Estimating and Managing Degradation of Li-Ion BESS Under Value-Stacked Duty Cycles in Electric Grid

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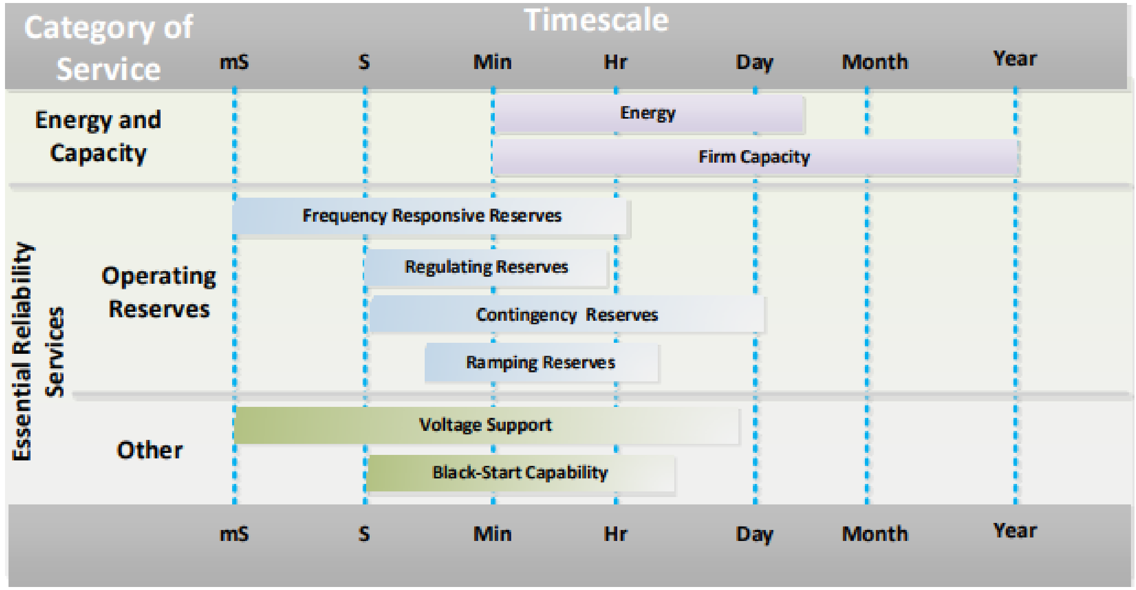
We gratefully acknowledge the funding provided by SwRI's Internal Research Program
that made this work possible

Terminology

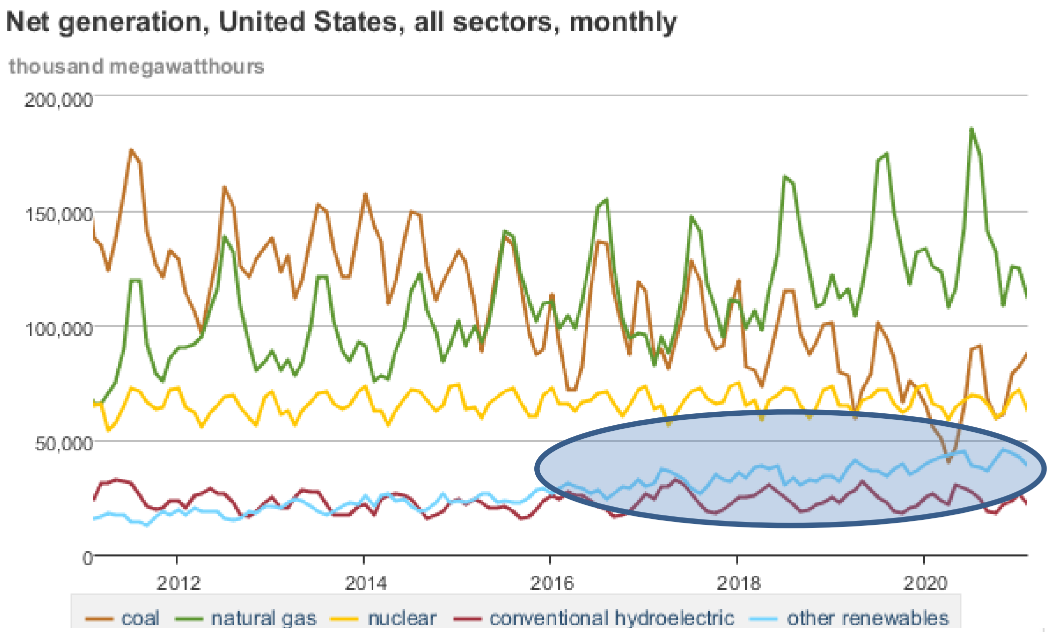
- Grid services – categorize energy and capacity services into one, and the remaining into the ERS (essential reliability service) category
- Value-stacking* – bundling of grid applications, creating multiple value streams, which can improve the economics for distributed energy resources

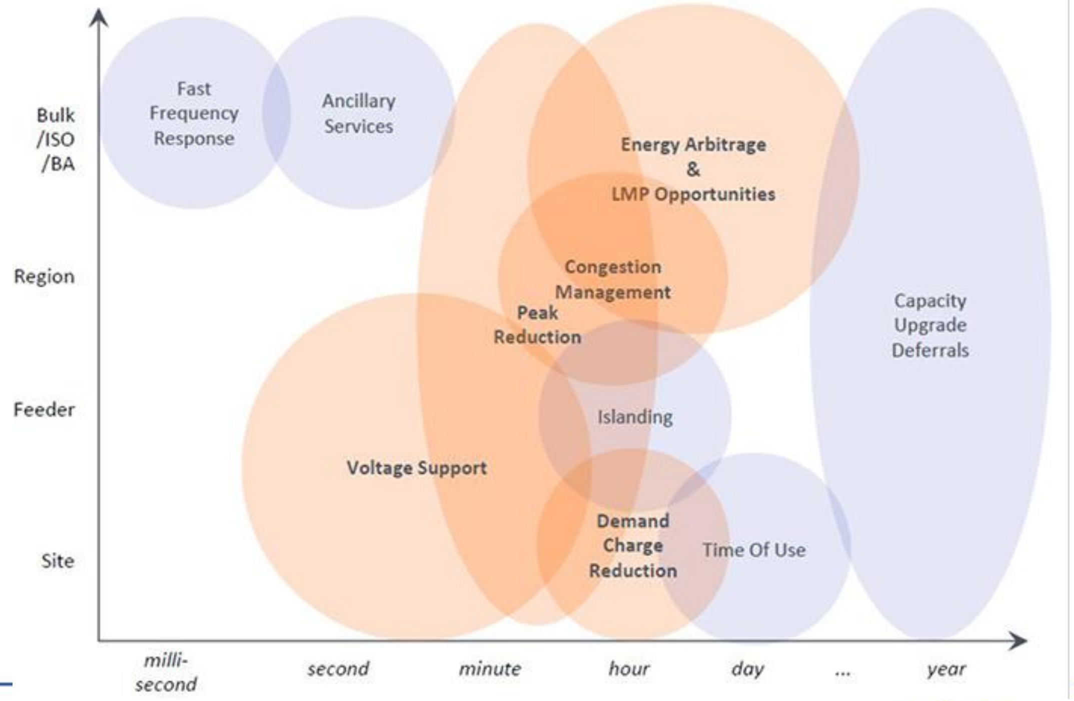


*Source: Smart Electric Power Alliance

Project Motivation

- Energy storage is a key enabler of the modern electric grid:
  - Integrate variable generation
  - Provide infrastructure services
  - Defer infrastructure upgrade
- Challenge: Unclear how batteries will do under mixed-duty (timescale, location, intensity) in the long run
  - Performance degradation – life-cycle cost; capex
  - Likelihood of fire – safety; opex
- Project: Apr-2021 – Mar-2023/Dec-2023

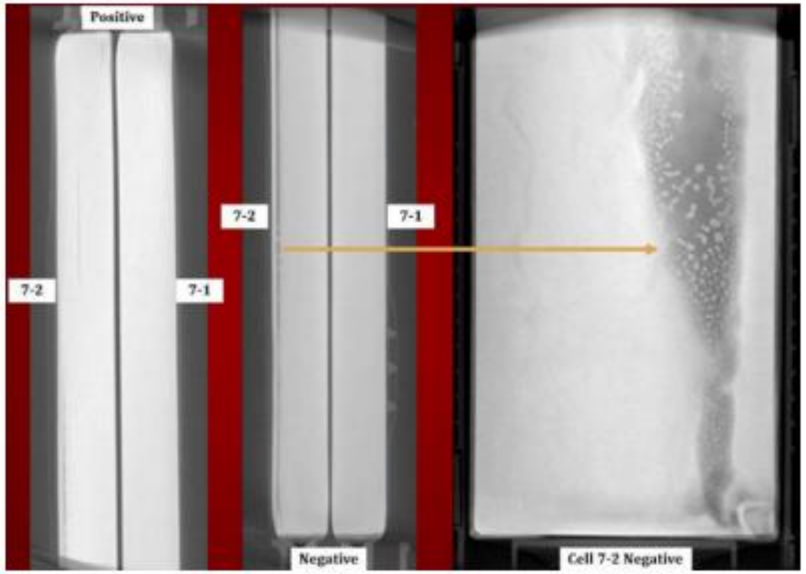


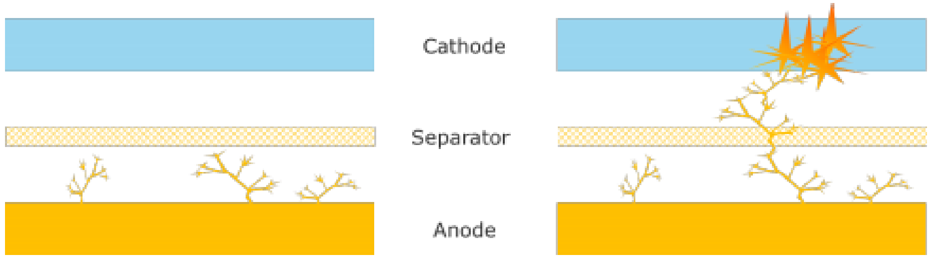


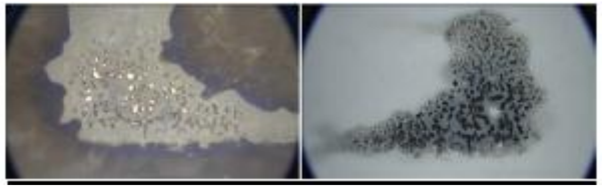
Source: EIA (top), IEEFA/DOE (bottom)

Project Motivation: Lithium-Ion Battery Fires are Real

Location	Energy (MWh)	Power (MW)	Module Type	Application	Installation	Event Date
Scotland, Aberdeenshire, Rothienorman						21 February 2025
England, Essex, Tilbury	600	300		Frequency Regulation, Capacity Market, Balancing Mechanism, Wholesale Power Markets	Substation	19 February 2025
US, CA, Moss Landing	1,200	300	LG Energy Solution	Solar Integration	Power Plant	16 January 2025
South Africa, Table Mountain				Backup energy resource	Indoor	25 October 2024
Canada, ON, Brantford				Peak Shaving	Commercial	12 September 2024
Singapore				UPS	Data center	10 September 2024
US, CA, Escondido	120	30			Substation	5 September 2024
US, CA, Santa Ana				Industrial		17 July 2024
USA, CA, San Diego	250	250	LG Chem	Energy shifting		15 May 2024
US, CA, Kearny Mesa	80	20	LFP		Substation	29 April 2024







"…aggressive load-shifting could increase battery fire risk…"

"…current approaches for monitoring and preventing fires may be inadequate…"

Source: EPRI's BESS Failure Incident Database, APS/DNVGL

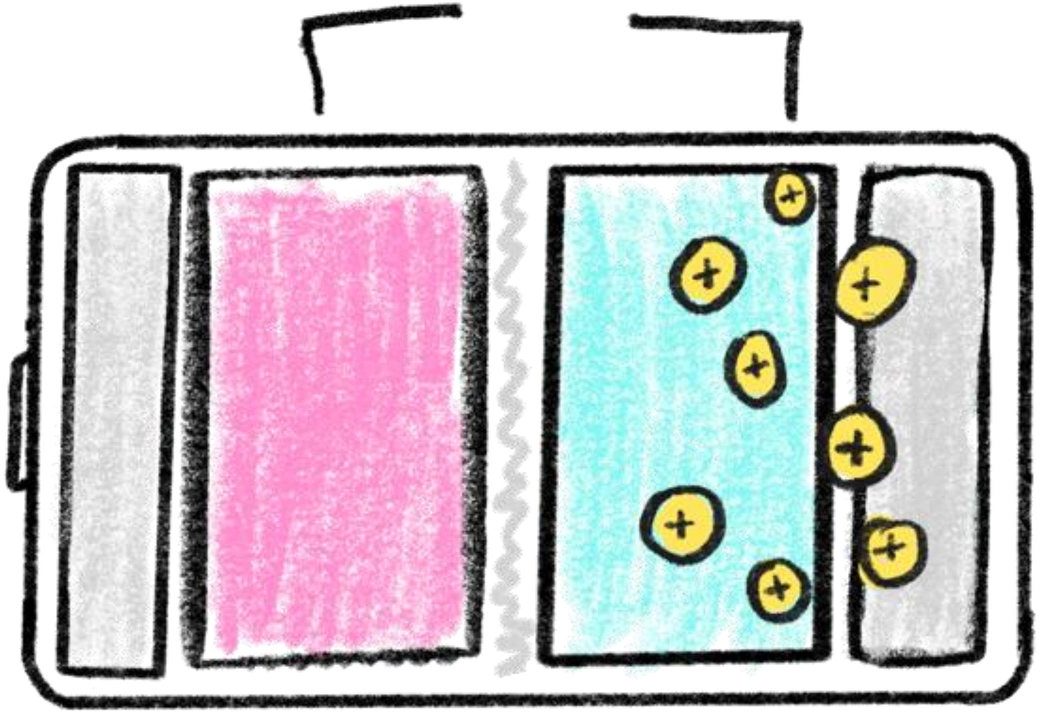
Projects Themes

- Field data: operating envelop
- Modeling a Li-ion cell: mechanisms, structure, and parameters
- Laboratory testing: guided by field operation and likely Li-ion failure mechanisms
- Keeping the model “honest”: monitor degradation, adapt parameters
- Implementation and demonstration: research BESS at SwRI

