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Statistical Design of Experiment for Li-ion Cell Formation Parameters using "Gen3" Electrode Materials: Final Summary

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Overview

Timeline	Barriers
Project Start: Oct. 2005 Project End: Dec. 2008 Percent Complete*: 100% * Effort was part-time over the shown period. Existing tools can be used on a case-by-case basis to address future SEI formation issues.	It is common knowledge that interfacial films and processes can govern Li-ion cell performance under many conditions of interest. The cell formation process accomplishes surface passivation of electrodes in Li-ion cells by building SEI films, and thus it is a very important first step in producing stable cells that will exhibit good power and energy characteristics over long life. *More knowledge is needed regarding the formation process tied to each unique cell chemistry.*
Budget	**Partners**
Funding Received: FY 08: $150K FY 09: $50K (task completion)	INL has collaborated with ANL regarding SEI formation issues related to this study (D. Abraham).

Scope

Objectives

1. To perform a systematic evaluation of the foremost formation parameters for the ABRT Gen3-type chemistry to gain further understanding of the formation process, and to provide insights for improving battery performance and life.
2. Use resultant statistical model to optimize the formation protocol by minimizing the total formation time while meeting a performance baseline.

Approach

A Design of Experiment (DOEx) was devised to provide a statistical basis for exploring the relationship between key formation parameters and cell performance, covering six (6) foremost formation parameters over 31 test conditions split between three stages.

Standard statistical analyses were used to determine the order-of-influence for the parameters and their interactions as well as accomplish a formation optimization case study.

Milestones

(refer to Technical Accomplishments)

Technical Accomplishments in 2008

1. All remaining laboratory work was completed.
2. All remaining statistical analyses were completed.
3. An optimization case study was performed by applying the resultant response variable expressions within a broad range of interpolated and extrapolated conditions. The target was to minimize the time required for formation.

❖ *__Note:__ some of the materials that follow are from FY 07, and are included herein to provide project continuity.*

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Parameters and Fixed Conditions

Experimental Parameters:

- Temperature, **T**: 0, 30*, 50 °C
- Upper Cutoff Voltage, **UCV**: 3.7, 4.0*, 4.2 V
- Charge Cycling Rate, $\mathbf{C_{ch}}$: C_1/24, C_1/10*
- Discharge Cycling Rate, $\mathbf{C_{dis}}$: C_1/24, C_1/10*
- Time at OCV rest after each charge or discharge, $\mathbf{t_{OCV}}$: 0*, 4 Hr
- Total formation cycles, $\mathbf{n_{cyc}}$: 2*, 3

Initially-suspected relative influence of main effects on SEI formation:

$T > UCV > C_{ch} > C_{dis} > t_{OCV} > n_{cyc}$

Fixed Conditions:

- Lower Cutoff Voltage (LCV) at 3.0 V
- Current-limited taper charge on reaching UCV

* default conditions

Chemistry and Test Platform

Chemistry

- Electrodes: Gen3, *single-sided coating*
  - Cathode: lithiated $Ni_{1/3}$-$Co_{1/3}$-$Mn_{1/3}$ –oxide
  - Anode: MCMB 10-28
- Electrolyte: Gen2 (EC-EMC (3:7) + 1.2M $LiPF_6$)
- Separator: Celgard 2325 or equivalent

Test Cells

- Button Cells (2032-type)
- Six (6) cells per test condition (a total of 186 button cells were built, formed, and tested in this work)

After formation, cells underwent a suite of initial characterization tests and measurements, were cycle-life tested, and then underwent final characterization. Except where specified, all post-formation characterization was done at 30 °C, whereas the cycle-life testing was performed at 50 °C.

Data Analysis: Basis and Approach

Data from all stages were used for final statistical analyses, where we modeled all main effects and desired first-order interactions simultaneously through response variable expressions (RVEs):

Standard Form for Data: $$y = y_o + \sum_i a_i x_i + \sum_i \sum_j a_{ij} x_i x_j + \sum_i e_i$$

Interpolative/Extrapolative: $$y = y_o \exp\left\{\sum_i a_i x_i + \sum_i \sum_j a_{ij} x_i x_j + \sum_i e_i\right\}$$

Two Responses are examined in this summary:

Capacity	Interfacial Conductance
$C_m = (C_i C_f)^{1/2}$ [mAh]	$K_m = (R_i R_f)^{-1/2}$ [Ω^{-1}]
(per C1 cycling)	(per EIS interfacial impedance arc)

where these geometric mean values are based on initial and final data related to cycle-life testing at 50 °C.

