\frac{RT}{2 i_o n F \beta_o A_e} \right)$$

But these quantities are functions of T, SOC, and pulse time (need to standardize each).

→ **<u>These metrics collectively help define the age or "mileage" of a battery.</u>**

DEFINING TWO KEY TERMS RELATED TO CELL CAPACITY

f_θ Fraction of Active, Available Sites (FAAS) remaining at time *t* for Li^+ charge transfer and intercalation; specific to charge or discharge conditions.

f_{Li^+} Fraction of Available Labile Li^+ (FALL) remaining at time *t* which is a fraction of Li^+ within the bulk electrolyte, SEI, and solid particles (both cathode and anode) that is available for transport between electrodes.

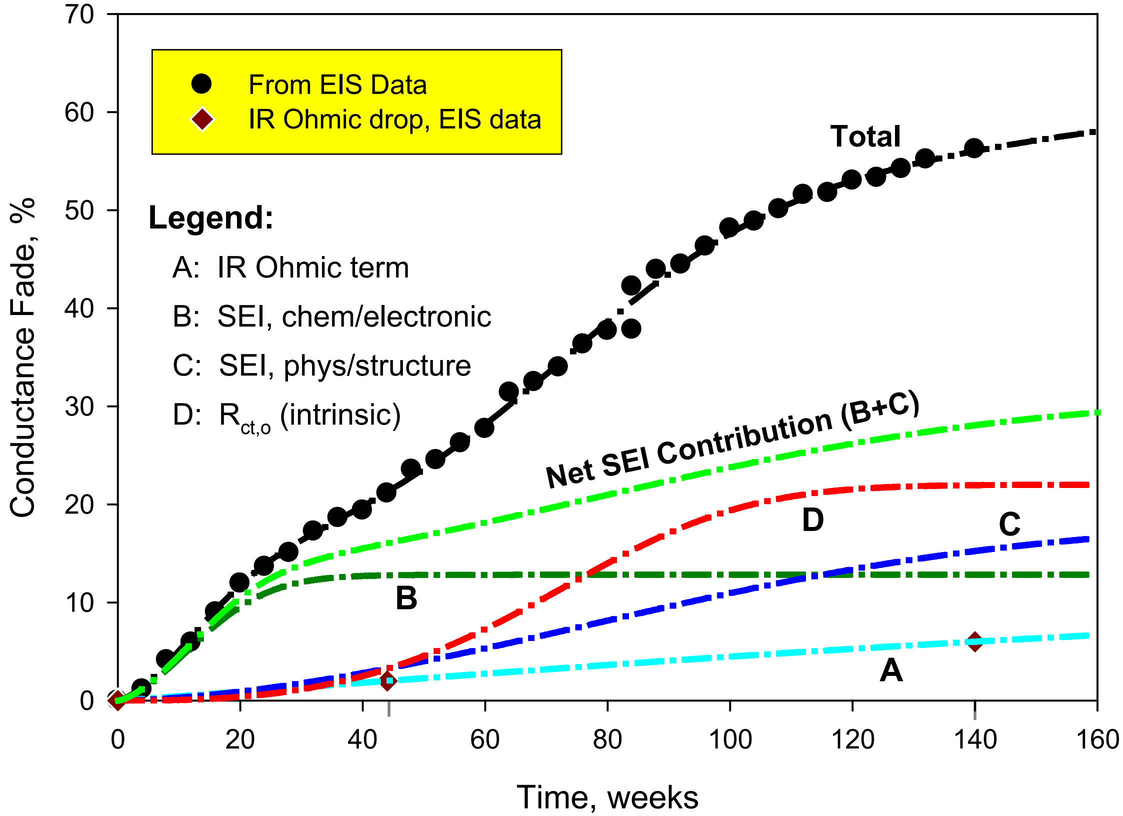
We need both healthy FAAS and FALL for a Li-ion cell to function well. FAAS and FALL can both change over time, decreasing due to various mechanisms:

1. Permanent blockage of intercalation pathways at particle surface, including conductively-dead SEI.
2. "Poisoning" of intercalation sites by contaminants or by products from irreversible chemical reactions.
3. Mechanical degradation of solid state.
4. Temporary (reversible) blockage of intercalation pathways via phase transition at particle interface.

1. Irreversible consumption of Li^+ in SEI.
2. Irreversible consumption of Li^+ in other side reactions, including formation of Li°.
3. Reversible consumption of Li^+ in temporary phase transitions as f(T), e.g., solid solvates.
4. Li^+ trapped/sequestered in the solid state.

Modeling Cell Conductance Fade

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



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.

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

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.