Understanding Degradation Mechanisms in a Li-ion Cell

Generic mechanisms – down-selected to the case of the electric grid

Operation of a Li-ion Cell and its Models



Source: Bloomberg

Mechanistic

- Natural laws; e.g., conservation of charge

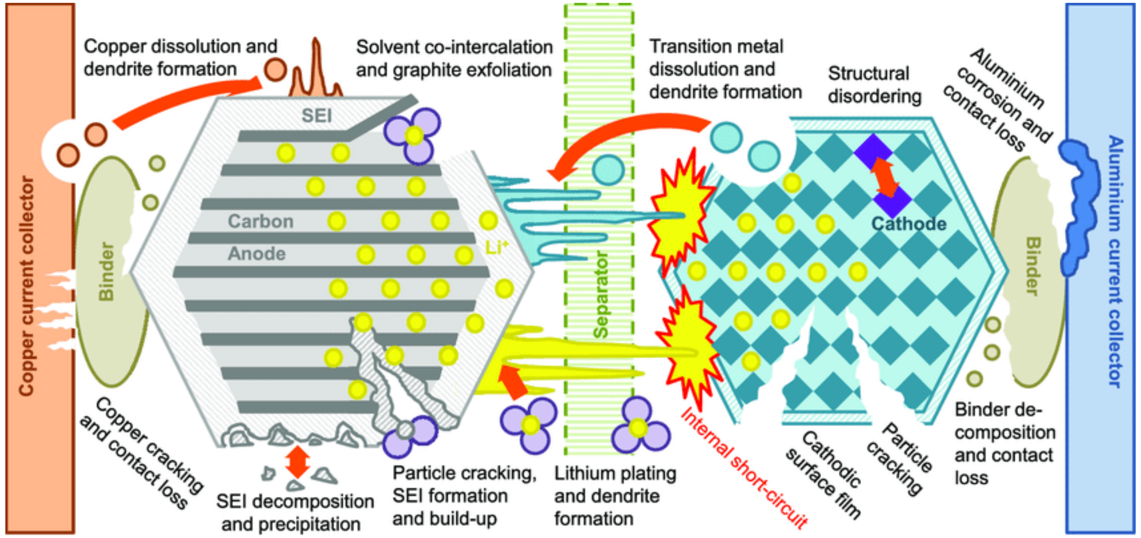
Modes/Effects

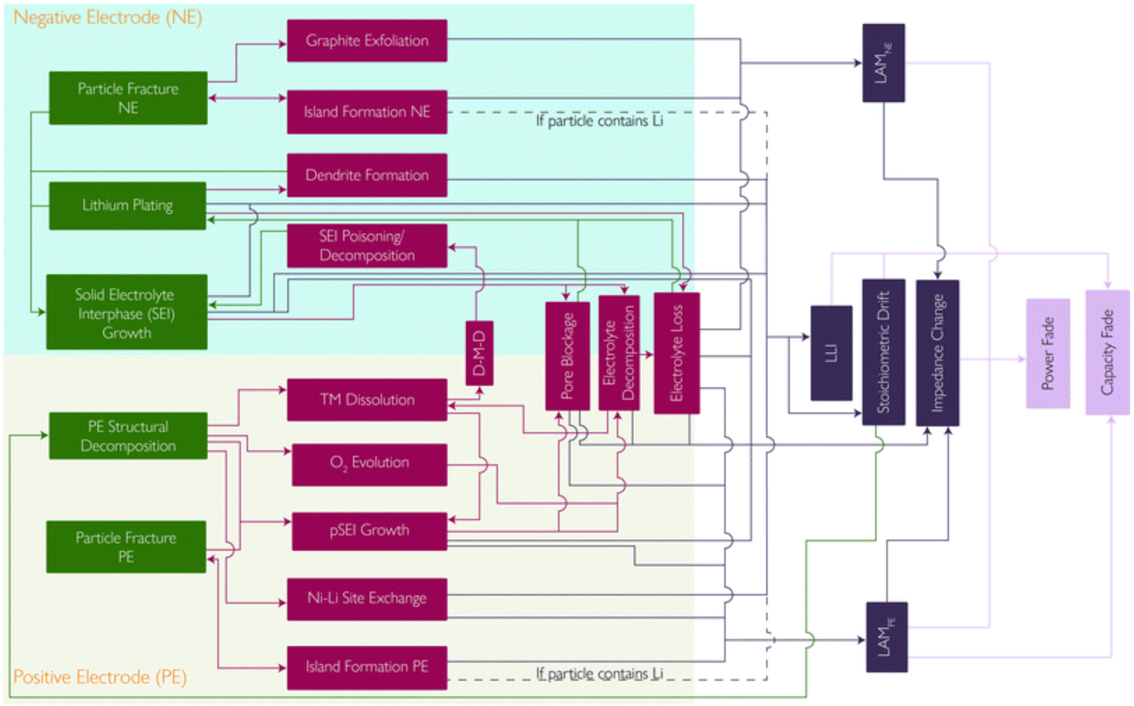
- Abstracted effects explained by underlying mechanisms; e.g., loss of cyclable lithium

Behavioral

- Externally observable metrics; e.g., reduced capacity

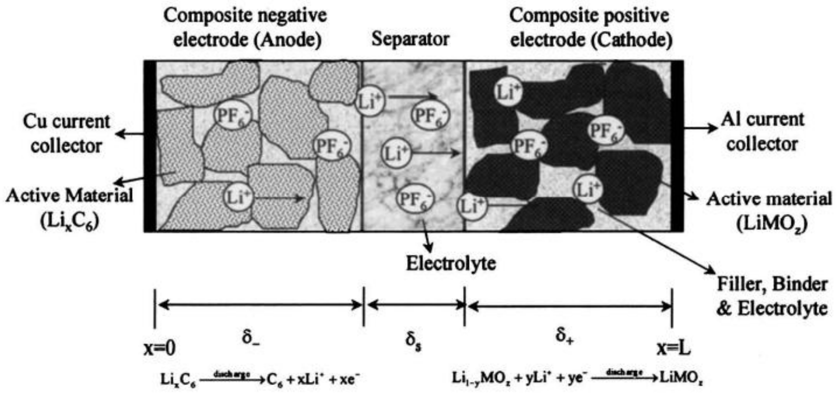
Understanding Degradation Mechanisms and Interactions

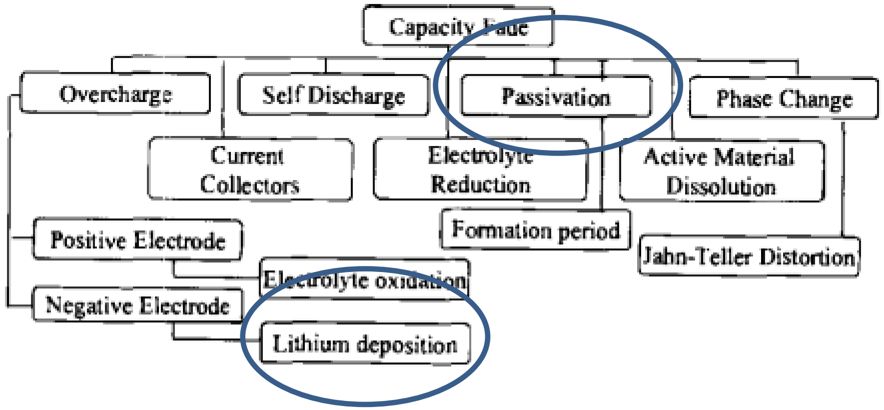


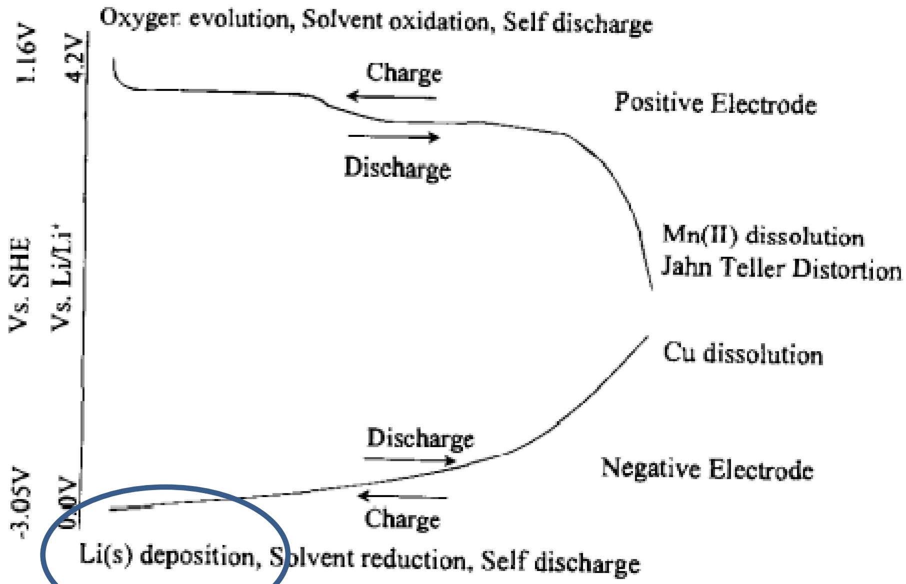


https://www.researchgate.net/publication/311577607_Degradation_diagnostics_for_lithium_ion_cells
https://pubs.rsc.org/en/content/articlehtml/2021/cp/d1cp00359c

Capacity Fade Mechanisms and Side Reactions







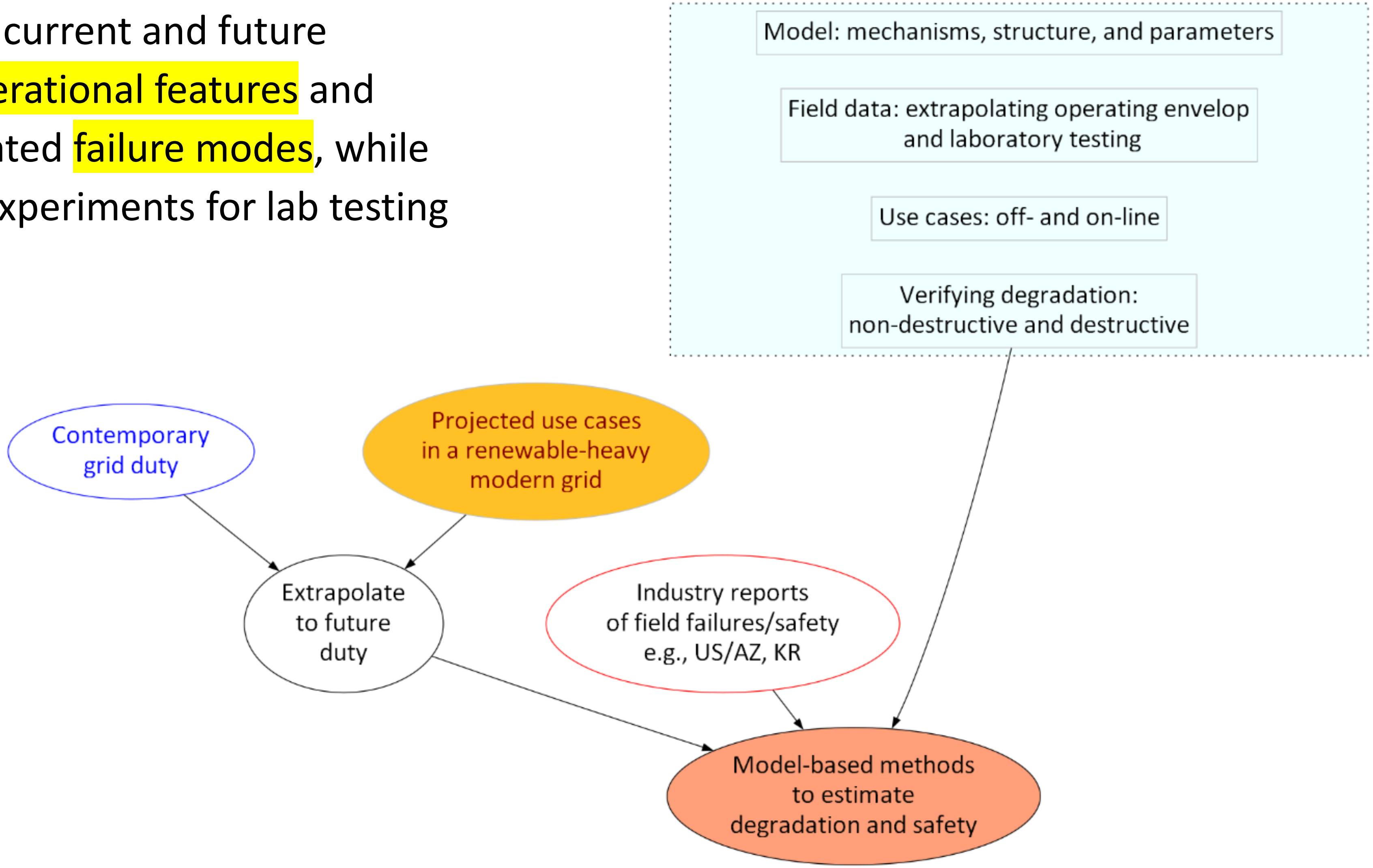
*Capacity Fade Mechanisms and Side Reactions in Lithium-Ion Batteries, Pankaj Arora and Ralph E. White
J. Electrochemical Soc., Vol. 145, No. 10, October 1998

Analysis of Operational Field Data and Design of Experiments

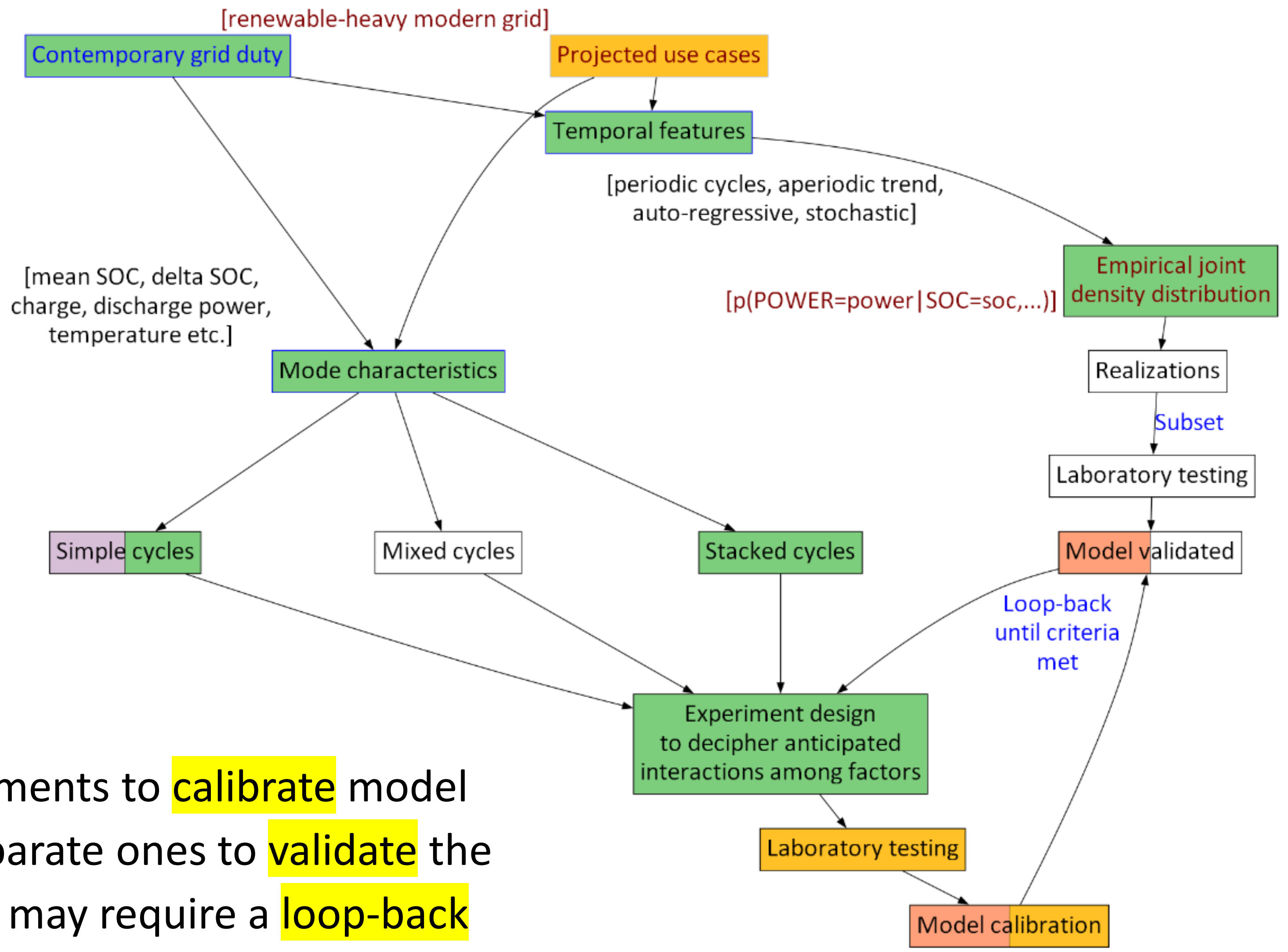
Modal and temporal

Example Considerations for Design of Experiments

We considered current and future application/operational features and known/anticipated failure modes, while designing the experiments for lab testing



Field Data: Operating Envelop and Laboratory Testing



We designed experiments to calibrate model parameters, and separate ones to validate the model… some cases may require a loop-back