Summary Results: RVE Analysis of Data

		T	UCV	C_{ch}	C_{dis}	t_{OCV}	n_{cyc}
Capacity:	Best (1.57):	50	4.2	$C_1/10$	$C_1/24$	4	3
(R^2 = 0.754)	Worst (0.52):	0	4.0	$C_1/10$	$C_1/10$	0	2

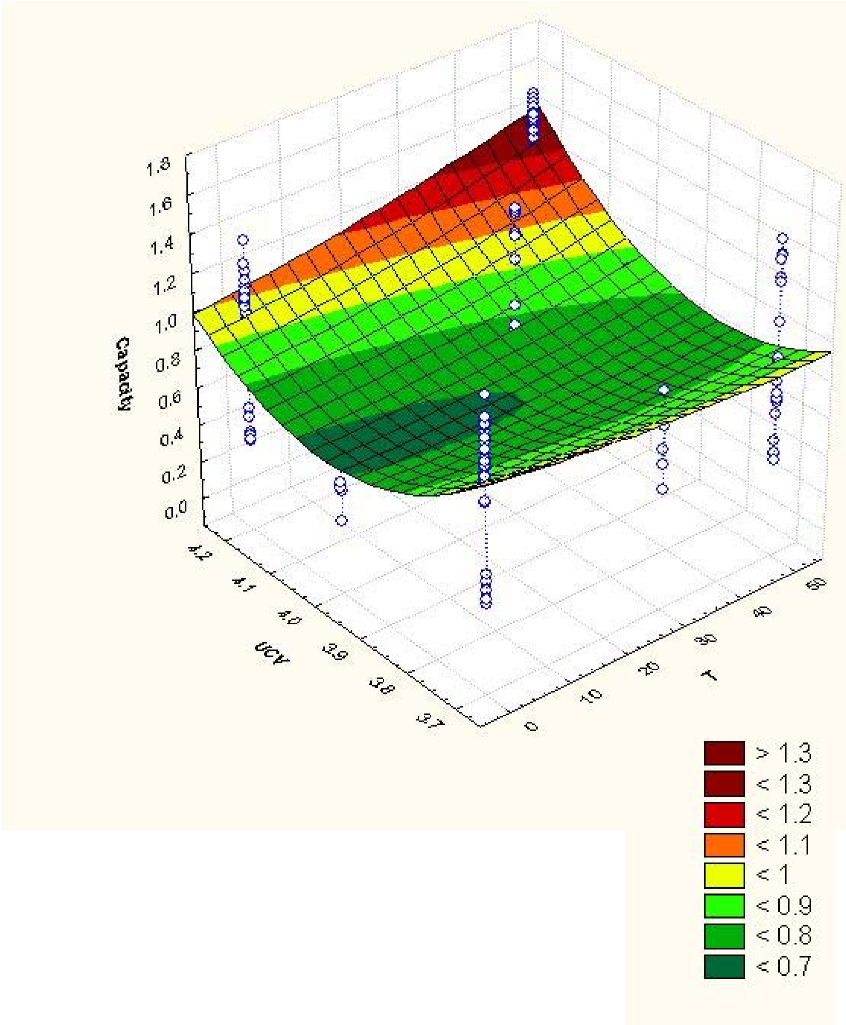
order-of-influence: C_{dis}> C_{ch}> C_{ch}*C_{dis}> T*UCV> T> t_{OCV}*n_{cyc}> t_{OCV}> UCV> n_{cyc}> y_o

		T	UCV	C_{ch}	C_{dis}	t_{OCV}	n_{cyc}
Conductance:	Best (0.24):	50	4.2	$C_1/10$	$C_1/24$	4	3
(R^2 = 0.777)	Worst (0.08):	0	4.0	$C_1/10$	$C_1/10$	0	2

