Study of Li-ion Cell Formation Parameters using “Gen3” Electrode Materials: Summary of Stage 1-3 Experiments

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This presentation does not contain proprietary or confidential information

Scope

Purpose

To perform a systematic evaluation of the foremost formation parameters for the ATD Gen3-type chemistry to: gain further understanding of the formation process, and to provide insights for improving battery performance and life.

Barriers

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.*

Approach

A Design of Experiment (DOEx) was devised to provide a statistical basis for exploring the relationship between key formation parameters and cell performance.

The complete study covered six (6) foremost formation parameters, using 31 test conditions split between three stages. A total of 186 button cells were built, formed, and tested in this work.

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

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 Batteries

- Button Cells (2032-type)
- Six (6) cells per test condition

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

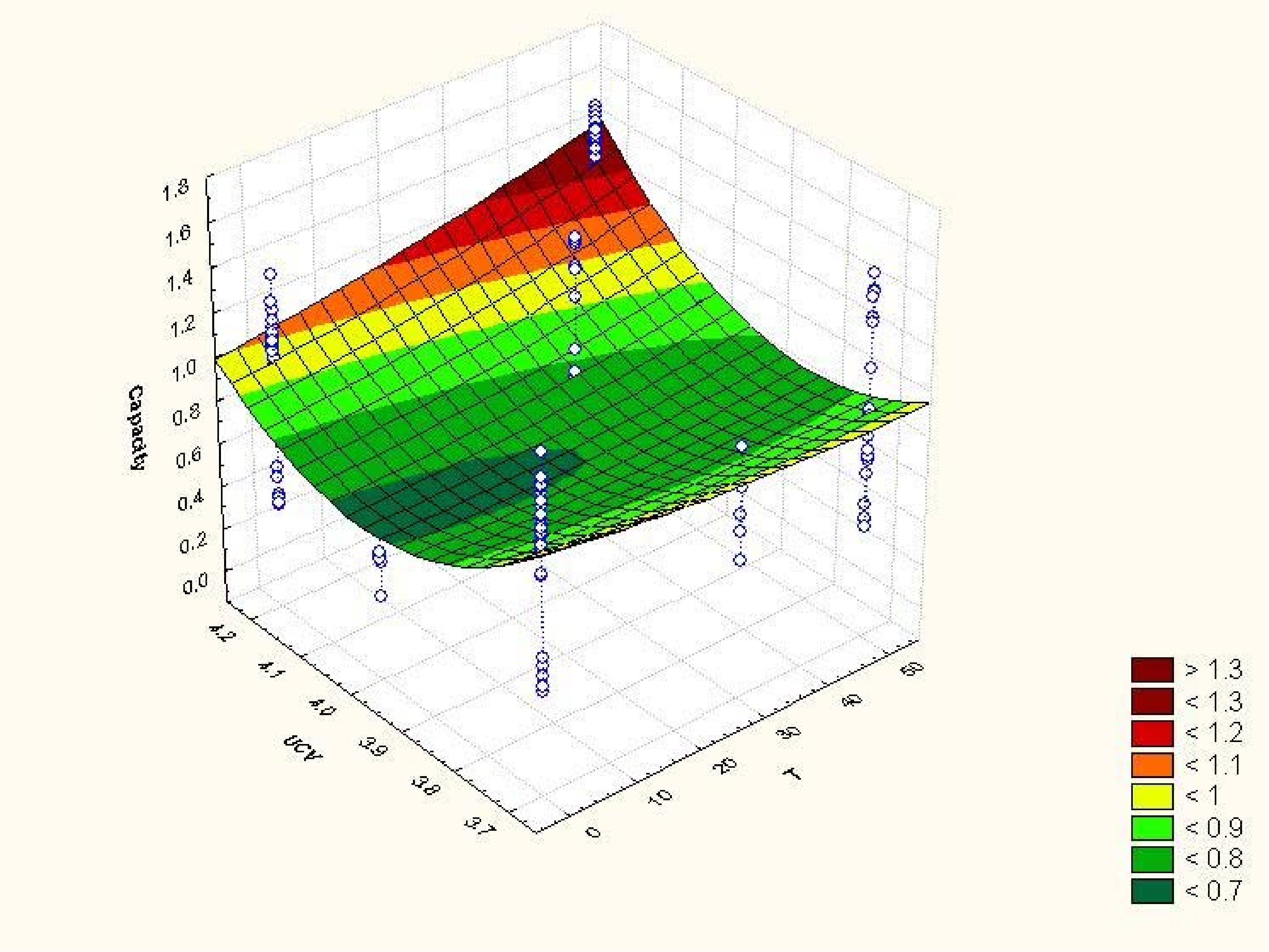
Data from all stages were used for final statistical analyses, where we modeled all main effects and desired first-order interactions simultaneously through response variable expressions (RVEs).

