

Supplemental information for

Health diagnosis and recuperation of aged Li-ion batteries with data analytics and equivalent circuit modeling

Riko I Made,¹ Jing Lin,² Jintao Zhang,¹ Yu Zhang,² Lionel C. H. Moh,¹ Zhaolin Liu,¹ Ning Ding,¹ Sing Yang Chiam,¹ Edwin Khoo,^{2,*} Xuesong Yin^{1,4,*} and Guangyuan Wesley Zheng^{3,*}

¹ Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis #08-03, Singapore 138634, Republic of Singapore.

² Institute for Infocomm Research (I²R), Agency for Science, Technology and Research (A*STAR), 1 Fusionopolis Way, #21-01 Connexis, Singapore 138632, Republic of Singapore.

³ Posh Robotics, 3501 Breakwater Court, Hayward, CA 94545, United States.

⁴ Lead contact

*Correspondence: yinxs@imre.a-star.edu.sg, edwin_khoo@i2r.a-star.edu.sg and wesley@poshrobotics.com

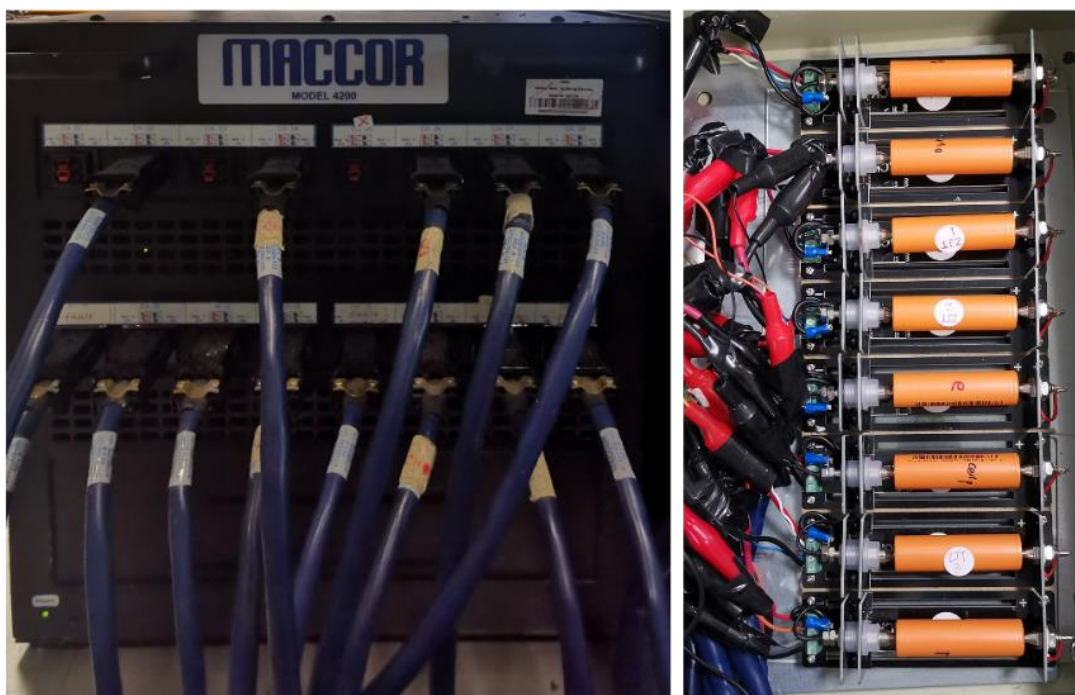
This file includes:

13 supplemental figures

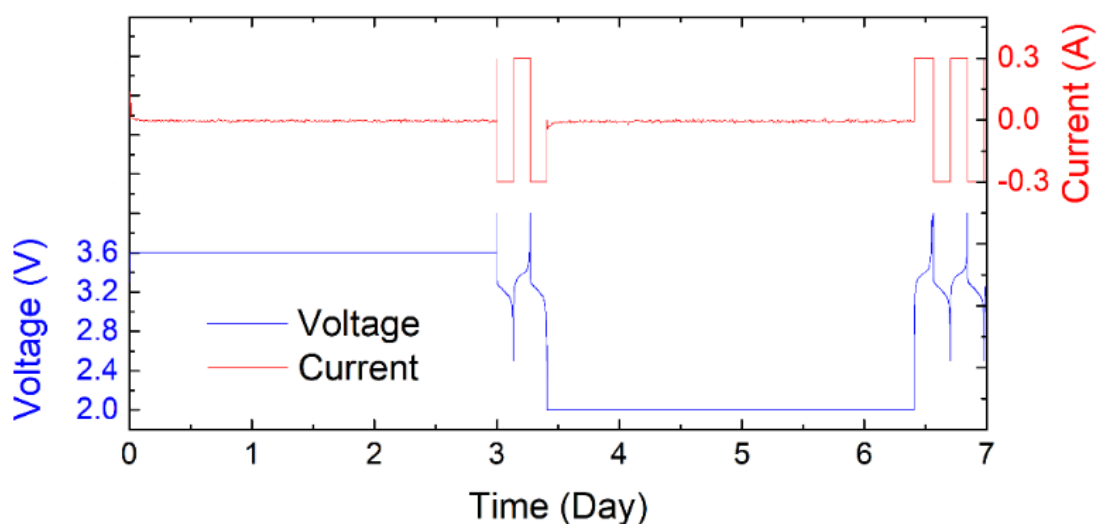
4 supplemental tables

1 supplemental method

1. Supplemental Figures

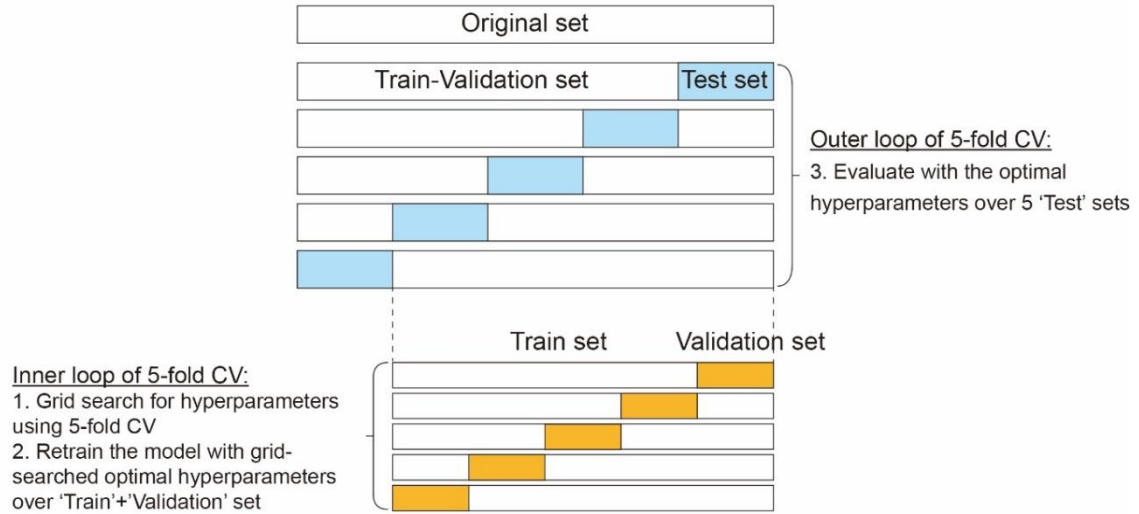


Supplemental Figure S1. Battery tester and cell holder used for cell cycling. The tester is connected with battery cells by multiple cables. Each cable has 4 crocodile clips, which are connected with four terminals in the battery holder for each channel. The distance between two ends of each channel can be adjusted by screws and a spring, so the cell can be firmly clamped.