Objectives for Analysis of Operational Field Data

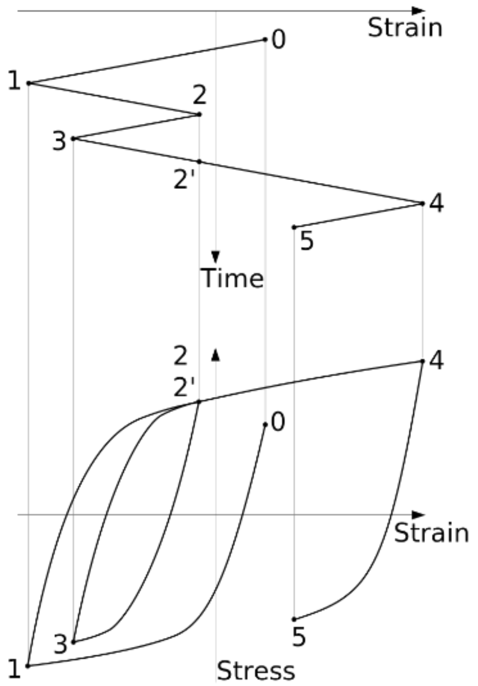
- Battery makers and third-party testers report aging under "simple" cycles
  - Can we identify such simple cycles (modes) in the field data?
    - Common ancillary services: load shifting and frequency regulation
    - Mean SOC, delta SOC, charge power, discharge power
    - Charge and discharge durations decided implicitly
- For "mixed" duty, only one service offered at a time
- For "stacked" duty, more than one service offered at a time
- Initially planned to perform aging under simple- and mixed-mode cycles
  - Revised plan to only perform aging under stacked-mode cycles
  - Limited by the number of Samsung 94 Ah cells and cycler channels
  - Matches the use case of a modern inverter-heavy electric grid

Identifying Simple-Modes

Using a modified rain-flow method

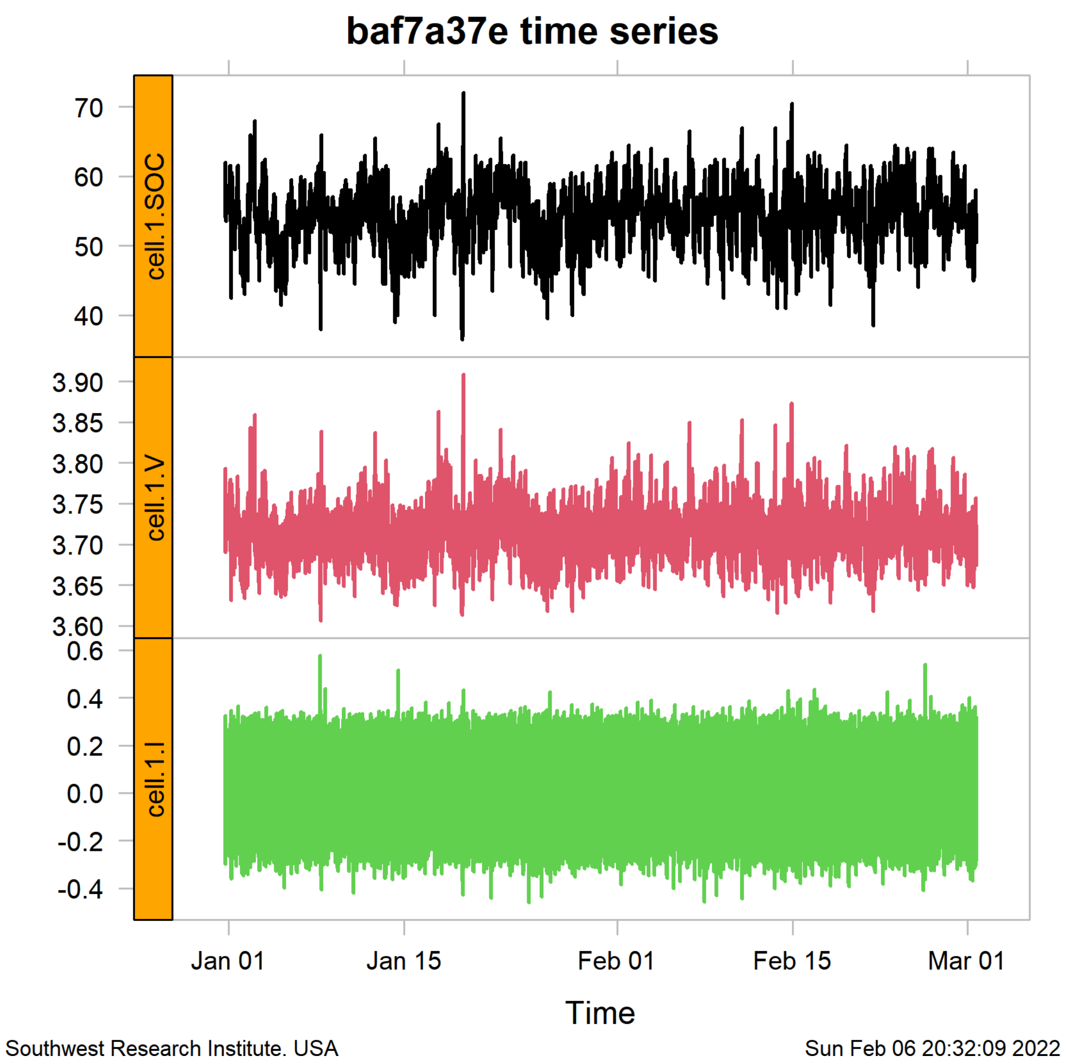
Analysis of Operational Field Data – Modal

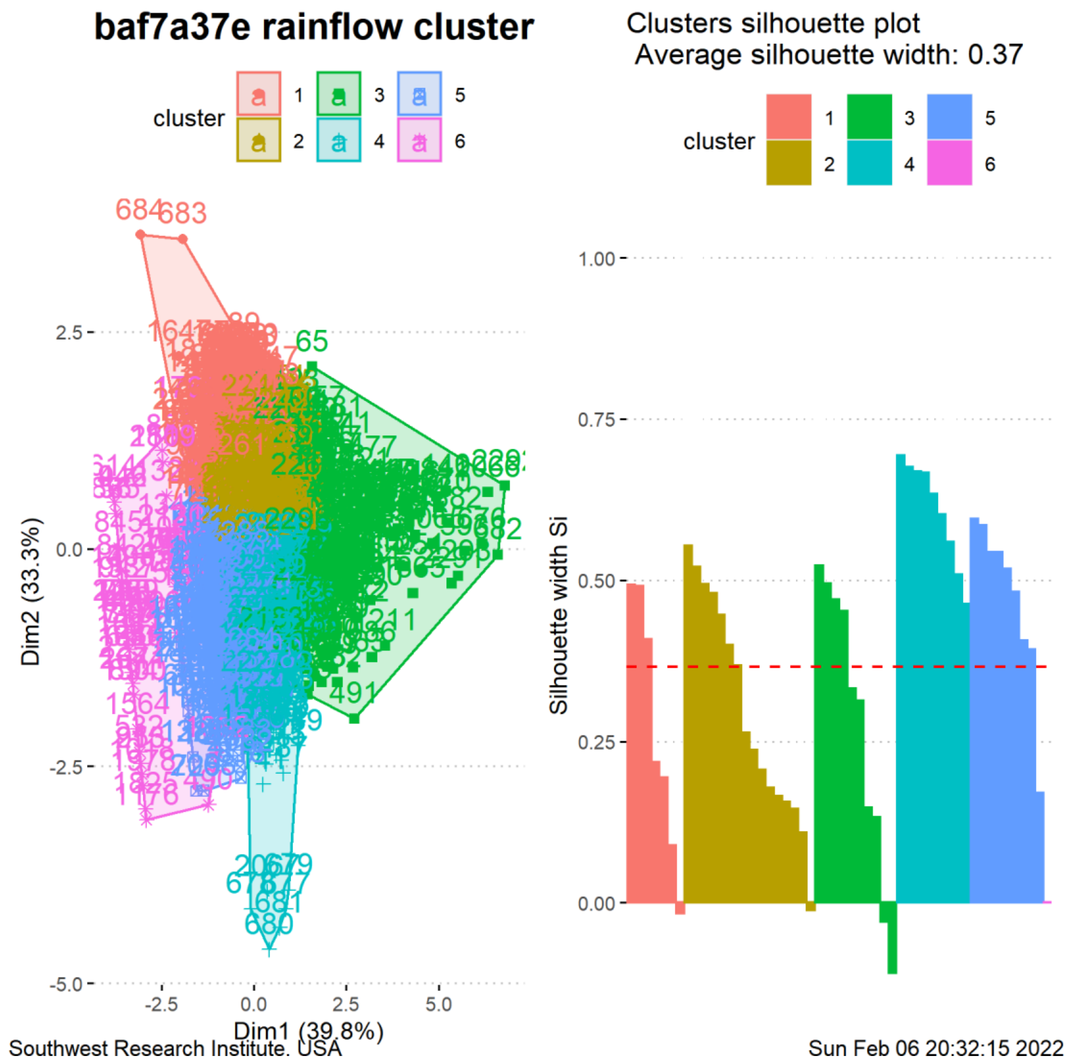
- Rain-flow counting
  - SwRI has applied this fatigue-inspired method to batteries for over 10 years
- Simple repetitive loading is “easy”
- Randomly varying loading is difficult
- Convert random loading to simple cycles via rain-flow counting
- Accumulate damage



https://en.wikipedia.org/wiki/Rainflow-counting_algorithm

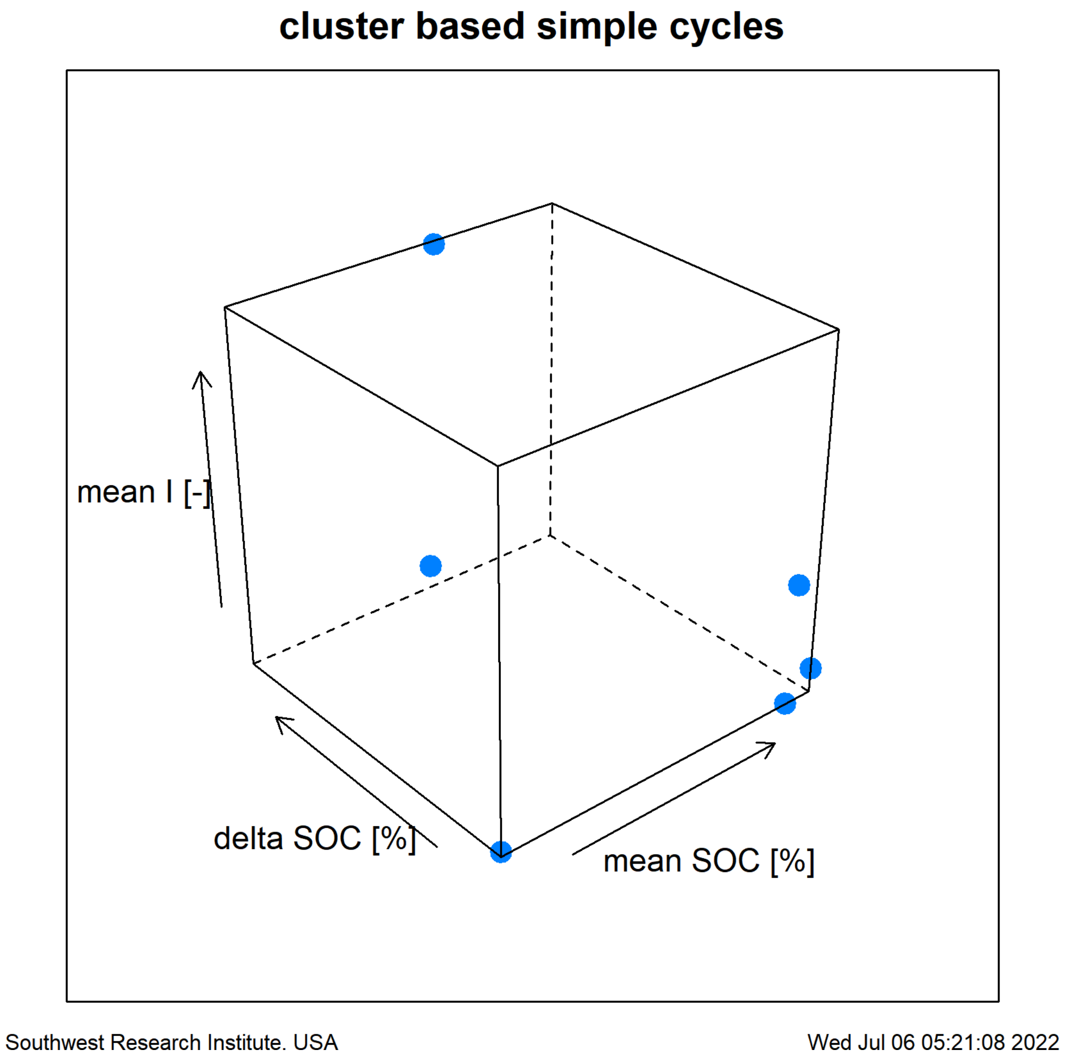
Source: baf7a37e





Simple Cycles Based on Operational Field Data

This is for record only
No lab testing under simple cycles



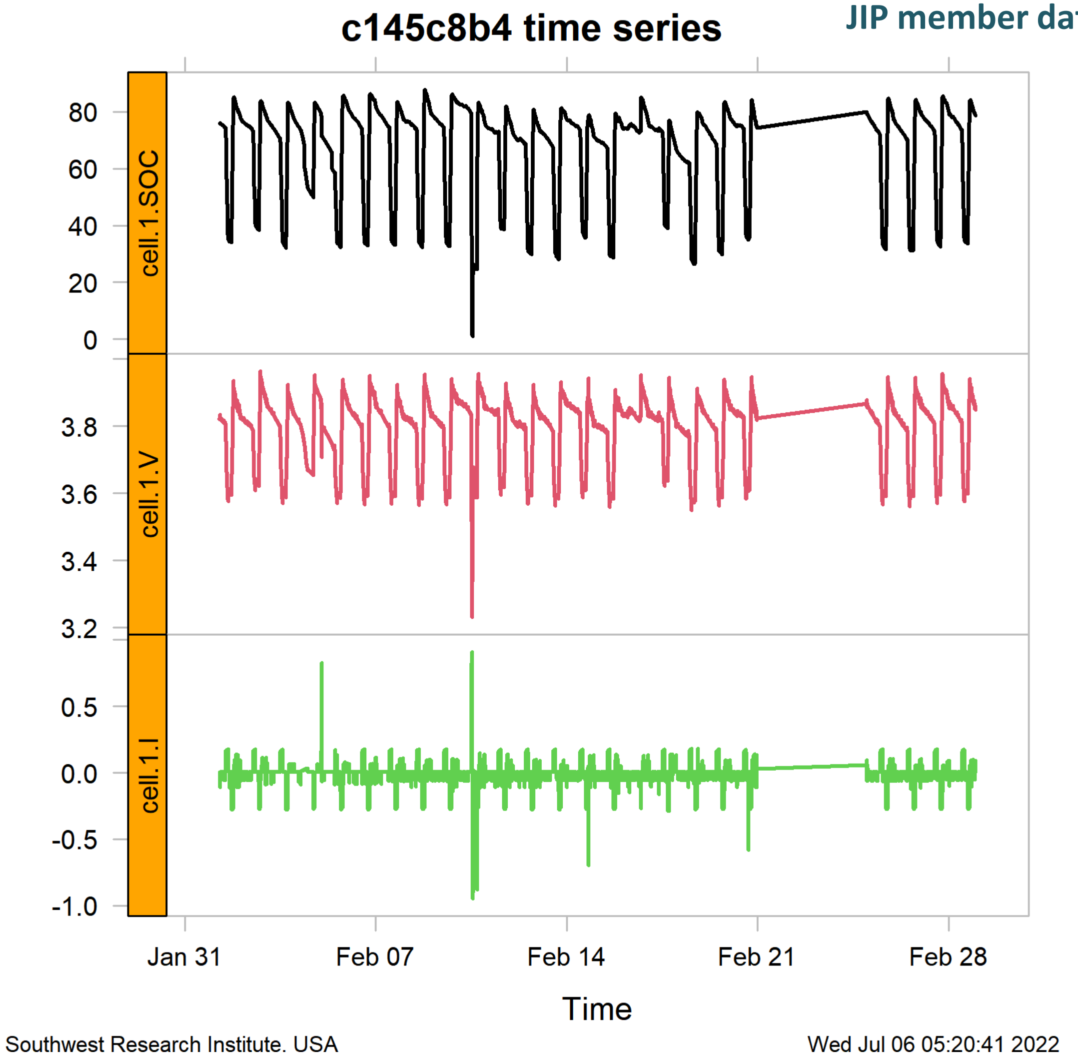
.id	mean SOC [%]	delta SOC [%]	mean I [-]	count [%]
07848e9c	25.0	0.23	0.03	1%
f757df9e	49.2	0.03	0.04	21%
baf7a37e	55.8	0.25	0.30	3%
88ff33e5	50.4	9.55	0.01	9%
c145c8b4	82.3	0.05	0.01	35%
c145c8b4	73.8	0.15	0.01	38%
c145c8b4	31.8	0.02	0.00	14%
c145c8b4	58.5	27.05	0.03	5%
c145c8b4	74.3	0.10	0.12	3%
c145c8b4	58.3	26.80	0.19	5%