Two Responses are examined in this summary:

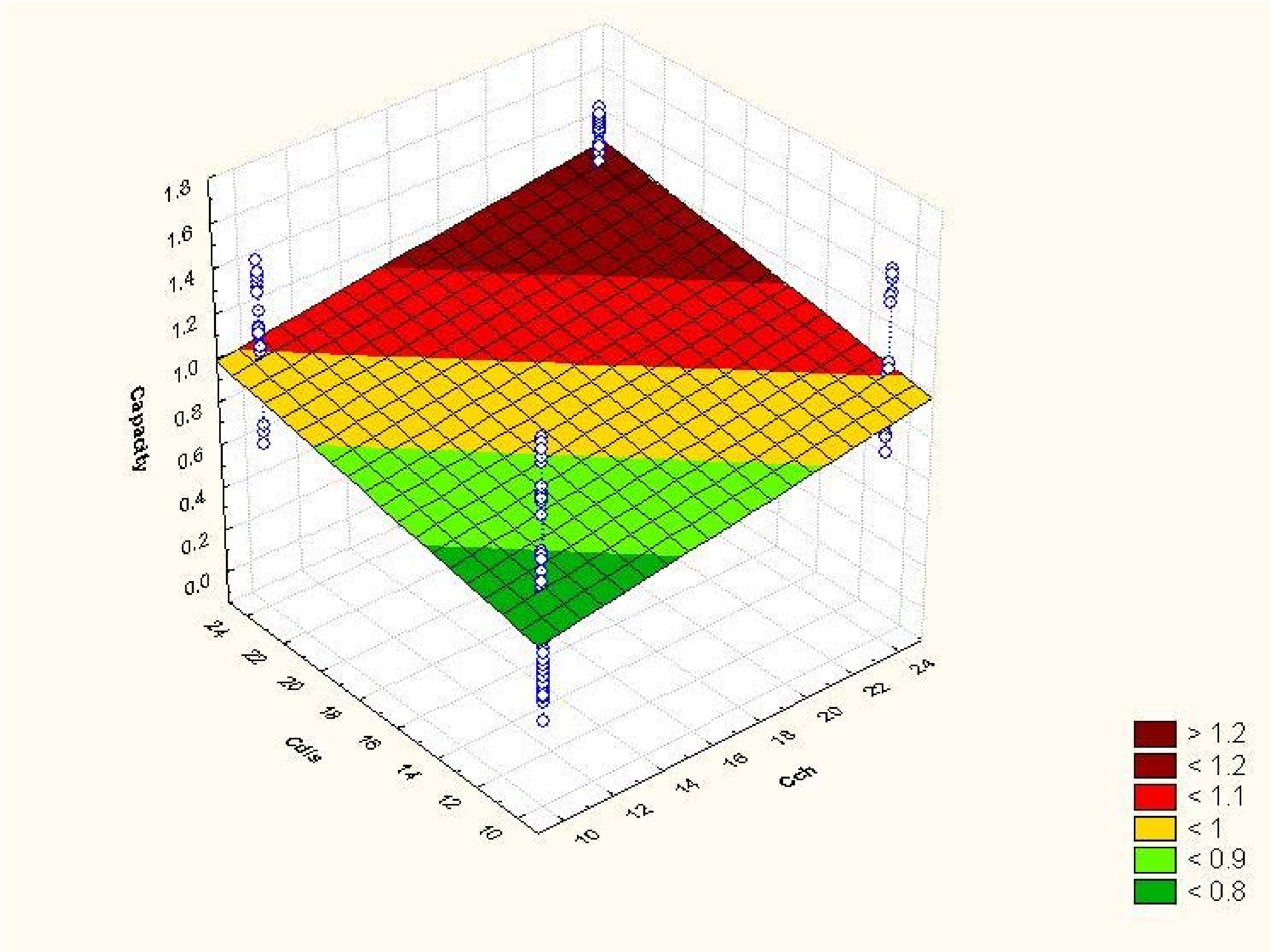
Capacity	Interfacial Conductance
$C_m = (C_i C_f)^{½}$ [mAh]	$K_m = (R_i R_f)^{-½}$ $[\Omega^{-1}]$
(per C1 cycling)	(per EIS interfacial impedance arc)