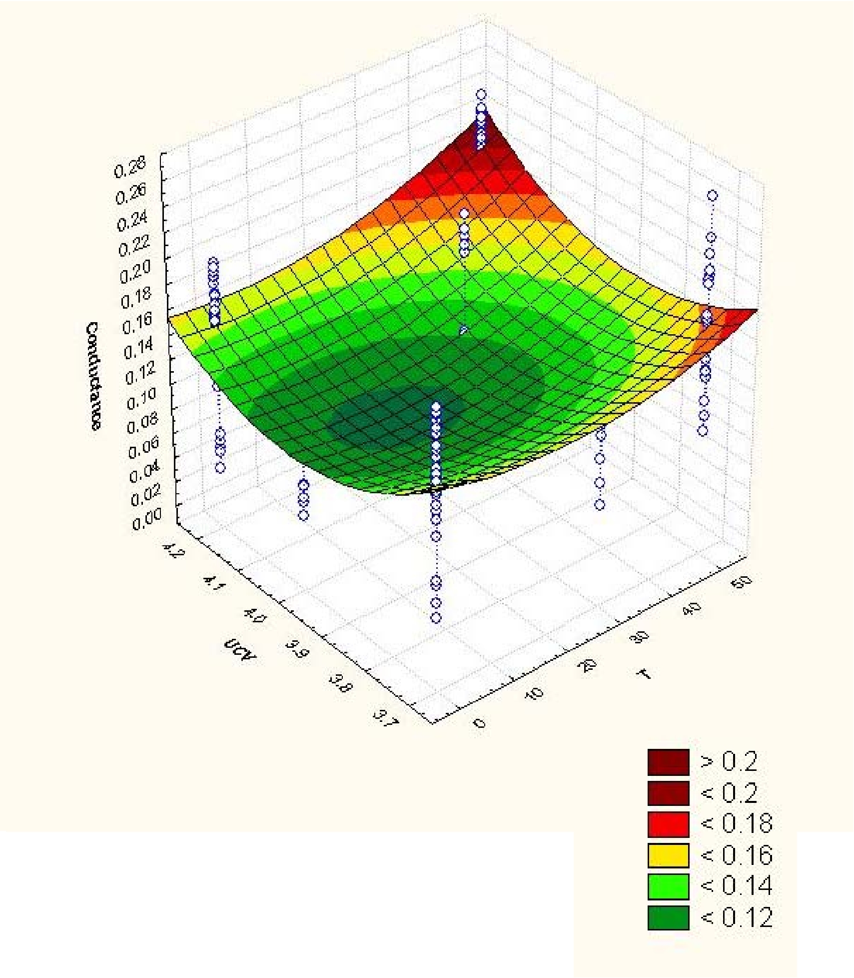
order-of-influence: C_{dis}> C_{ch}> C_{ch}*C_{dis}> T*UCV> T> UCV> t_{OCV}*n_{cyc}> t_{OCV} > y_o > n_{cyc}

Responses as f(UCV, T)