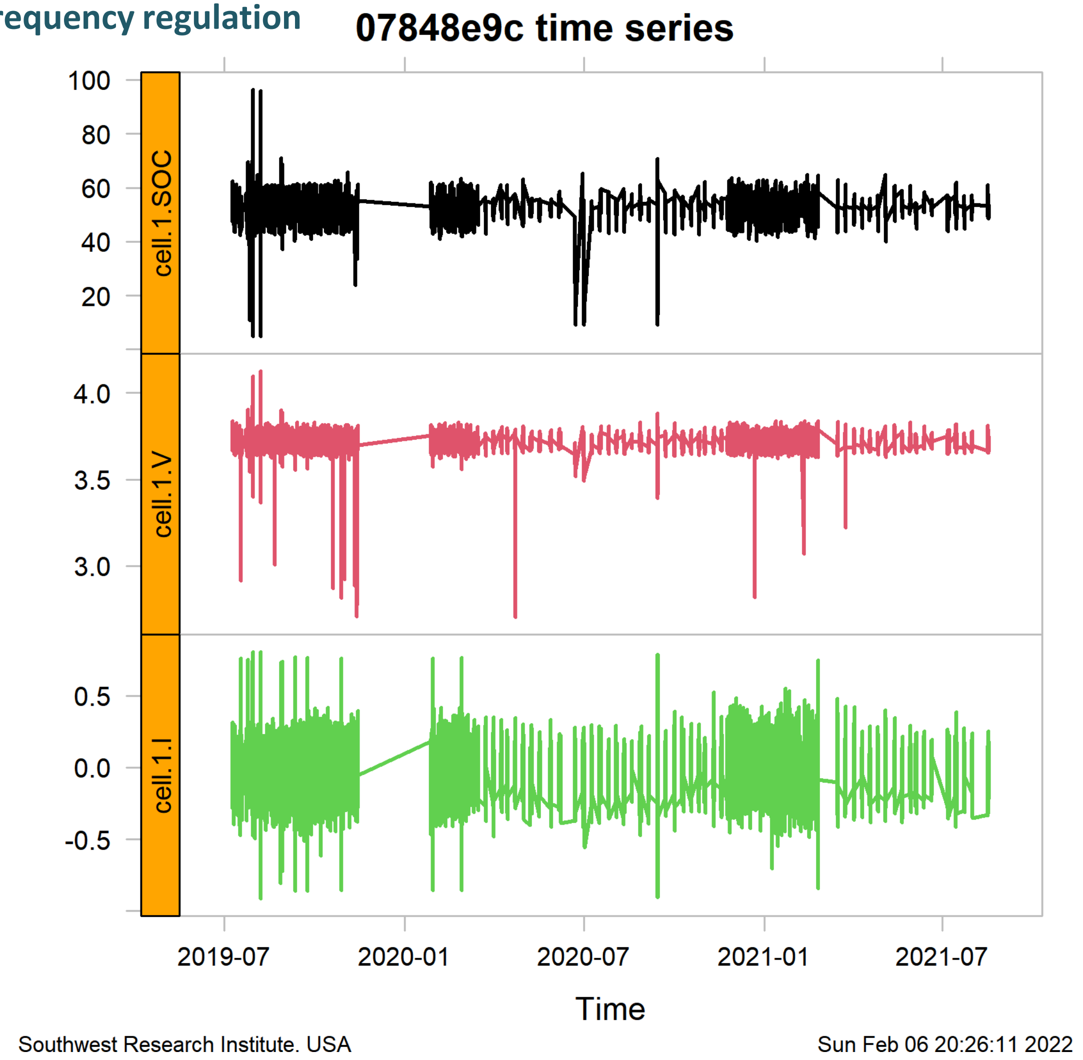
Extracting Other Characteristics in Preparation for Stacked Operation

Using empirical joint probability distribution of (SOC, power) and (duration, power)

Source: c145c8b4 and 07848e9c

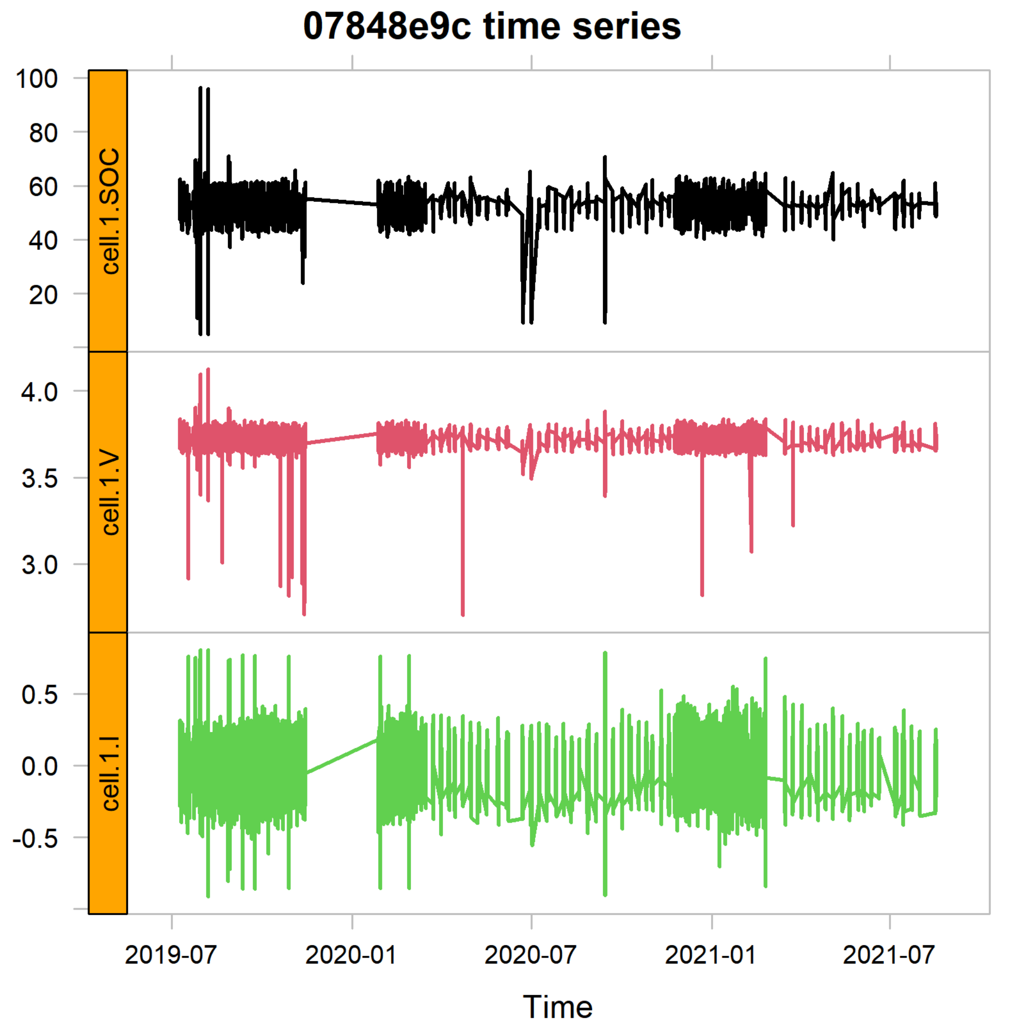
Third-party data
Mixed mode operation - some frequency regulation, some load shifting
JIP member data – frequency regulation

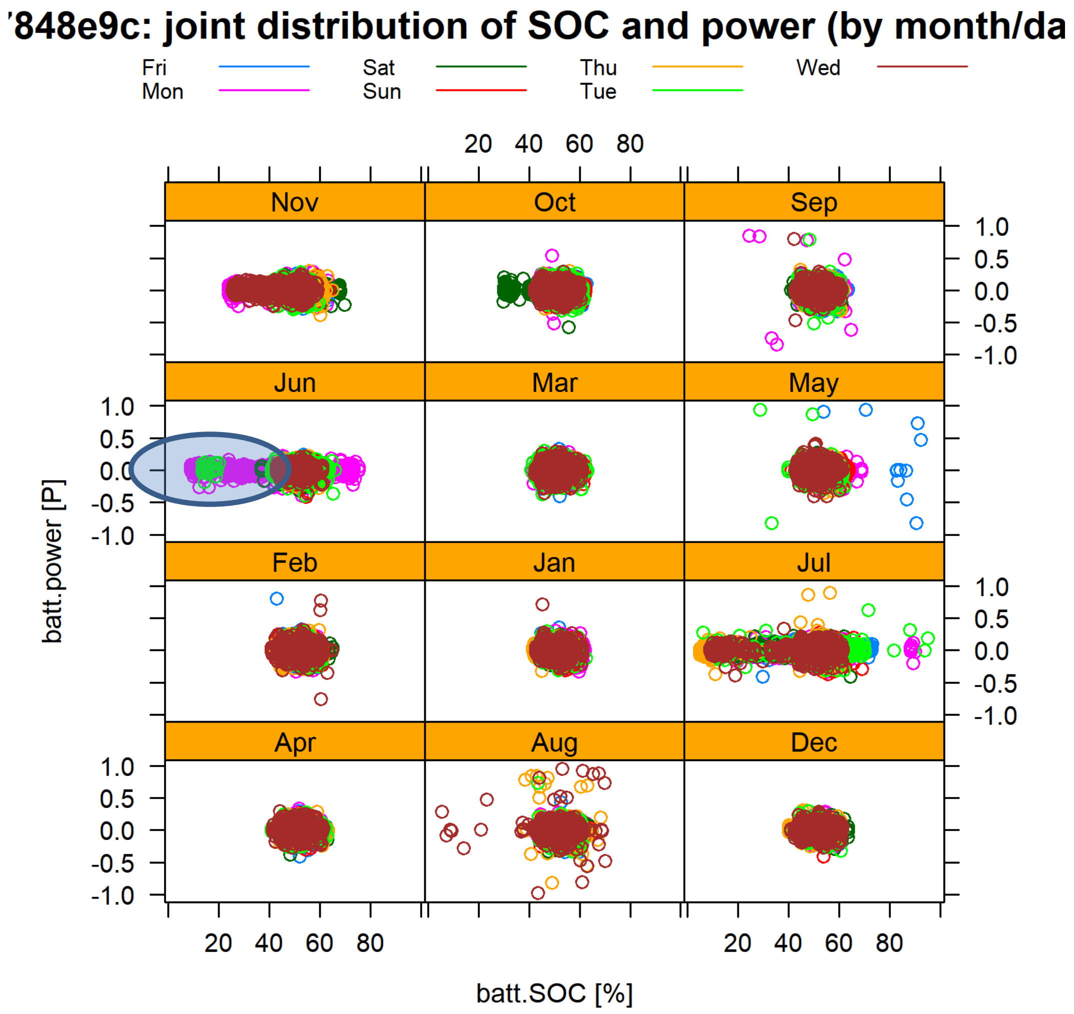




Source: 07848e9c

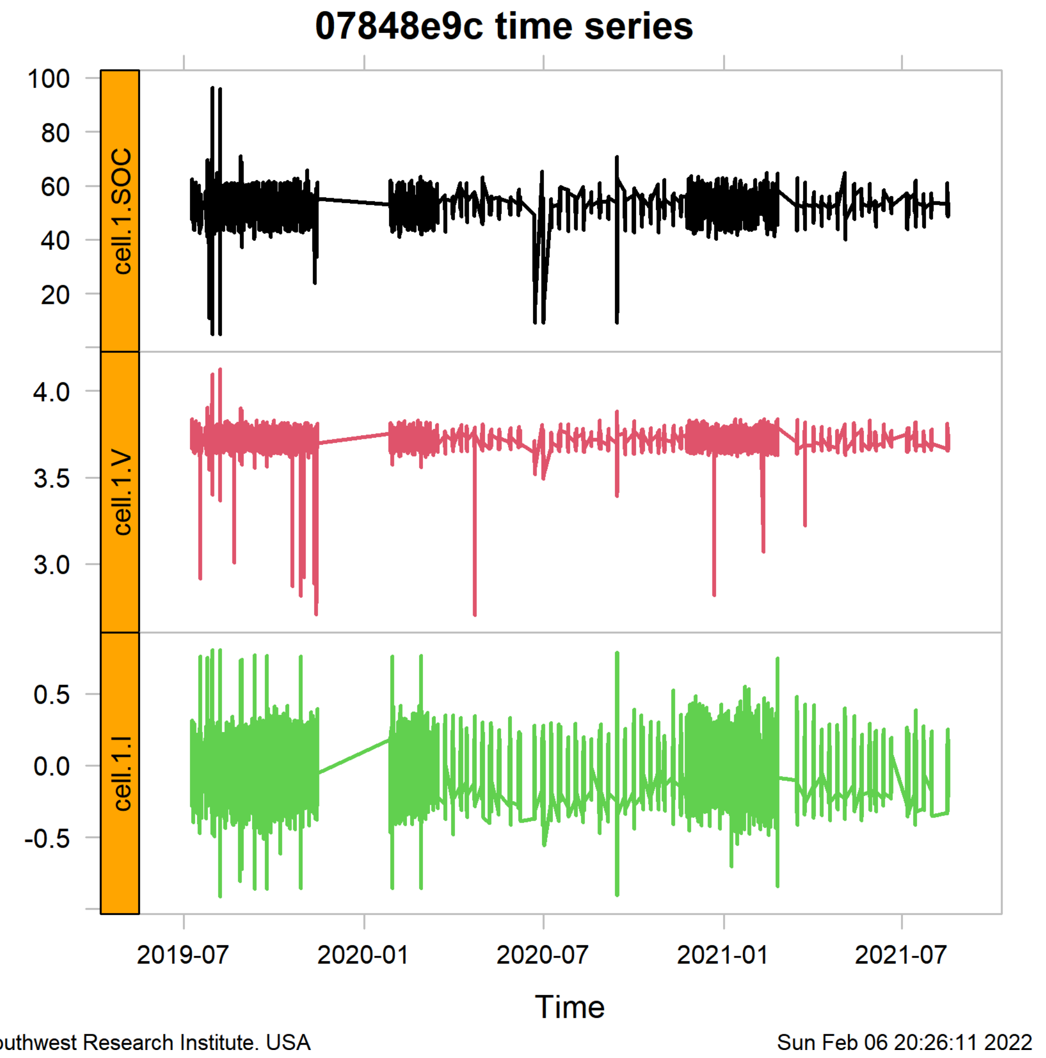
Split time-series in segments of positive/zero/negative power
Note seasonal and daily patterns in the joint distribution
Battery dispatched "conservatively" – within +-0.3 P