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

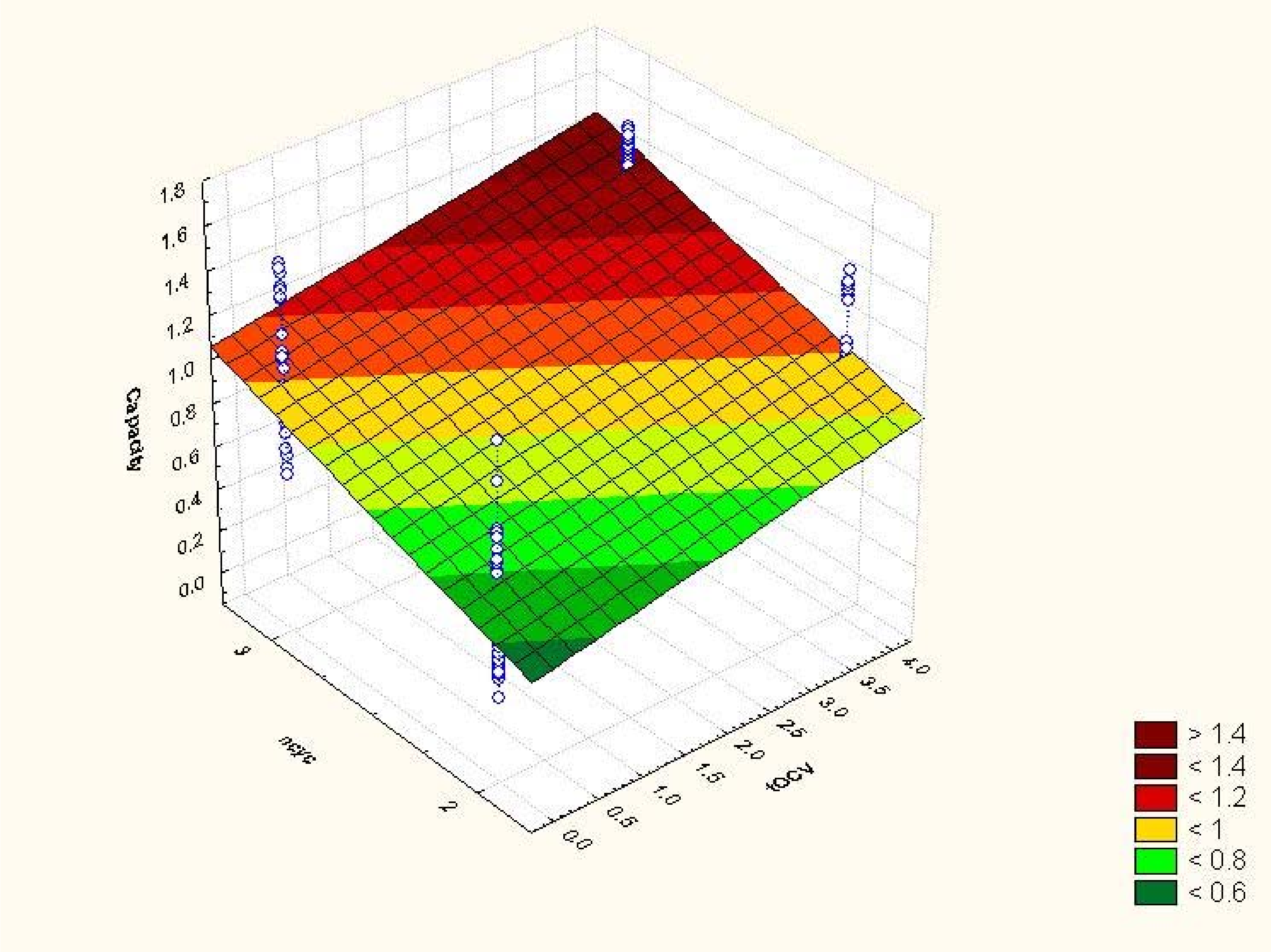
Capacity as f(UCV, T)