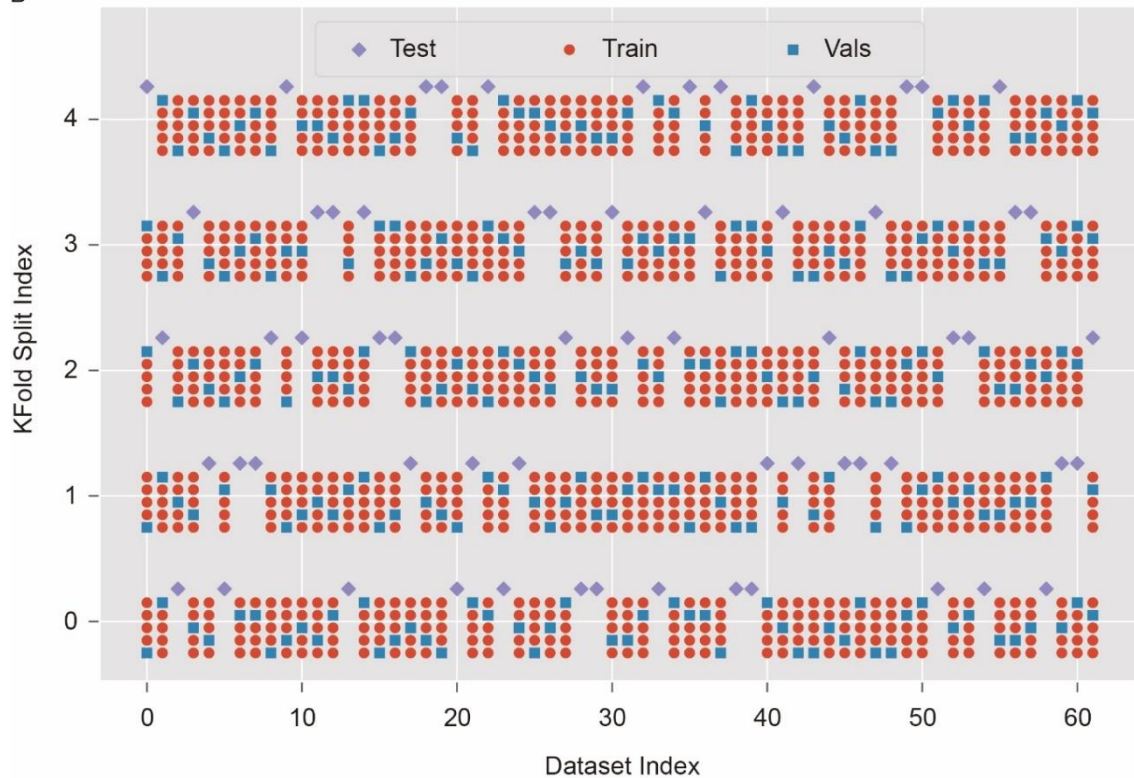


Supplemental Figure S2. Typical current and voltage profiles during reconditioning and capacity check. The reconditioning is conducted with a cell at fully charged state. When a potential of 3.6 V is applied, the cell current becomes 0 A in a short period and keeps around 0 A for 72 h. Then the cell is discharged to 2.5 V at 0.3 A and charged to 4.0 V at 0.3 A and then discharged to 2.5 V again. After that, a potential of 2.0 V is applied for another 72 h with the cell current around 0 A. In the end, the cell is cycled between 2.5 V and 4.0 V at 0.3 A for 2 cycles for a capacity check-up.