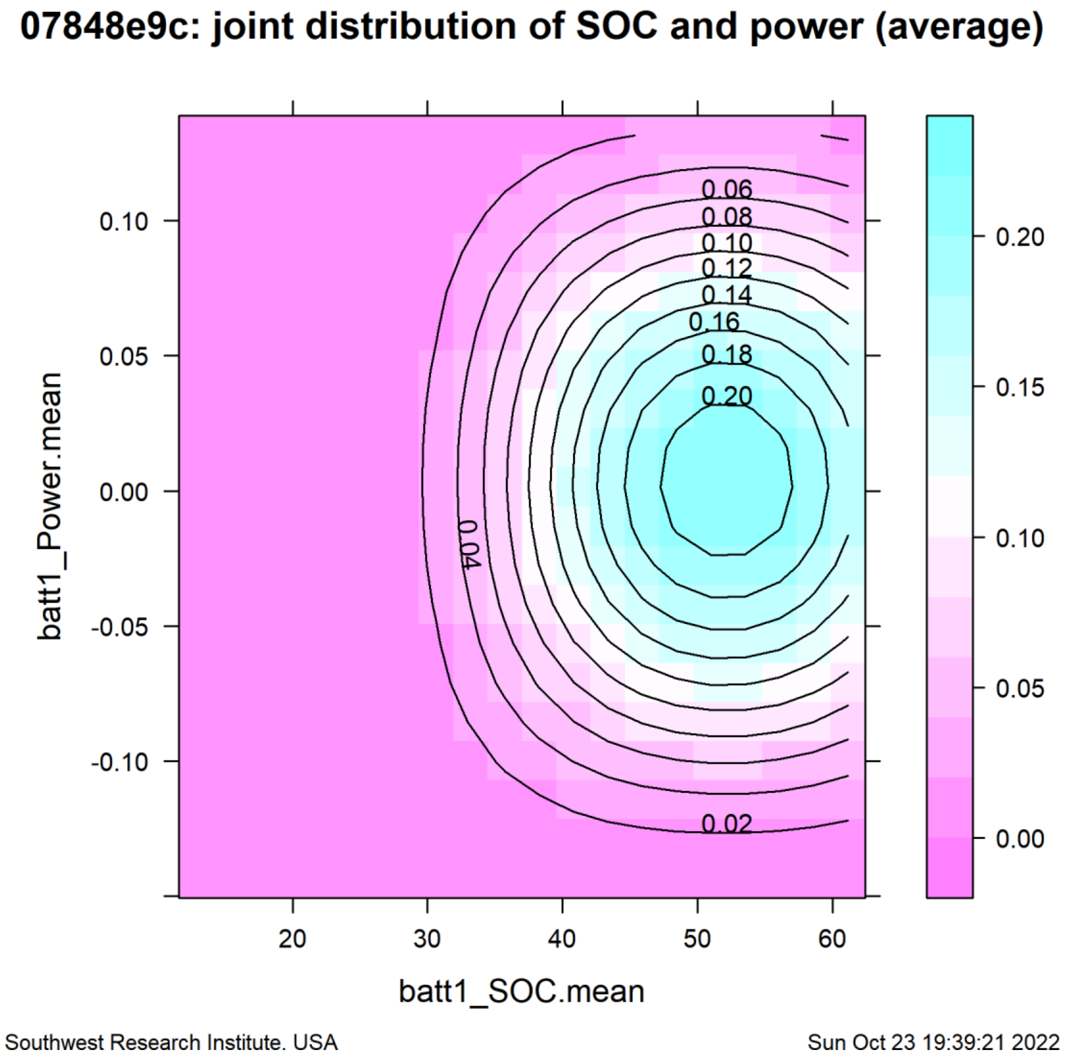




Source: 07848e9c

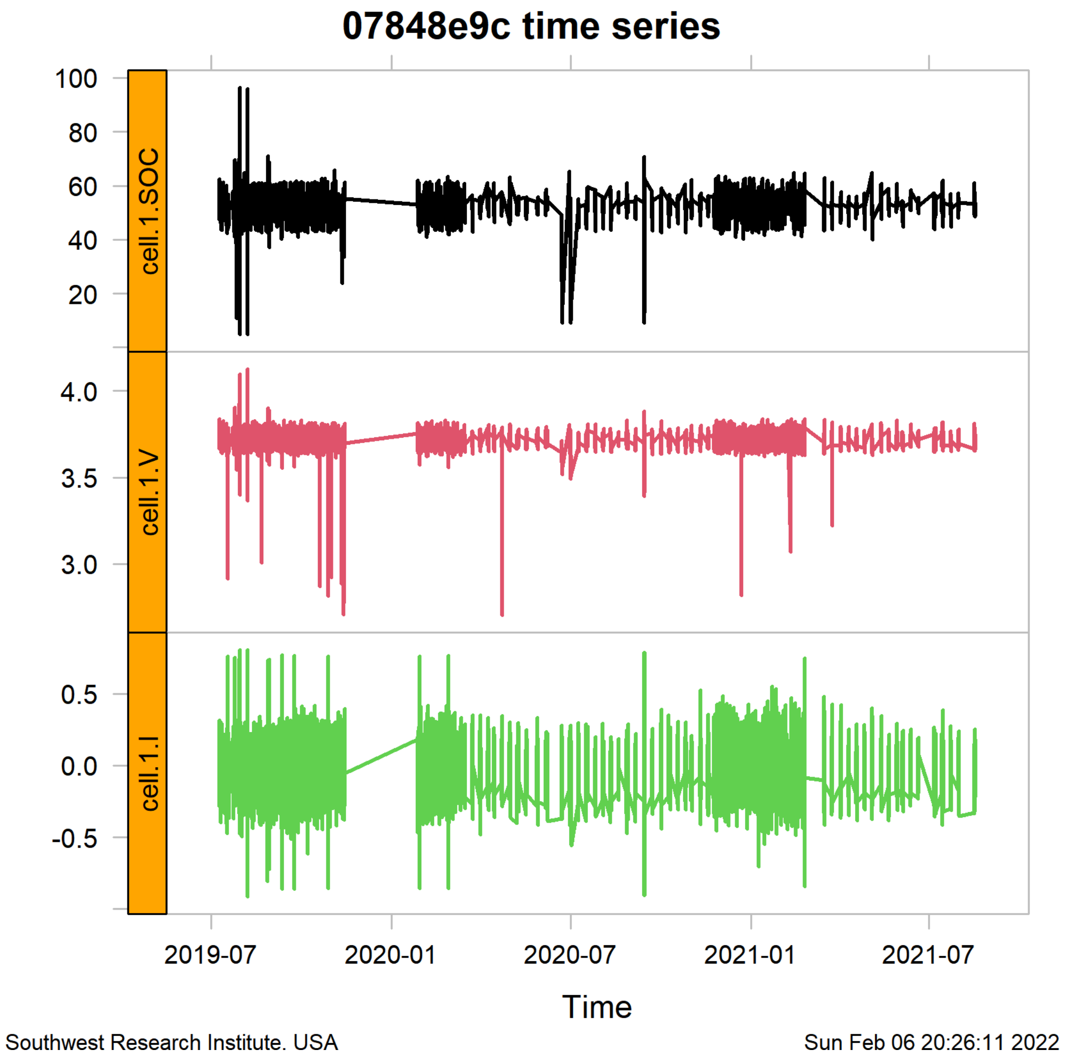
Note slight bias in SOC to the right of 50 [%]
Majority of operation "light" – within +- 0.1 P
How far can we push the BESS – safely?

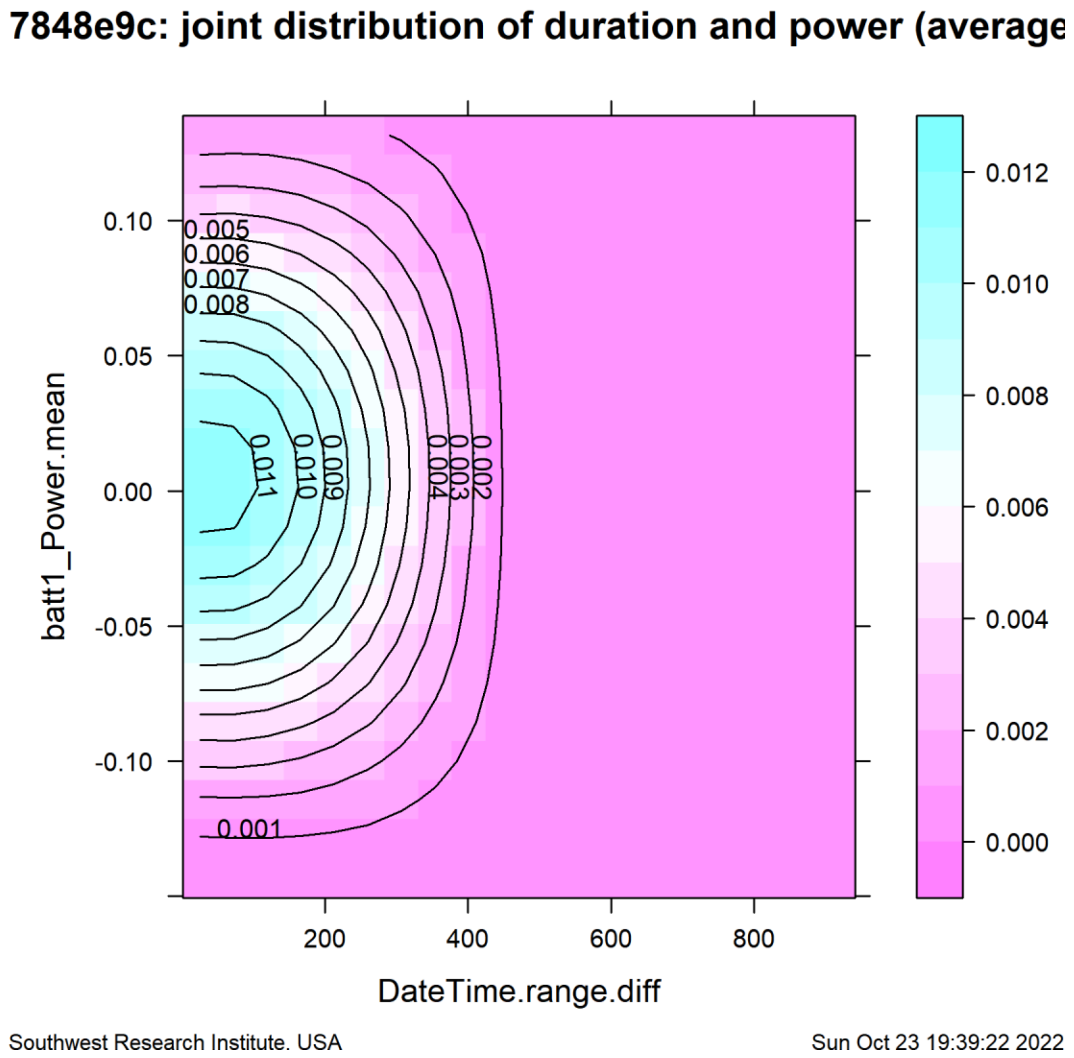




Source: 07848e9c

Majority of duration at any power within 200 [s]
Frequency regulation is work (or charge) neutral over horizons of several minutes





Experiments for Mixed/Stacked Grid Duty

Combining modal and temporal characteristics, and expanding operating envelope

Designing Experiments for Mixed/Stacked Grid Duty

- Multiple services
- Mixed: Timewise disjoint – one service at a time
- Stacked: Simultaneous – more than one service at a time

- Given the field data, we currently consider only two services*

- SHFT (load shift)
  - Large change in SOC
  - Longer duration – 2-, 4-, 6-hour operation common
  - Reasonable power
- FREQ (frequency regulation)
  - Smaller change in SOC
  - Shorter duration – several sec to min
  - Potentially higher power
  - Work- (or charge-) neutral over short horizons – either inherently so or forced by the BMS
  - Likely no rest/idle operation

Designing Experiments for Mixed/Stacked Grid Duty

- Parameters for Samsung 94 [Ah]
- Discharge
  - continuous = 346 [W]
  - peak = 427 [W]
- Charge
  - continuous = -346 [W]
  - peak = -500 [W]
- SOC
  - max = 95 [%]
  - min = 5 [%]

- SHFT (load shift)
  - Large change in SOC
  - Longer duration – 2-, 4-, 6-hour operation common
  - Reasonable power
- FREQ (frequency regulation)
  - Smaller change in SOC
  - Shorter duration – several sec to min
  - Potentially higher power
  - Work- (or charge-) neutral over short horizons – either inherently so or forced by the BMS
  - Likely no rest/idle operation

Example: Experiments for Mixed/Stacked Grid Duty

No “single-service” experiments

Statistical power is acceptable (typical threshold 1-beta=0.8)

Test	shft.dp [W]	shft.cp [W]	freq.dp [W]	freq.cp [W]	soc.min [%]	soc.max [%]	shft.dp.duration [s]	shft.cp.duration [s]	T [C]
1	57.7	-132	85.3	-208	5	95	29.2	12	25
2	173	-132	171	-208	35	95	14.6	12	25
2a	173	-132	171	-208	35	95	14.6	12	-10
3	57.7	-44.2	256	-208	5	95	9.73	12	25
4	173	-44.2	85.3	-208	35	95	29.2	12	25
5	173	-132	85.3	-69.2	5	95	29.2	36	25
5a	173	-132	85.3	-69.2	5	95	29.2	36	-10
6	57.7	-132	256	-69.2	35	95	9.73	36	25
6a	57.7	-132	256	-69.2	35	95	9.73	36	-10
7	173	-44.2	171	-69.2	5	95	14.6	36	25
8	57.7	-44.2	85.3	-69.2	35	95	29.2	36	25
9	57.7	-132	85.3	-208	5	65	29.2	12	25
10	57.7	-132	256	-208	35	65	9.73	12	25
11	173	-44.2	85.3	-208	5	65	29.2	12	25
12	173	-44.2	171	-208	35	65	14.6	12	25
13	173	-132	171	-69.2	5	65	14.6	36	25
14	173	-132	85.3	-69.2	35	65	29.2	36	25
14a	173	-132	85.3	-69.2	35	65	29.2	36	-10
15	57.7	-44.2	256	-69.2	5	65	9.73	36	25
16	57.7	-44.2	85.3	-69.2	35	65	29.2	36	25

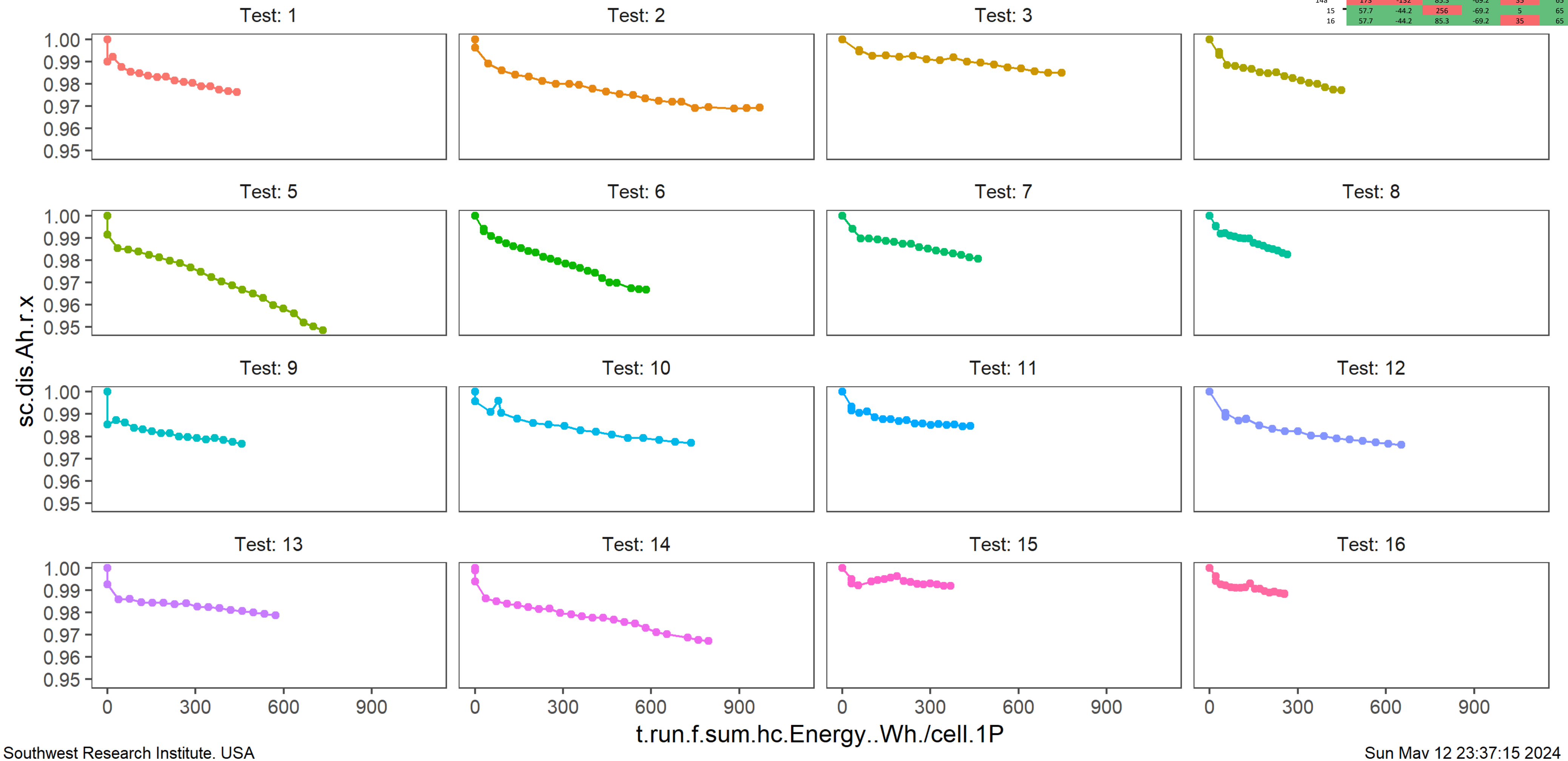
parameter	type	power
(Intercept)	effect.power	0.90
shft.dp	effect.power	0.90
shft.cp	effect.power	0.93
freq.dp	effect.power	0.77
freq.cp	effect.power	0.93
soc.min	effect.power	0.93
soc.max	effect.power	0.93
shft.cp:soc.max	effect.power	0.93
freq.cp:soc.max	effect.power	0.93
(Intercept)	parameter.power	0.90
shft.dp	parameter.power	0.90
shft.cp	parameter.power	0.93
freq.dp	parameter.power	0.77
freq.cp	parameter.power	0.93
soc.min	parameter.power	0.93
soc.max	parameter.power	0.93
shft.cp:soc.max	parameter.power	0.93
freq.cp:soc.max	parameter.power	0.93