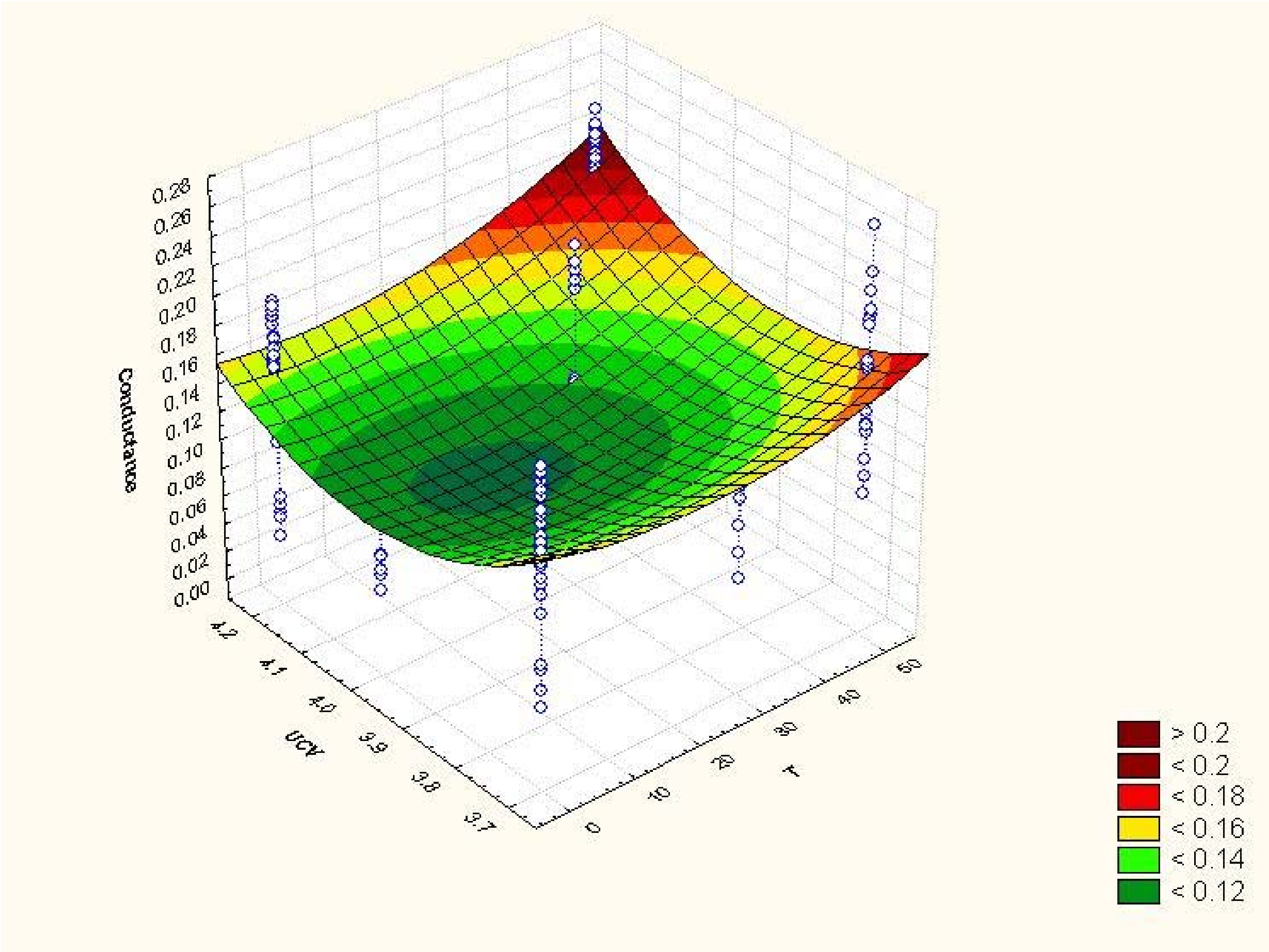
Capacity as f(C_{dis}, C_{ch})