A



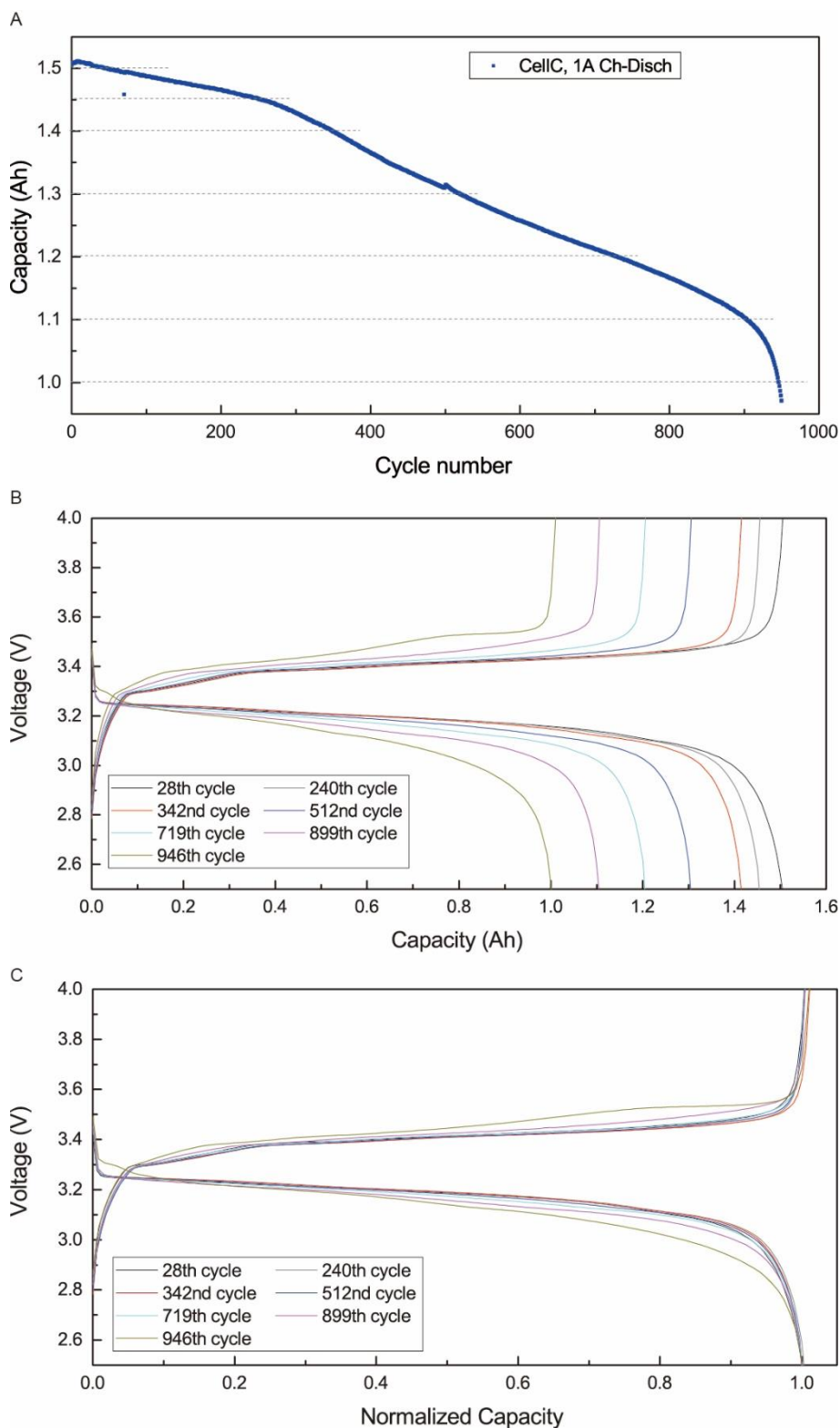
B



Supplemental Figure S3. Data splitting and partition of the Train, Validation and Test set.

(A) Dataset splitting scheme between outer loop (Train-Validation, Test) and inner loop (Train and Validation set) for nested cross-validation (CV). The inner loop is used to find the optimal hyperparameters across the 5-fold Train-Validation set. The model with the best performance is retained and finally retrained on the Train-Validation set, which is then evaluated on the respective Test set.

(B) The generated data partition of the Train, Validation and Test set, is represented with red-circle, blue-square, and purple-diamond symbols, respectively. The dataset index represents the row numbers of the dataset.

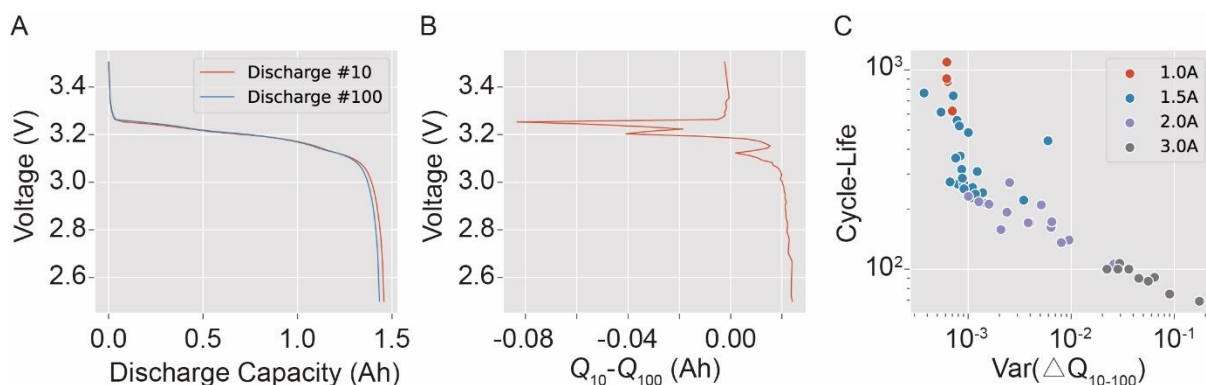


Supplemental Figure S4. Cycling behaviors of Cell C cycled at 1.0 A.

(A) Capacity decay with respect to cycle number. The cell has an initial capacity slightly above 1.50 Ah. The capacity is slowly decreased to 1.45 Ah. After 250 cycles, the speed of capacity decay increases until a residual capacity of 1.10 Ah around 900 cycles. An even faster capacity drop appears in the next 50 cycles with an end-up capacity of 1.00 Ah at 950 cycles.

(B) Charge-discharge curves at different capacities of 1.50 Ah (28th cycle), 1.45 Ah (240th cycle), 1.40 Ah (342nd cycle), 1.30 Ah (512th cycle), 1.20 Ah (719th cycle), 1.10 Ah (899th cycle) and 1.00 Ah (946th cycle).