Capacity Degradation by Eq Work Cyc

Test	shft.dp [W]	shft.cp [W]	freq.dp [W]	freq.cp [W]	soc.min [%]	soc.max [%]	shft.dp.duration [s]	shft.cp.duration [s]	T [C]
1	57.7	-132	85.3	-208	5	95	29.2	12	25
2	173	-132	171	-208	35	95	14.6	12	25
2a	173	-132	171	-208	35	95	14.6	12	-10
3	57.7	-44.2	256	-208	5	95	9.73	12	25
4	173	-44.2	85.3	-208	35	95	29.2	12	25
5	173	-132	85.3	-69.2	5	95	29.2	36	25
5a	173	-132	85.3	-69.2	5	95	29.2	36	-10
6	57.7	-132	256	-69.2	35	95	9.73	36	25
6a	57.7	-132	256	-69.2	35	95	9.73	36	-10
7	173	-44.2	171	-69.2	5	95	14.6	36	25
8	57.7	-44.2	85.3	-69.2	35	95	29.2	36	25
9	57.7	-132	85.3	-208	5	65	29.2	12	25
10	57.7	-132	256	-208	35	65	9.73	12	25
11	173	-44.2	85.3	-208	5	65	29.2	12	25
12	173	-44.2	171	-208	35	65	14.6	12	25
13	173	-132	171	-69.2	5	65	14.6	36	25
14	173	-132	85.3	-69.2	35	65	29.2	36	25
14a	173	-132	85.3	-69.2	35	65	29.2	36	-10
15	57.7	-44.2	256	-69.2	5	65	9.73	36	25
16	57.7	-44.2	85.3	-69.2	35	65	29.2	36	25

Longer tests 2a, 5a, 6a, 14a at -10 deg C

2359 JIP normalized capacity vs equivalent cycles (transacted work)



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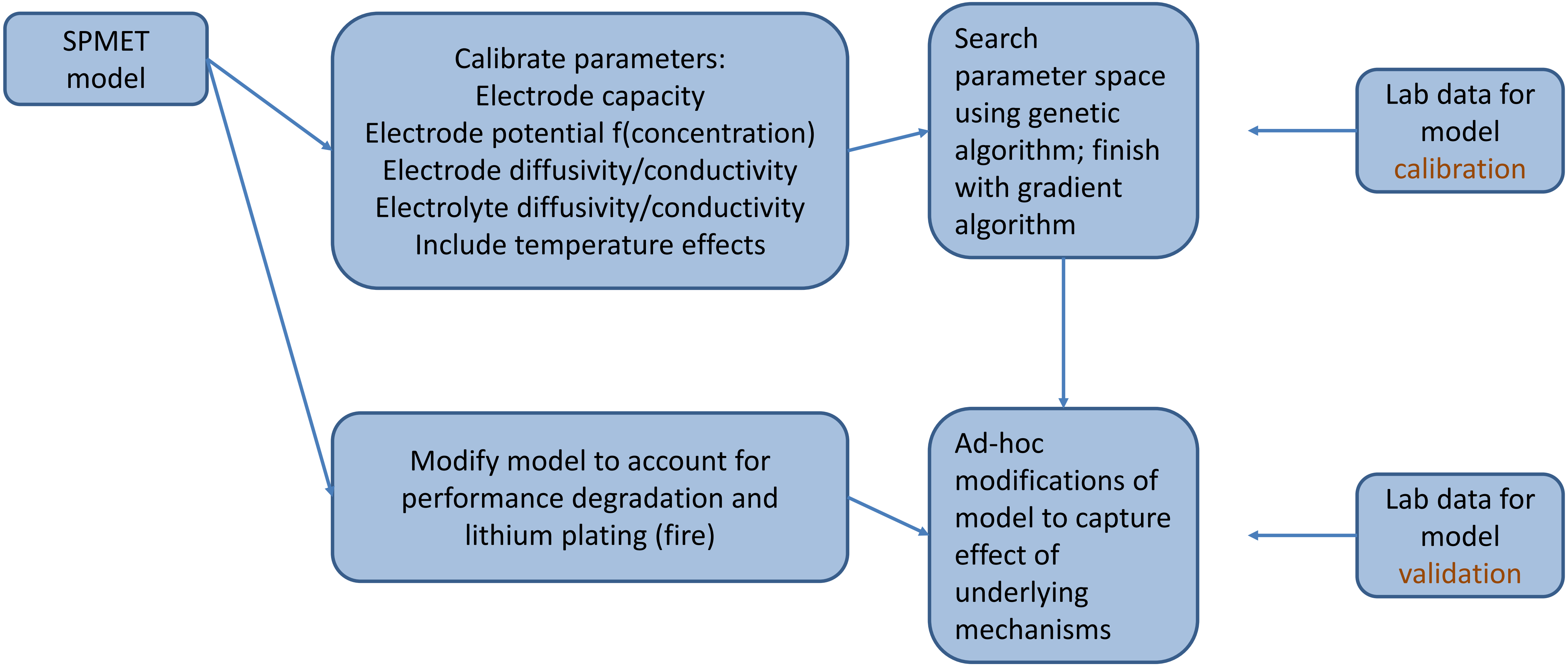
Capacity Degradation

- Statistical model fitted
  - Model form inspired by various physical processes – Arrhenius, Butler-Volmer, diffusion, …
  - Regressors include work/charge transacted, power/current, duration, SOC, …
- Conclusions regarding detrimental effects from the fitted model
  - Low temperature + high SOC + high current
  - High temperature
  - High current + long duration
  - …

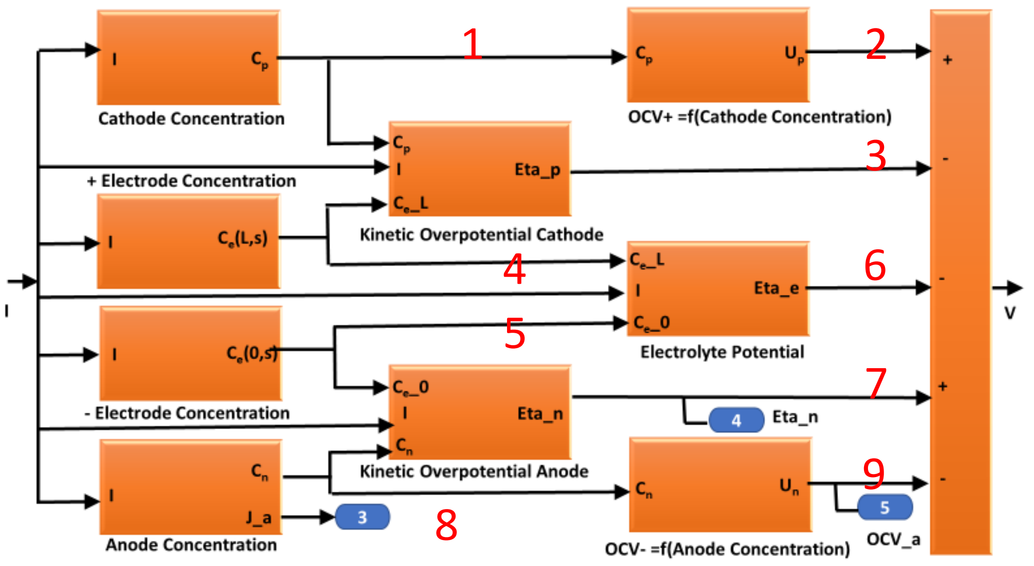
Calibrating and Validating the Model

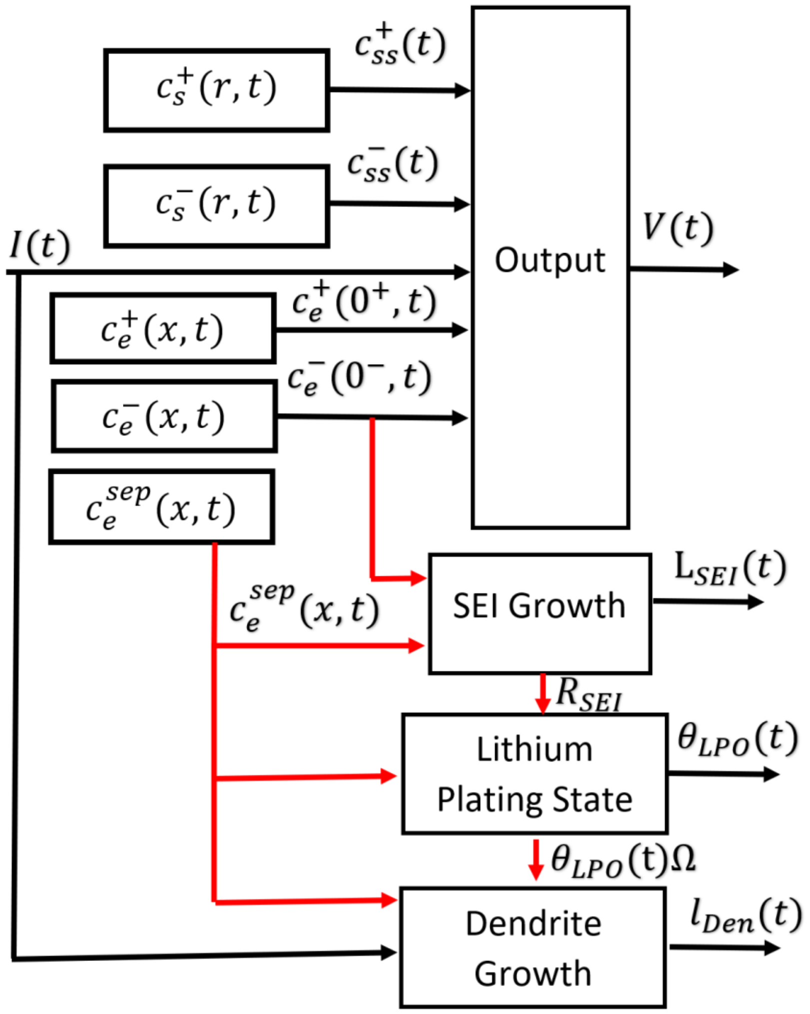
Using lab data to parameterize the physics-informed extended SPMeT model

Modeling


SPMET model
Calibrate parameters:
Electrode capacity
Electrode potential f(concentration)
Electrode diffusivity/conductivity
Electrolyte diffusivity/conductivity
Include temperature effects
Search parameter space using genetic algorithm; finish with gradient algorithm
Lab data for model calibration
Modify model to account for performance degradation and lithium plating (fire)
Ad-hoc modifications of model to capture effect of underlying mechanisms
Lab data for model validation

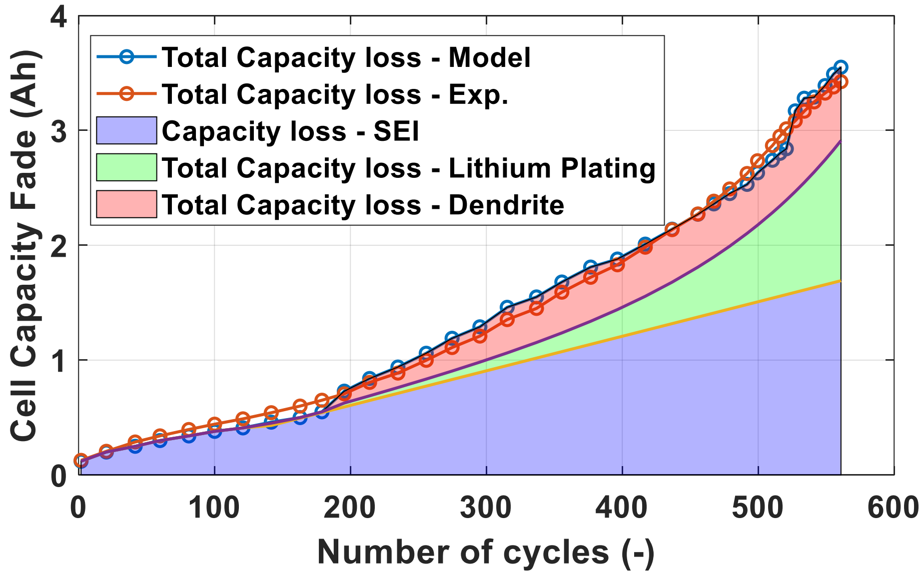
Transcribing “Essential Understanding” to a Model





Validating the Model – Considering Capacity Fade

- Compare experimental and model-predicted capacity loss for LG M50T
- Slope changes in capacity fade at 180 and 520 cycles correctly predicted by onset of lithium plating and dendritic growth
- The additional component of dendritic growth to explain the second slope change is a novel and matches the experimental observations



Positive feedback between SEI and Li plating → "run-away"

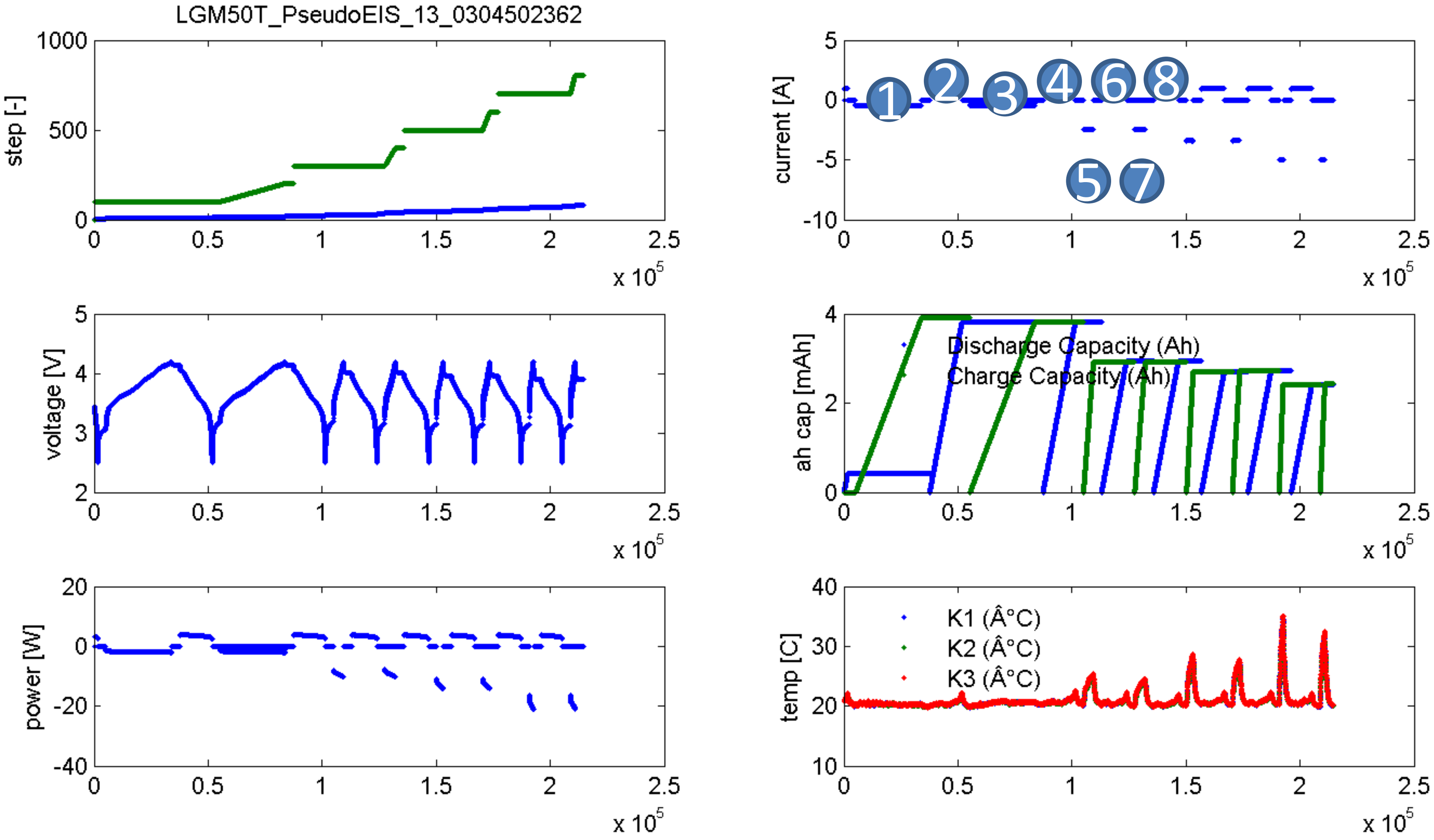
On-line Check – The Modified Pseudo-EIS*