Capacity, mAh

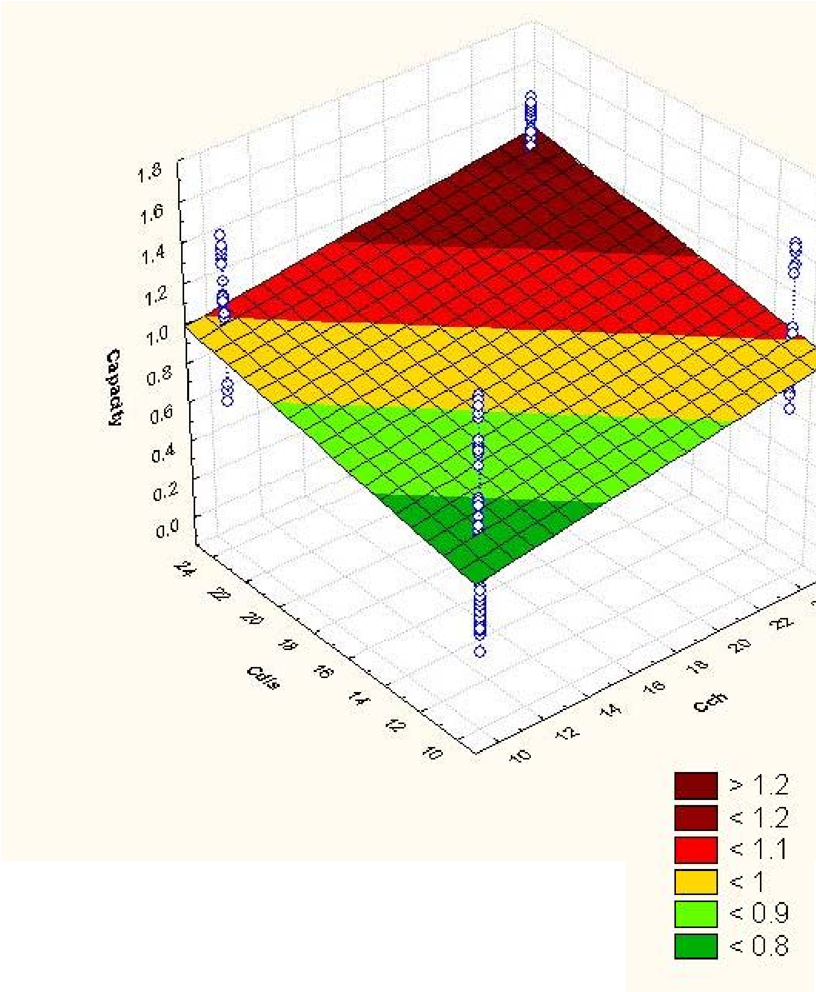


Conductance, Ω^{-1}

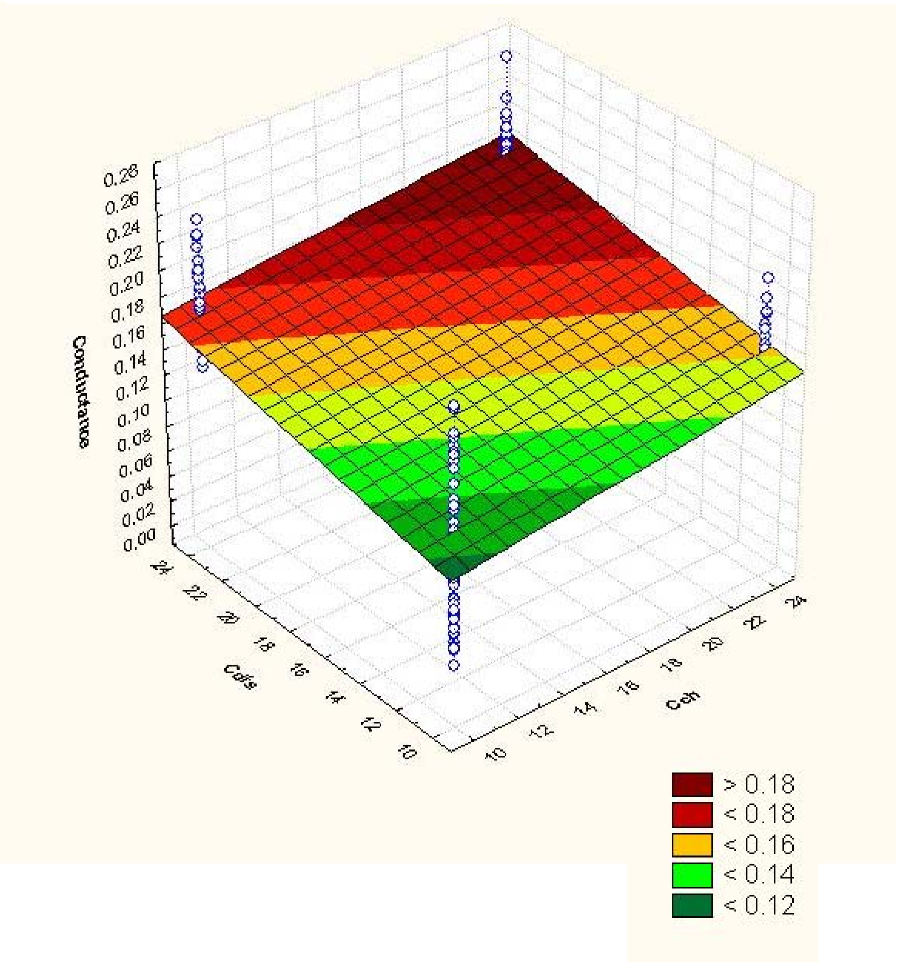


Responses as f(C_{dis}, C_{ch})