(C) Normalized charge-discharge profiles of Cell C at different capacities in (B). In addition to the decrease of capacities observed in (C), the over-potential of each cycle, i.e. the gap between charge and discharge curve, increases with increasing cycle numbers. It indicates an increased resistance in the cell during cycling ageing.



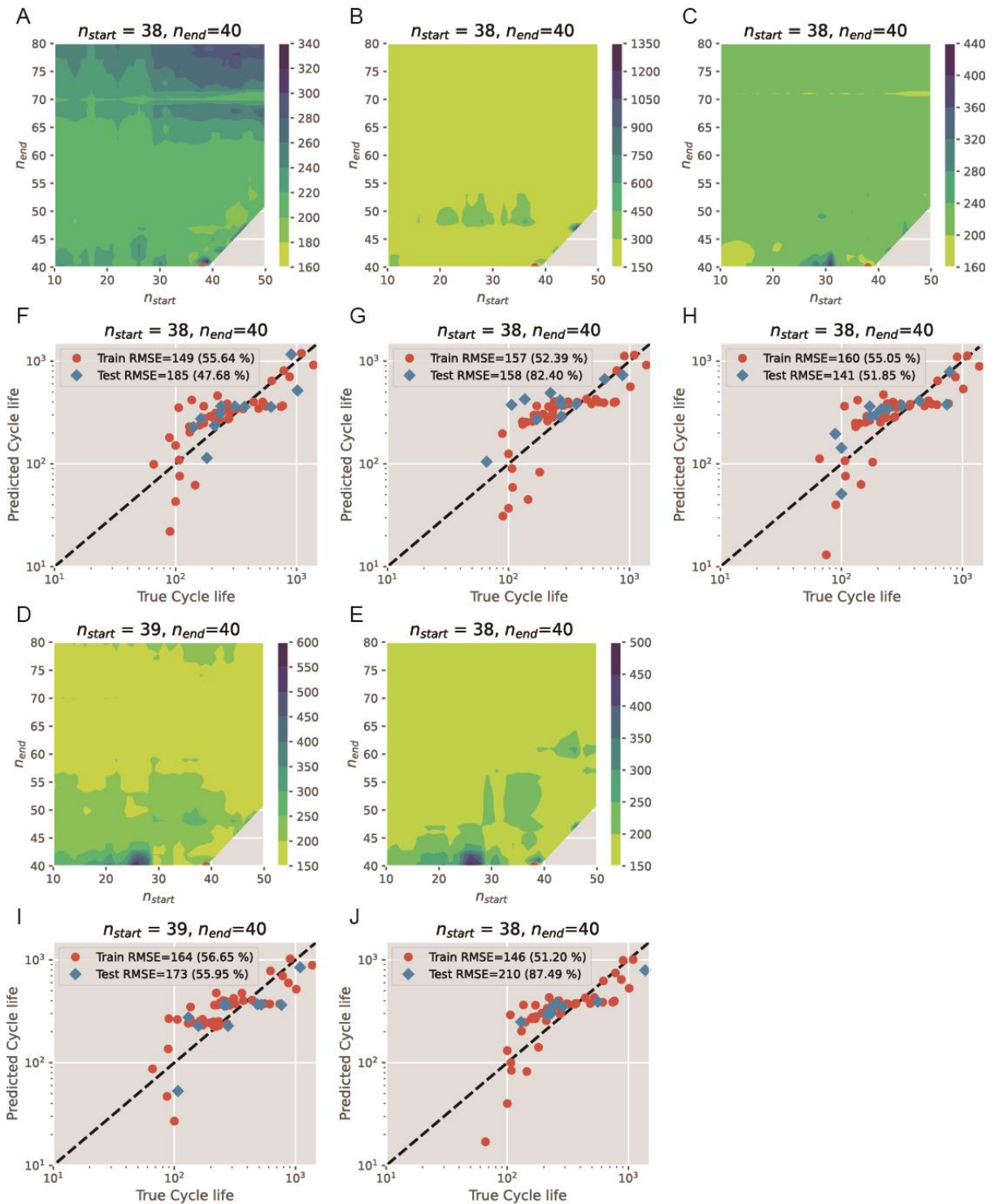
Supplemental Figure S5. Features $\text{var}(\Delta Q_{n_{start}-n_{end}})$.

(A) Discharge voltage curves from two selected cycles; here for illustration, we plot those from cycles 10 and 100.