Keeping the physics-informed model honest by periodic adjustment of parameters

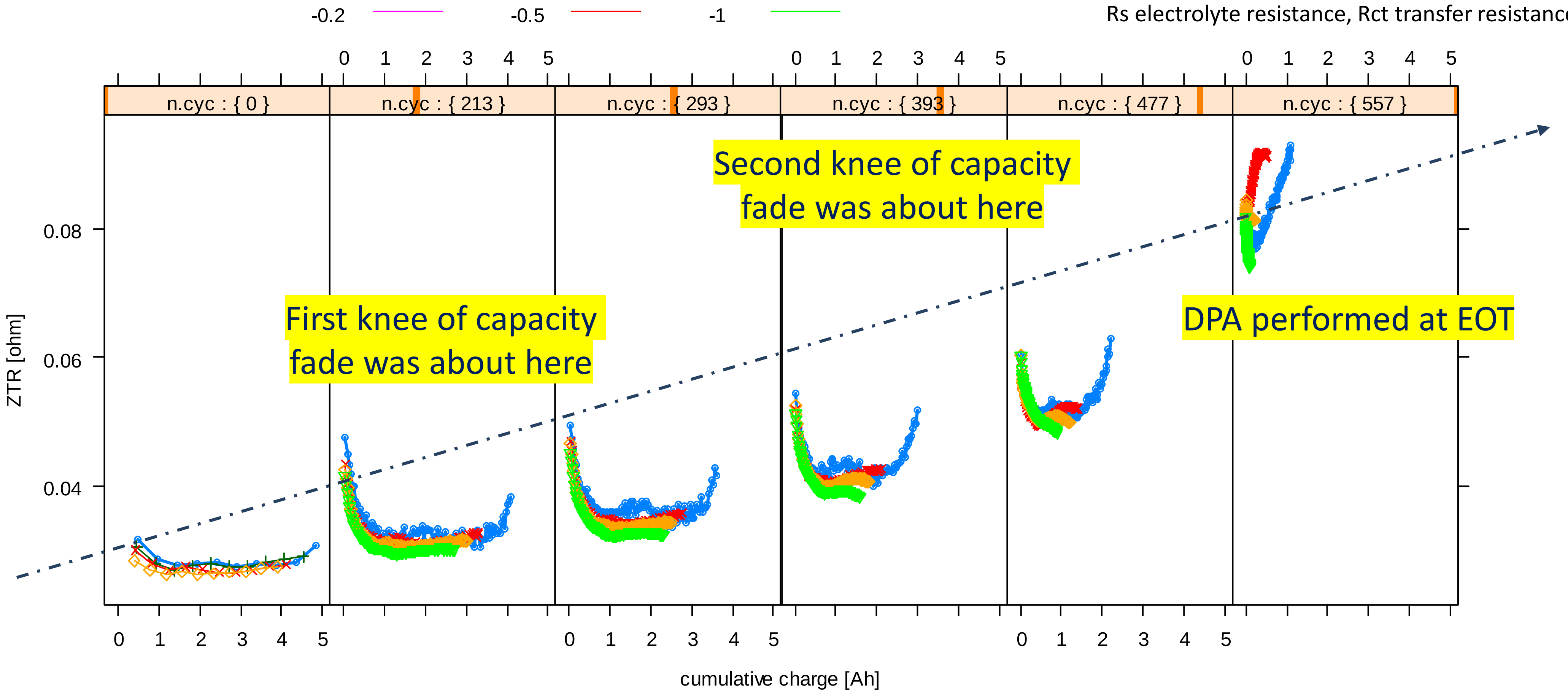
* Pseudo-Electrochemical-Impedance-Spectroscopy; Patent Pending

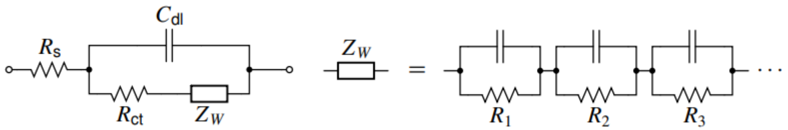
Pseudo-EIS – Z = f(SOC,I_charge_level_n)

(1) Charge at const current (level 1)
(2) Discharge at const std current – measure static cap
(3) Charge at const current (level 1); interrupt current for 3 [sec] after gaining 1 [%] SOC
(4) Discharge at const std current
(5) Charge at const current (level 2)
(6) Discharge at const std current – measure static cap
(7) Charge at const current (level 1) and interrupt current for 3 [sec] after gaining 1 [%] SOC
(8) …



Pseudo-EIS on LG M50T sample ID 0304502362





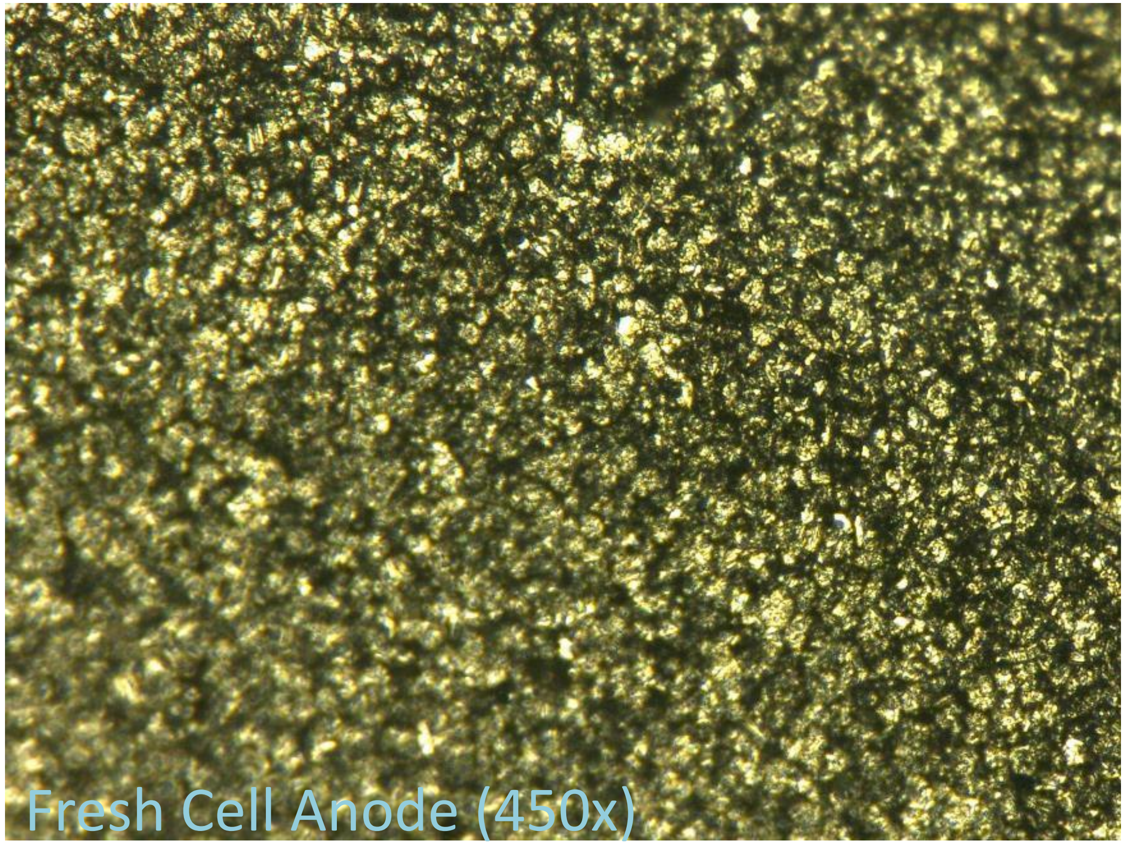
Rs electrolyte resistance, Rct transfer resistance

LG_M50T_pseudo_EIS_ZTR_conditioned_on_alias_

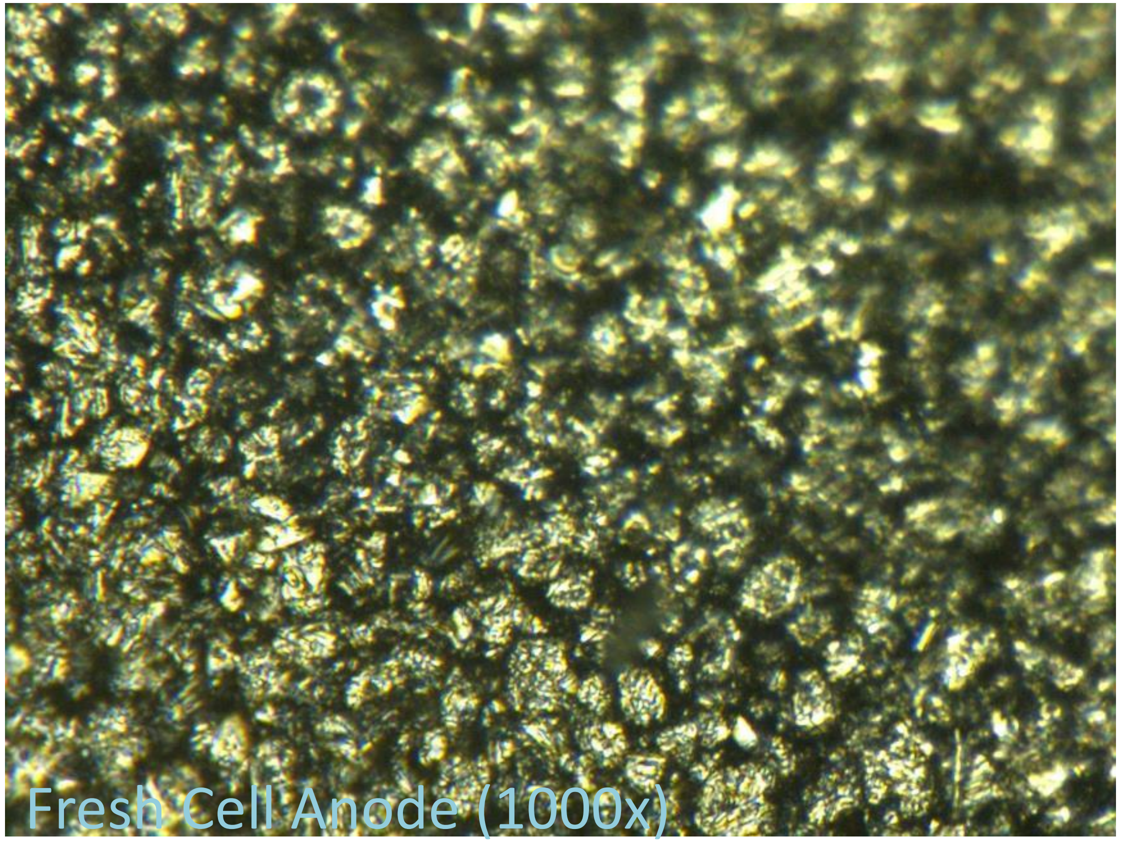
* Patent Pending

Mon Jan 2 18:42:02 2023

Optical Microscopic Analysis of Fresh Cell

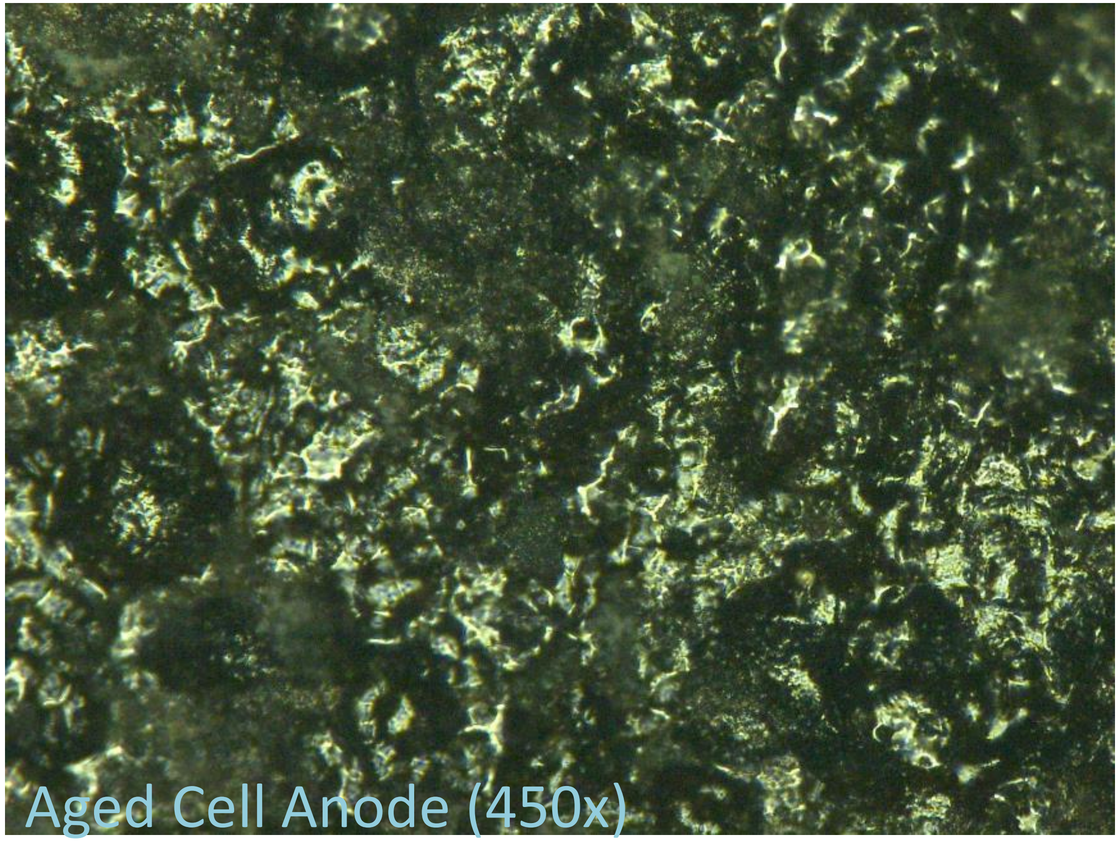


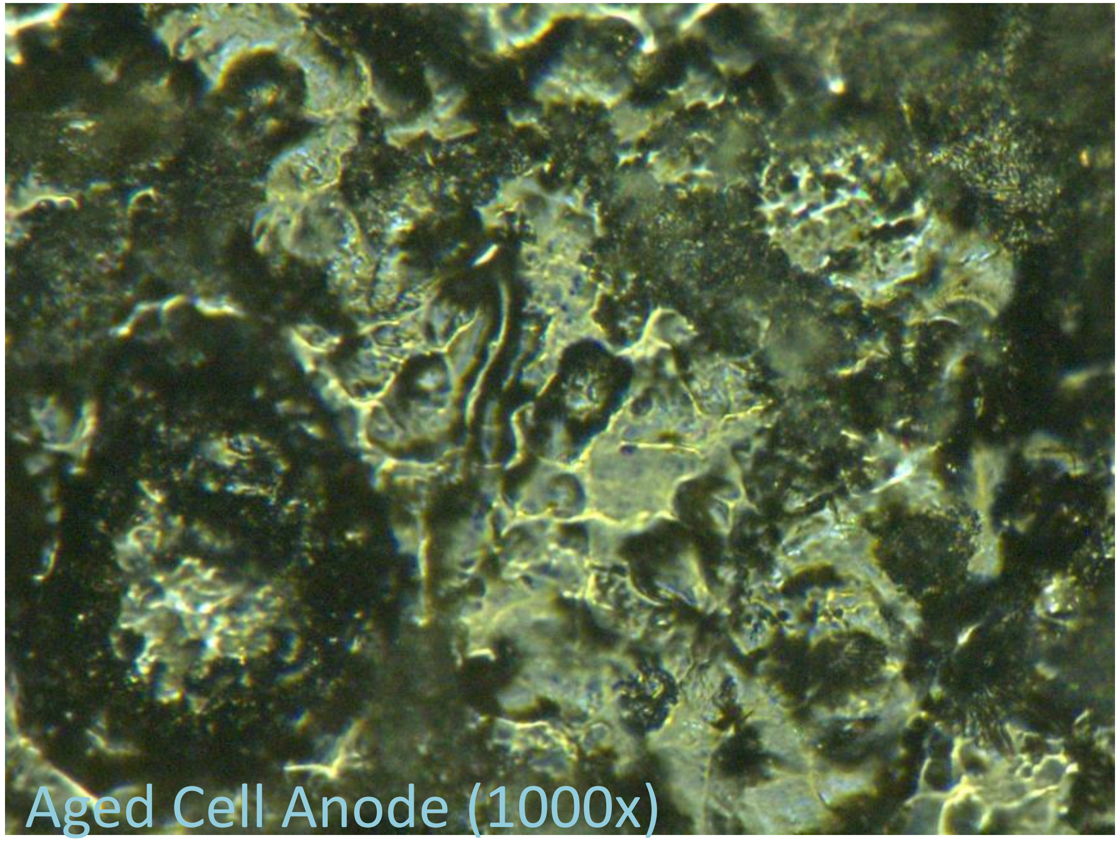
Fresh Cell Anode (450x)