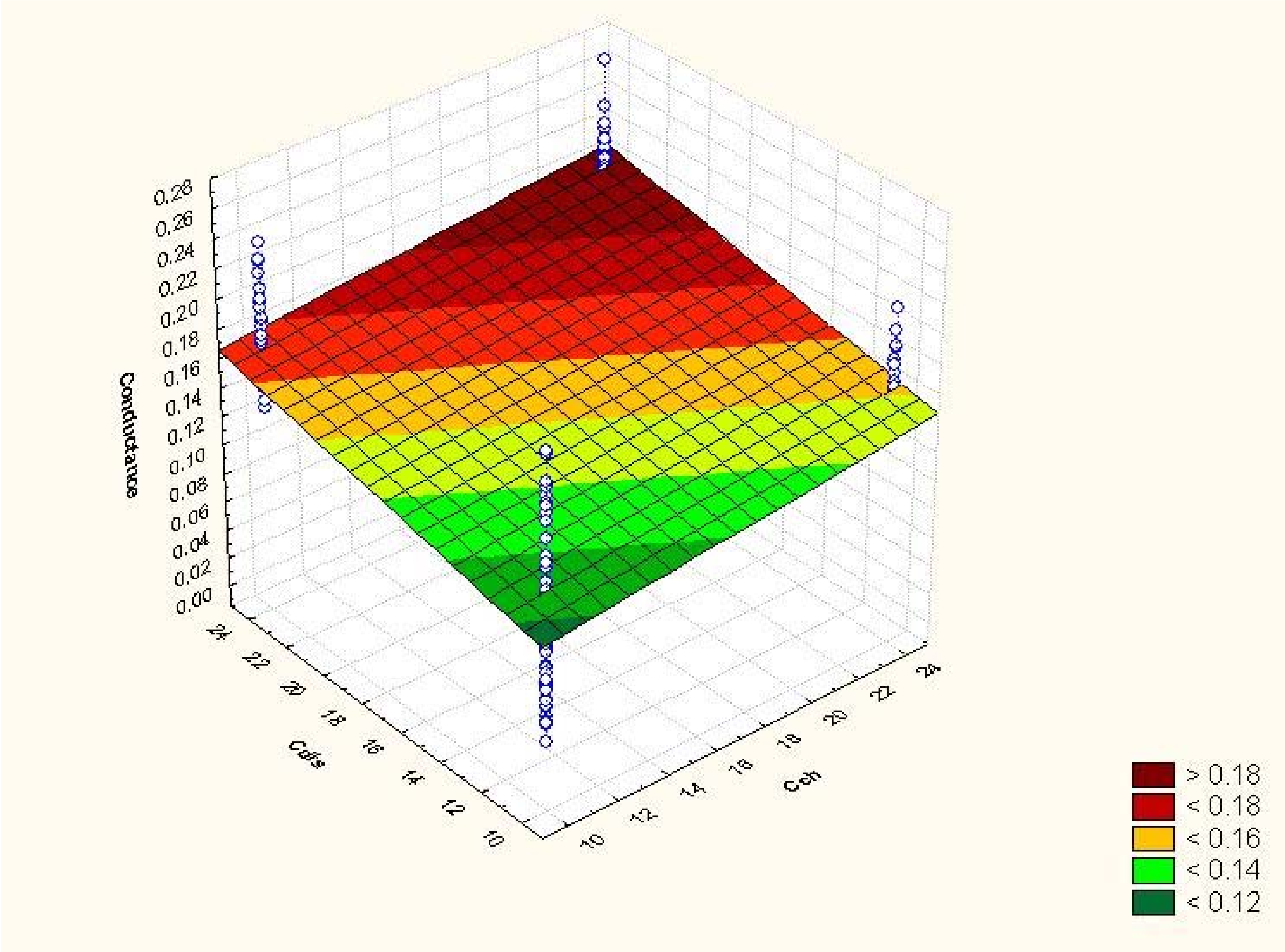
Capacity as f(n_{cyc}, t_{OCV})