Capacity, mAh

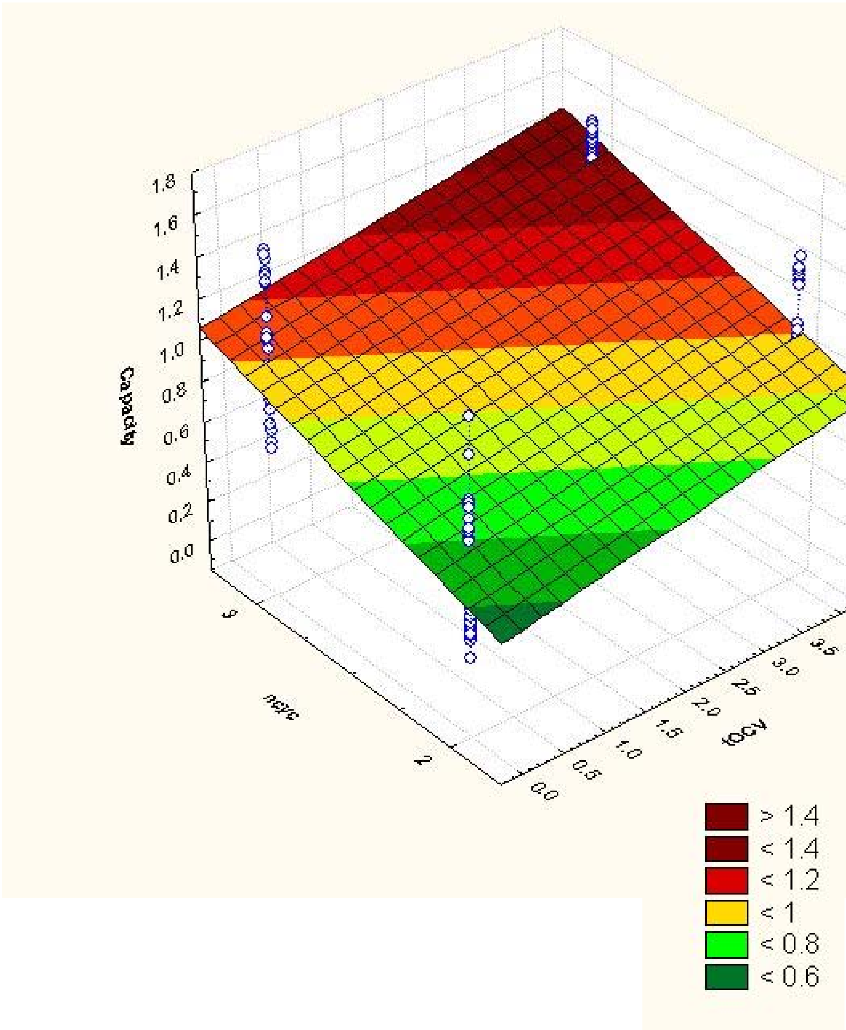


Conductance, Ω^{-1}

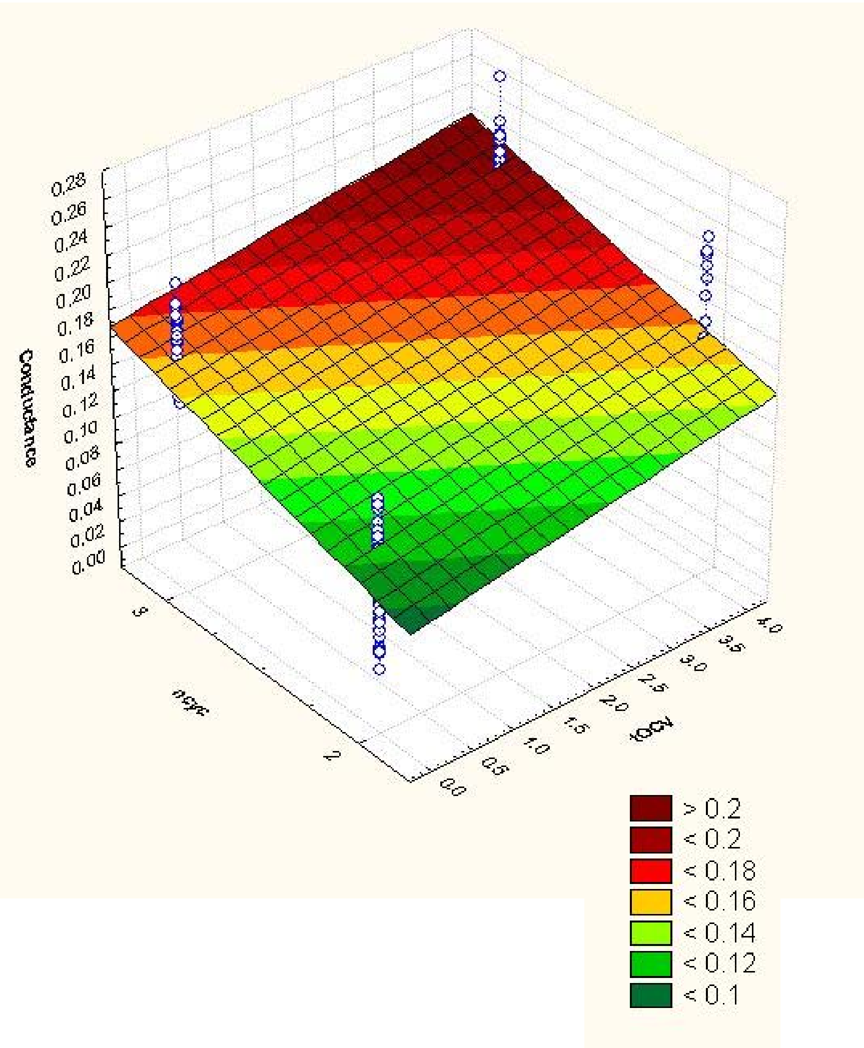


Responses as f(n_{cyc}, t_{OCV})

Capacity, mAh



Conductance, Ω^{-1}



Results: Optimization Case Study

A case study was performed to look at abbreviated formation protocols (more economical production) and optimizing such to minimize formation time. We varied the time-related variables (t_{ocv}, n_{cyc}, and C_{ch} (= C_{dis})), and considered the question:

"What cell formation protocol for the Gen3 chemistry done at 40°C and upper cutoff voltage of 4.2V will yield the shortest formation time while producing cells that maintain at least 50% of their capacity by the end of their life?"

From 81 conditions studied through RVE analysis, the following results were obtained:

Best Case 1: {C_{ch} = C_1/3, C_{dis} = C_1/3, t_{ocv}, = 5, n_{cyc}, = 4}, total formation of 44 hours

Best Case 2: {C_{ch} = C_1/10, C_{dis} = C_1/10, t_{ocv}, = 4, n_{cyc}, = 3}, total formation of 72 hours

A reasonable compromise: {C_{ch} = C_1/5, C_{dis} = C_1/5, t_{ocv}, = 4, n_{cyc}, = 4}, total formation of 56 hours

These results reveal that we can minimize total formation time by increasing t_{ocv} and maintaining good n_{cyc} , which collectively allow higher cycling rates. Thus, t_{ocv} should be placed at a higher priority for SEI formation studies aimed at abbreviated formation protocols.

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Formation Time Minimization Example

Variables:

t_{OCV} = 0,1,2,3,4,5,6,7,8

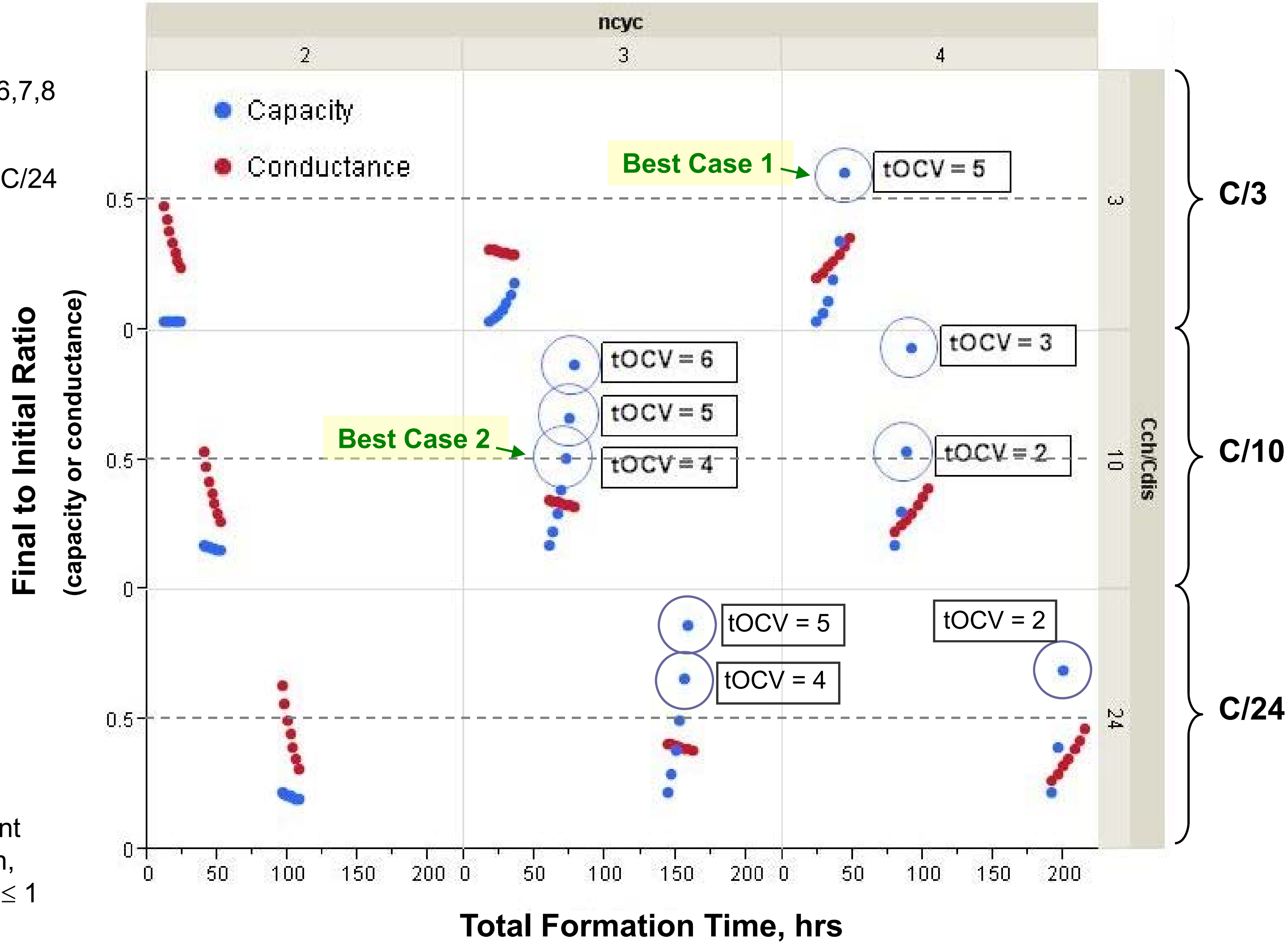
n_{cyc} = 2,3,4

C rate: C/3, C/10, C/24

Set Values:

T = 40 °C

UCV = 4.2V



Physically-relevant results are shown, where Cap. ratio ≤ 1

Summary / Conclusions

- Analysis of test data from the three-stage DOEx found the following formation conditions are preferred for good battery performance of the Gen3 chemistry: higher T, higher UCV, lower cycling rates, non-zero time at rest between cycles, and more instead of fewer total cycles.

- The order of influence of parameters regarding cell capacity data are:

  $$C_{dis} > C_{ch} > C_{ch}*C_{dis} > T*UCV > T > t_{OCV}*n_{cyc} > t_{OCV} > UCV > n_{cyc} > y_o$$

- The statistical models were adapted to improve the formation protocol by minimizing the total formation time while meeting a performance baseline of 50% capacity retention by end-of-life. By increasing t_{ocv} and maintaining good n_{cyc}, we can increase cycling rates, resulting in total formation times between 2-3 days instead of a week or more.

- While the results for the Gen3 chemistry are informative, the value of this study also lies in the generalized DOEx approach and analysis tools that are applicable to any Li-ion chemistry.

Future Work

- The general approach developed for this work is applicable to any Li-ion chemistry and configuration. Thus, our tools can be applied to other systems of interest to DOE-EERE VTP on a case-by-case basis.
- Where feasible, avenues will be sought to present and publish these results as a means to demonstrate the use of standard accepted statistical methods to answer questions relevant to battery development.

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