Fresh Cell Anode (1000x)

Optical Microscopic Analysis of Aged Cell



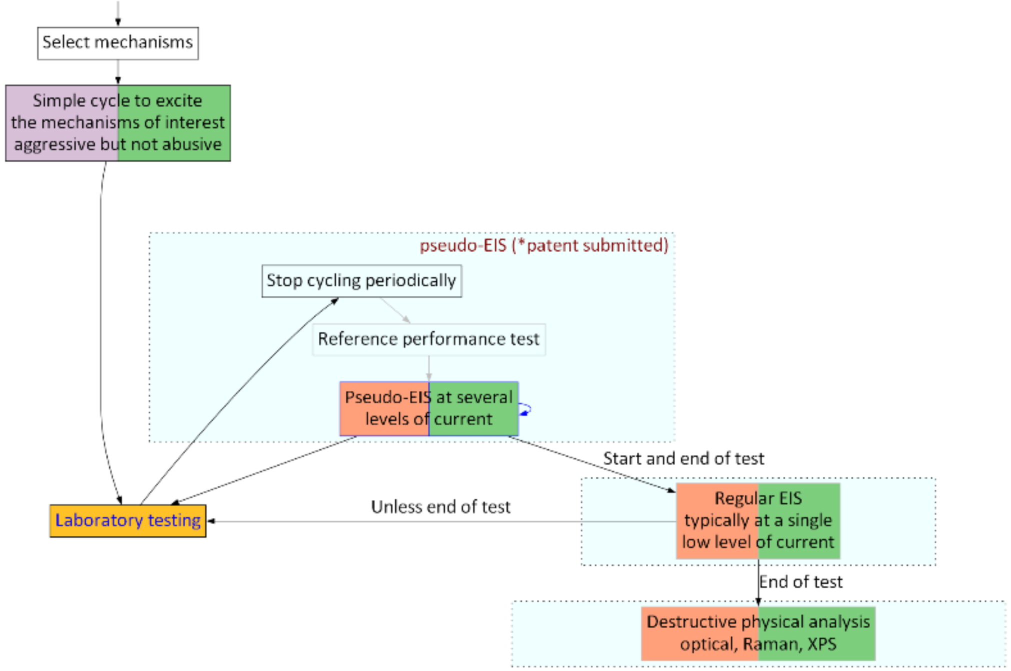


Evidence for Solids Precipitation on Anode Surface

Summary of Our Extension to Pseudo-EIS Method

- Detects (and quantifies) degradation and lithium plating
  - Plating verified in 0304502362
- Enables on-line adjustment of model parameters (and keeps model honest)
- Provides proactive management of current during (fast) charging to trade-off performance and safety
- Can be used offline to gauge SOH of second-life batteries before redeployment

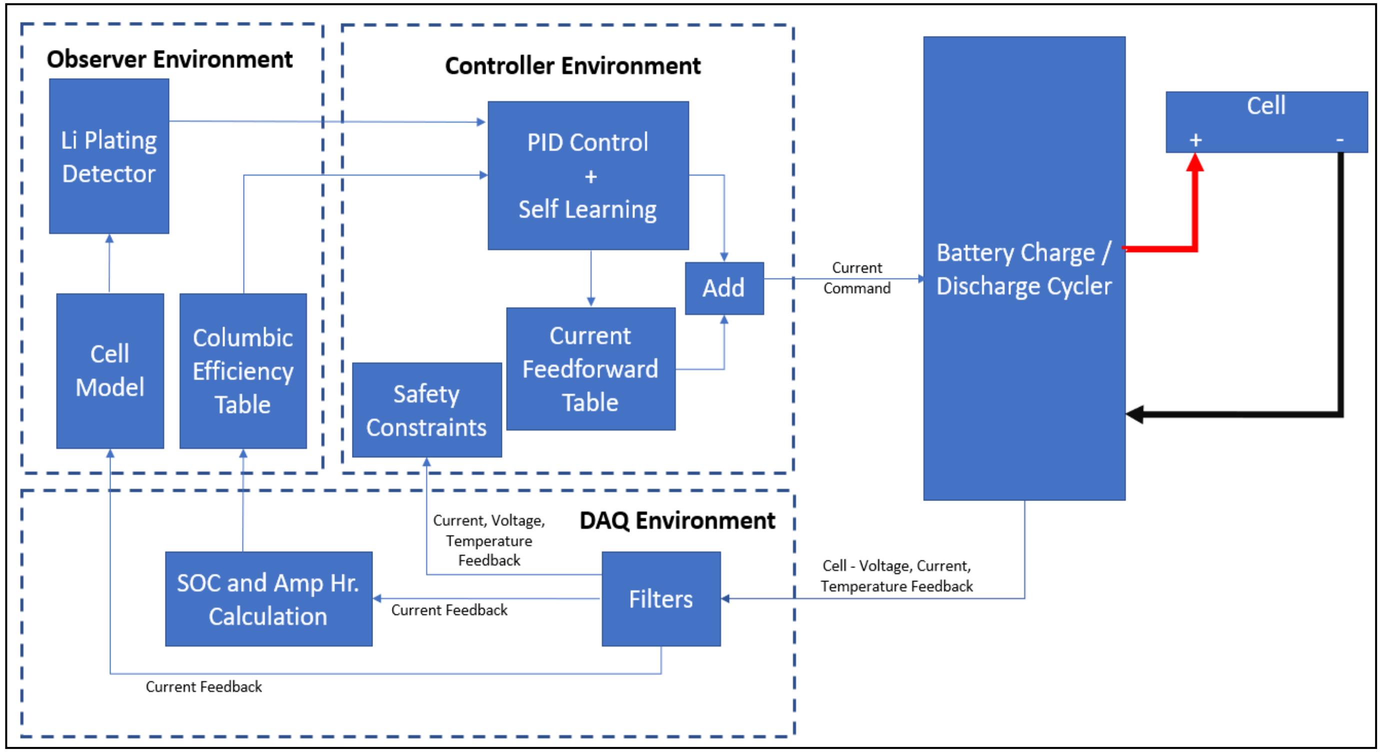
Approach readily amenable to real-time implementation in BMS for assessment of performance and safety



Implementation and Demonstration

Putting it all together on the research BESS on SwRI campus

Manage Charge/Discharge to Improve SOH/Extend Life

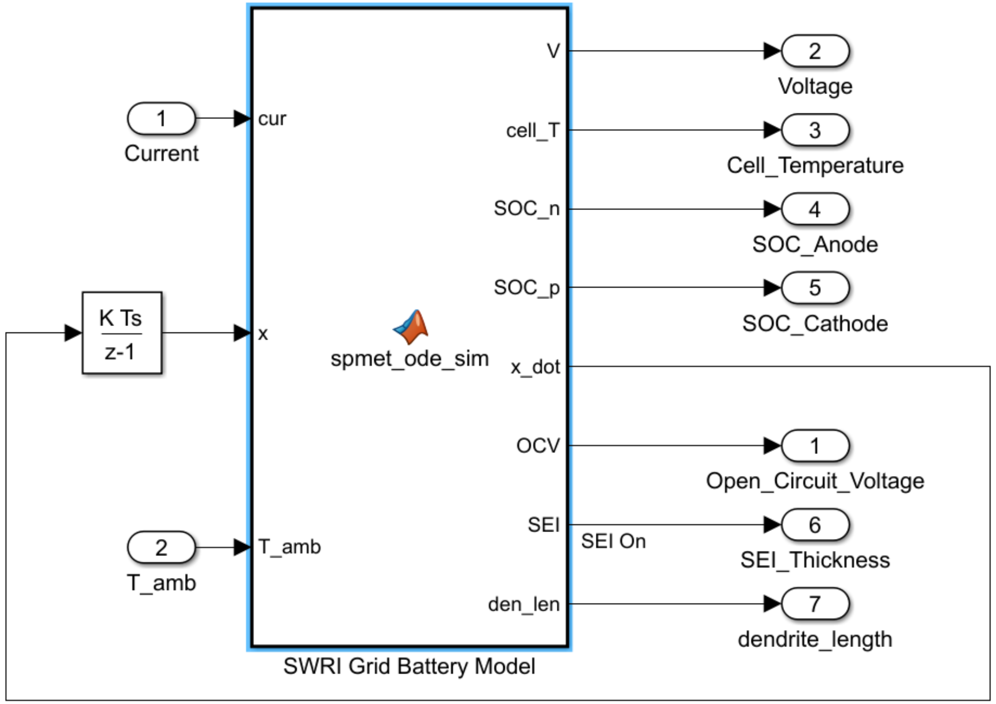


Inner Battery States:

1. Lithium concentration at cathode
2. Open circuit potential at cathode
3. Kinetic overpotential at cathode
4. Electrolyte concentration at the anode end (x=0)
5. Electrolyte concentration at the cathode end ($x=L_C$)
6. Electrolyte potential
7. Kinetic overpotential at anode
8. Lithium concentration at anode
9. Open circuit potential at anode

Controller Implementation in MATLAB/Simulink

- Inputs - current, ambient temperature
- Outputs - voltage, cell temperature, SOC anode and cathode, open circuit voltage, SEI thickness, dendrite length
- States – Li ion concentration in anode, cathode and electrolyte, temperature of pouch and cell, SEI thickness, dendrite length
- Time step size – 40 [ms] for C rate < 8

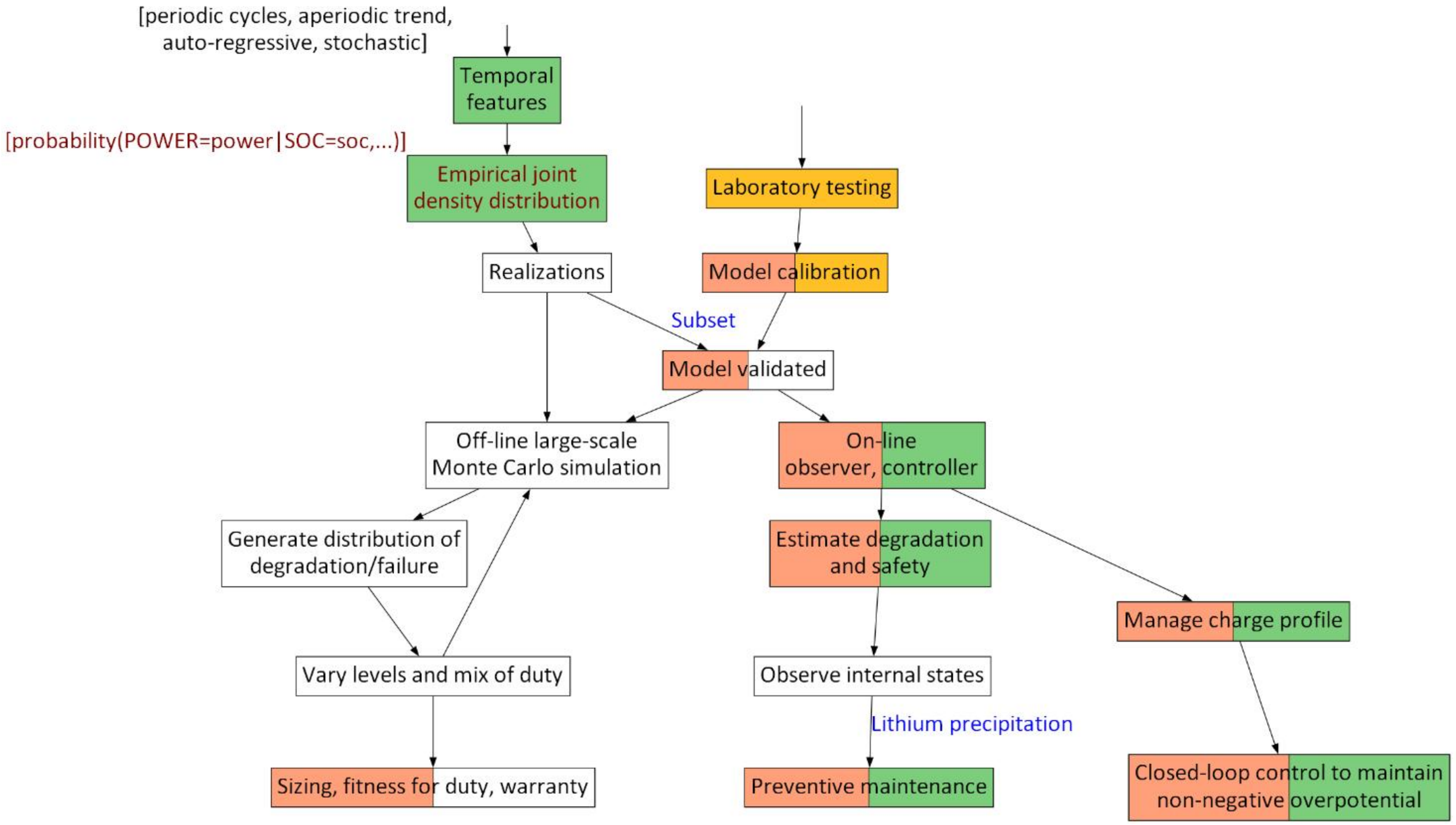


Embedded MATLAB Battery Model

Model Use Cases

- Model types
  - Electrochemical like SPMeT
  - Statistical
- Off-line
  - Which battery Li-ion chemistries suitable for which (stacked) grid services?
    - Model parameters (~6 calibratable) different for different chemistries
  - How much can a battery be pushed safely to maximize ROI?
  - Assessment of used batteries
- On-line
  - Charge management (via LPO)
  - Maintenance advisory based on as-used

Model: Use Cases



Summary

- Field data: operating envelop
- Modeling a Li-ion cell: mechanisms, structure, and parameters
- Laboratory testing: guided by field operation and likely Li-ion failure mechanisms
- Keeping the model "honest": monitor degradation, adapt parameters
- Implementation and demonstration: research BESS at SwRI
  - Currently operating in "observer" mode only
  - Looking for partners for a larger/longer field deployment

Questions/Comments?

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Thank you!