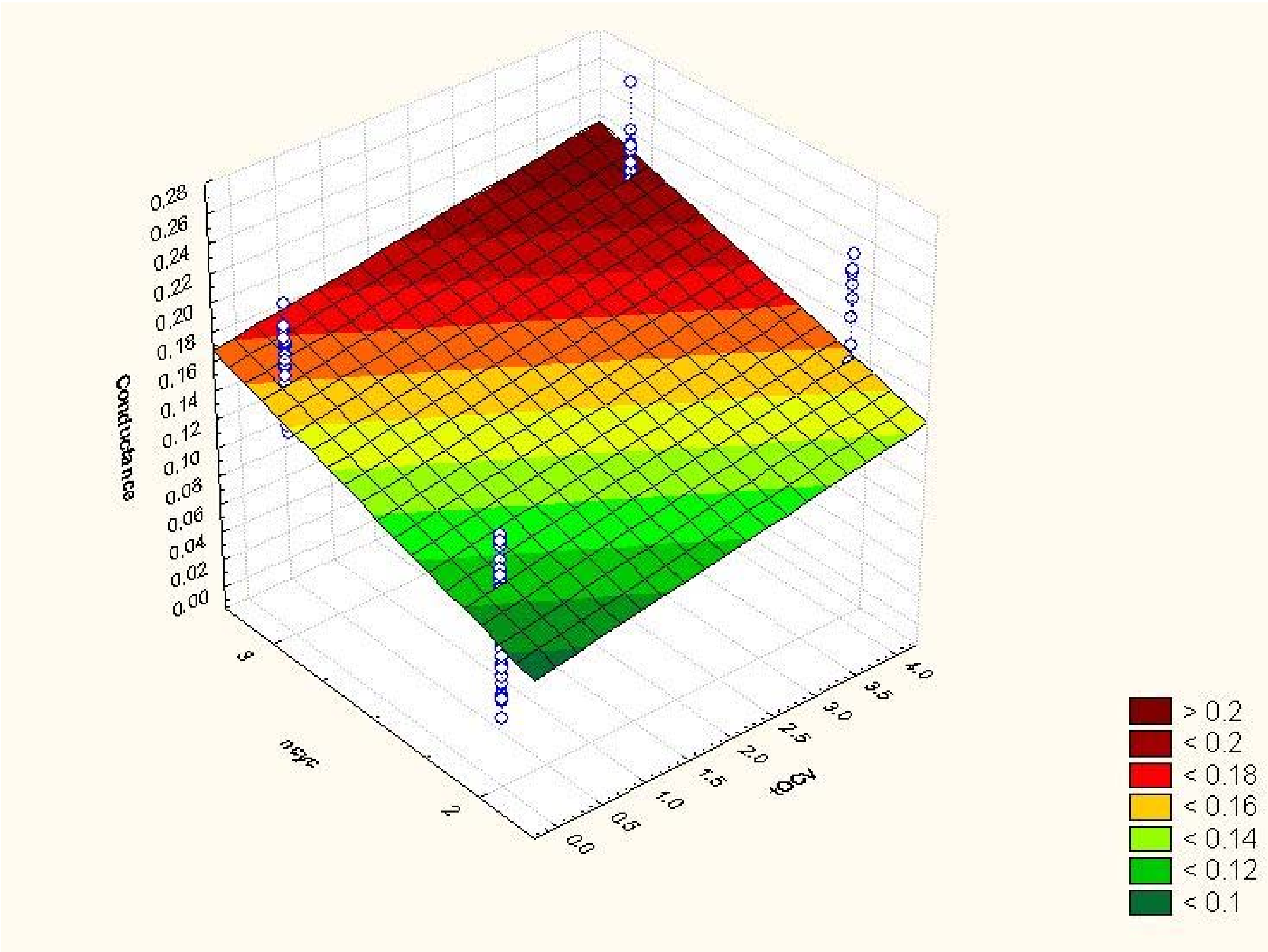
Conductance as f(UCV, T)



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



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



Relative Influence of Parameters

According to RVE-based Model Results, we can assign priority to the various formation parameters and key first-order interactions.

- For Capacity: $R^2 = 0.754$

Parameter	Coefficient Estimate	Standard Error	t Value	Uncertainty of Effect Pr > |t|
Intercept	0.0546599997	0.36842789	0.15	**0.8823**
T	-.0688099369	0.01072247	-6.42	<.0001
UCV	-.2094179229	0.08908598	-2.35	**0.0200**
Cch	0.1149770076	0.01682222	6.83	<.0001
Cdis	0.1155716068	0.01682222	6.87	<.0001
tOCV	-.5409750003	0.11805897	-4.58	<.0001
ncyc	-.1899673674	0.09755040	-1.95	**0.0533**
T*UCV	0.0181560595	0.00270543	6.71	<.0001
Cch*Cdis	-.0063677169	0.00094095	-6.77	<.0001
tOCV*ncyc	0.2379962392	0.04570070	5.21	<.0001

Thus, Capacity is most influenced by formation C_{dis}, C_{ch}, $C_{ch}*C_{dis}$, T*UCV, T, $t_{OCV}*n_{cyc}$, t_{OCV}

and least influenced by UCV, n_{cyc}, and the model intercept.

- For Conductance: $R^2 = 0.777$

Parameter	Coefficient Estimate	Standard Error	t Value	Pr > |t|
Intercept	0.0599056533	0.04797928	1.25	**0.2137**
T	-.0047427028	0.00139820	-3.39	0.0009
UCV	-.0337356958	0.01161563	-2.90	0.0042
Cch	0.0083225196	0.00219431	3.79	0.0002
Cdis	0.0095149575	0.00219431	4.34	<.0001
tOCV	-.0254130194	0.01540529	-1.65	**0.1010**
ncyc	0.0135671953	0.01272958	1.07	**0.2882**
T*UCV	0.0013717849	0.00035280	3.89	0.0001
Cch*Cdis	-.0004790771	0.00012274	-3.90	0.0001
tOCV*ncyc	0.0137126795	0.00596328	2.30	**0.0228**

Thus, Conductance is most influenced by formation C_{dis}, C_{ch}, $C_{ch}*C_{dis}$, T*UCV, T, UCV

and least influenced by $t_{OCV}*n_{cyc}$, t_{OCV}, the model intercept, and n_{cyc}.

Best and Worst Conditions

Based on regression results, the statistical model was used to predict mean capacity and conductance for all 144 possible test conditions of the full matrix (3x3x2x2x2x2).

		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
	Worst (0.52):	0	4.0	$C_1/10$	$C_1/10$	0	2
Conductance:	Best (0.24):	50	4.2	$C_1/10$	$C_1/24$	4	3
	Worst (0.08):	0	4.0	$C_1/10$	$C_1/10$	0	2

Summary / Conclusions

- The three-stage DOEx facilitated a systematic study of six foremost parameters regarding cell formation in the Gen3 chemistry, and found the following formation conditions are preferred for good battery performance: higher T, higher UCV, lower cycling rates, non-zero time at rest between cycles, and more instead of fewer total cycles.
- Results from RVE analyses allowed meaningful insights into main interactions and first-order binary interactions, and will help determine plausible mechanisms that relate cell formation to performance.
- With completion of all three stages and data analysis, we can now clearly determine optimal and worst formation conditions for the Gen3 chemistry, and are ready to consider off-test conditions.
- The results for the Gen3 chemistry studied herein might not be directly applicable to other Li-ion chemistries, but the general approach is valid regardless of the chosen system.

Future Work

- We will use the outcome of RVE regression analyses to predict the Gen3 formation outcome for conditions not directly studied. A prime example is to predict the effect of choosing abbreviated formation protocols (more economical) and optimizing such.
- We will examine plausible mechanisms that can explain the observed correlation between formation parameters and battery performance.
- This collective work will be published.

Other

Response to Previous Review Comments

The previous merit review of this work occurred in FY 06. Relevant comments that followed the intent and scope of the work were considered and adopted when feasible (trial randomization, inclusion of duplicate and baseline conditions, etc.).

Technology Transfer

DOE-ATD meetings provide some level of technology transfer between participants. Publication of this work will also serve as a technology transfer mechanism.

Publications / Patents

One or more peer-reviewed manuscripts are planned for this work.

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Supplemental Information

This material will not be presented

For Reviewer Reference Only

Approach -- Design of Experimental Matrix

The matrix is based on a **fractional factorial two-level screening study** of the six formation parameters, with a three-level study of the two most important parameters T and UCV.

The resultant approach is a **¼ fraction of a 2^6 factorial, resulting in 2^{6-2} (16) core conditions.** Added to this core matrix are:

- the necessary conditions to accommodate a full 3×3 matrix of T and UCV,
- one replicate condition (all parameters set at defaults),
- one control group (post-formation testing at 30 °C, not 50 °C),
- a "no formation" group
- Five supplemental conditions assessed after Stages 1 and 2.

∴ There were **31 total experimental conditions**.

At six cells per condition, **a population of 186 cells was required**.

Stage 3 Test Matrix (as completed)

Stage 1

Test Condition	T	UCV	C_{ch}	C_{dis}	t_{OCV}	n_{cyc}
7	0 °C	4.2	$C_1/10$	$C_1/10$	none	2
11	50	3.7	$C_1/10$	$C_1/10$	none	2
17	0	3.7	$C_1/10$	$C_1/10$	none	2
18	0	4.0	$C_1/10$	$C_1/10$	none	2
19	30	3.7	$C_1/10$	$C_1/10$	none	2
20[a]	30	4.0	$C_1/10$	$C_1/10$	none	2
21	30	4.2	$C_1/10$	$C_1/10$	none	2
22	50	4.0	$C_1/10$	$C_1/10$	none	2
23	50	4.2	$C_1/10$	$C_1/10$	none	2
24[a,b]	30	4.0	$C_1/10$	$C_1/10$	none	2

Stage 2

Test Condition	T	UCV	C_{ch}	C_{dis}	t_{OCV}	n_{cyc}
1	0°C	3.7V	$C_1/24$	$C_1/10$	none	3
4	0	3.7	$C_1/10$	$C_1/24$	4 hrs	2
5	0	4.2	$C_1/24$	$C_1/10$	4 hrs	2
6	0	4.2	$C_1/24$	$C_1/24$	4 hrs	3
9	50	3.7	$C_1/24$	$C_1/10$	4 hrs	2
12	50	3.7	$C_1/10$	$C_1/24$	none	3
14	50	4.2	$C_1/24$	$C_1/24$	none	2
25[a,c]	30	4.0	$C_1/10$	$C_1/10$	none	2
26[d]	N/A	N/A	N/A	N/A	N/A	N/A
27	30	4.0	$C_1/1$	$C_1/1$	none	2

Stage 3

Test Condition	T	UCV	C_{ch}	C_{dis}	t_{OCV}	n_{cyc}
2	0	3.7	$C_1/24$	$C_1/24$	none	2
3	0	3.7	$C_1/10$	$C_1/10$	4 hrs	3
8	0	4.2	$C_1/10$	$C_1/24$	none	3
10	50	3.7	$C_1/24$	$C_1/24$	4 hrs	3
13	50	4.2	$C_1/24$	$C_1/10$	none	3
15	50	4.2	$C_1/10$	$C_1/10$	4 hrs	3
16	50	4.2	$C_1/10$	$C_1/24$	4 hrs	2
28	0	3.7	$C_1/24$	$C_1/24$	4 hrs	3
29	0	4.2	$C_1/24$	$C_1/24$	4 hrs	3
30	50	4.2	$C_1/24$	$C_1/24$	4 hrs	3
31	30	4.0	$C_1/24$	$C_1/24$	4 hrs	3

Data Regression through RVEs

Sensitivity of data to the various formation parameters will be determined by performing regression analyses based on RVE written for specific responses *y* (e.g., final interfacial impedance, capacity, etc.). For example,

$$y = a_1 T + a_2 UCV + a_3 C_{ch} + a_4 C_{dis} + a_5 t_{OCV} + a_6 n_{cyc} + a_7 (T \times UCV) + a_8 (T \times C_{ch}) + a_9 (T \times C_{dis}) + a_{10}(UCV \times C_{ch}) + a_{11}(UCV \times C_{dis}) + a_{12}(C_{ch} \times C_{dis}) + a_{13}\{(C_{ch} \times n_{cyc})\ or\ (C_{dis} \times t_{OCV})\} + e_1 + e_2 + e_3 \tag{1}$$

where the T statistic test is used to determine whether or not coefficients are statistically significantly different from zero at some pre-determined confidence level. RVE coefficients that are found to be significant would be indicative of a significant effect of that parameter or parameter interaction on the response *y*.

Statistical Approach to Study of SEI Formation

Summary of Statistical Tasks:

1. Design of 2^{6-2} fractional factorial experiment (three stages) to determine optimum conditions of six formation parameters.

2. Regression analysis of button cell performance variables on formation parameters to determine formation parameters with significant effects on button cell performance and interactions between formation parameters.

3. Graphical investigation of first-order interactions between formation parameters to determine optimum (and worst) formation conditions.

Statistical Software:

- **SAS (version 9.1.3)**
  - **used for regression analysis and creation of input data for statistical graphics**

- **Statistica (release 7)**
  - **used for graphical assessment of first-order interactions and determination of optimum conditions**