(B) Calculated capacity differences from the two discharge cycles ΔQ .

(C) Cell cycle life as a function of variance of ΔQ ($\text{var}(\Delta Q)$), which shows an exponential decay relation.

Linear Regression Model Cross Validation

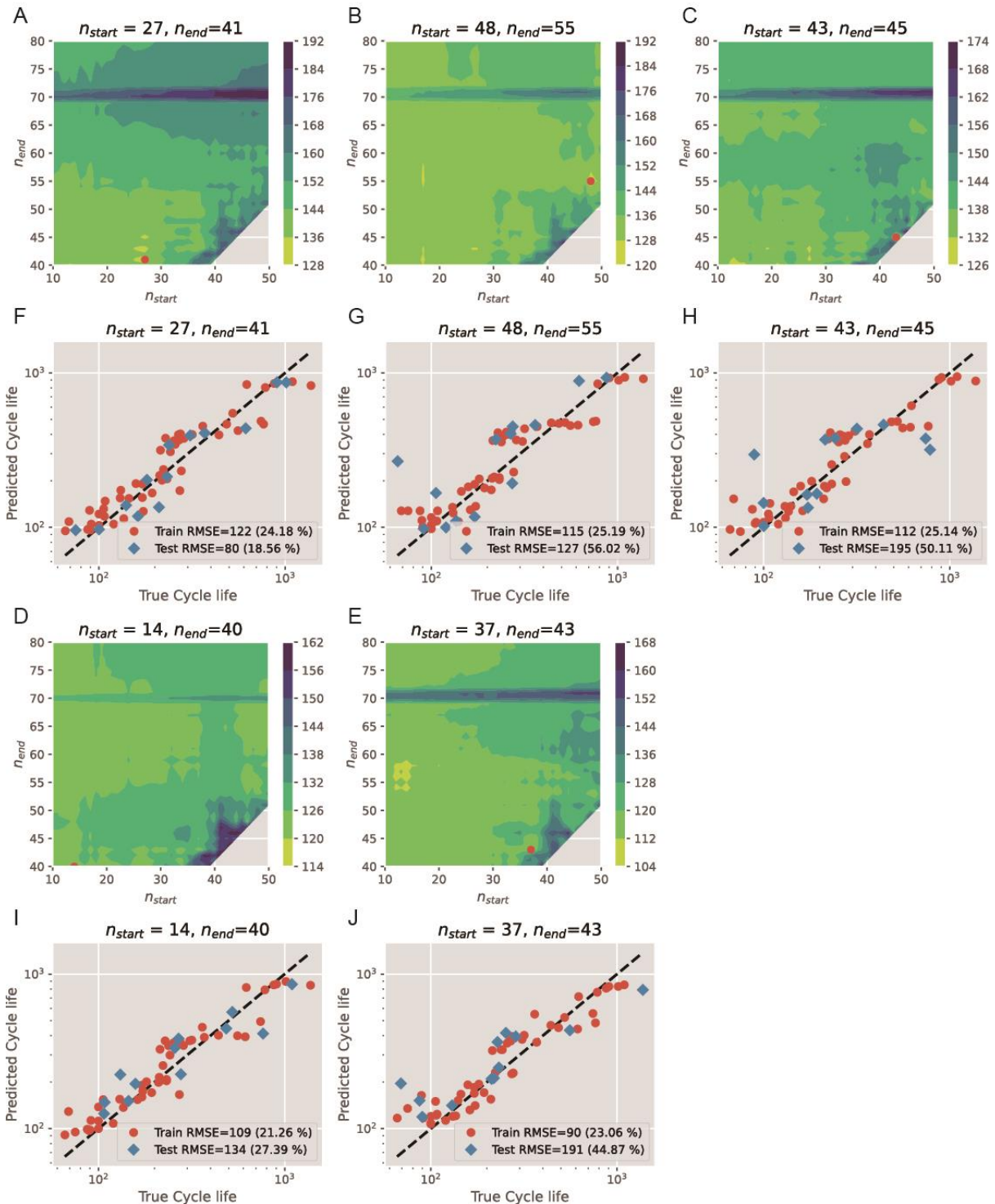


Supplemental Figure S6. Linear regression model cross validation.

(A-E) Linear regression contour map of the validation set's RMSE from 5-fold train-validation, with the red circular dot representing the best RMSE for each fold, respectively.

(F-J) Parity plot of the model performance from each outer loop folds – fold 0 to 4 from left to right, with the MAPE given inside the brackets in the legend.

GPR Regression Model Cross Validation

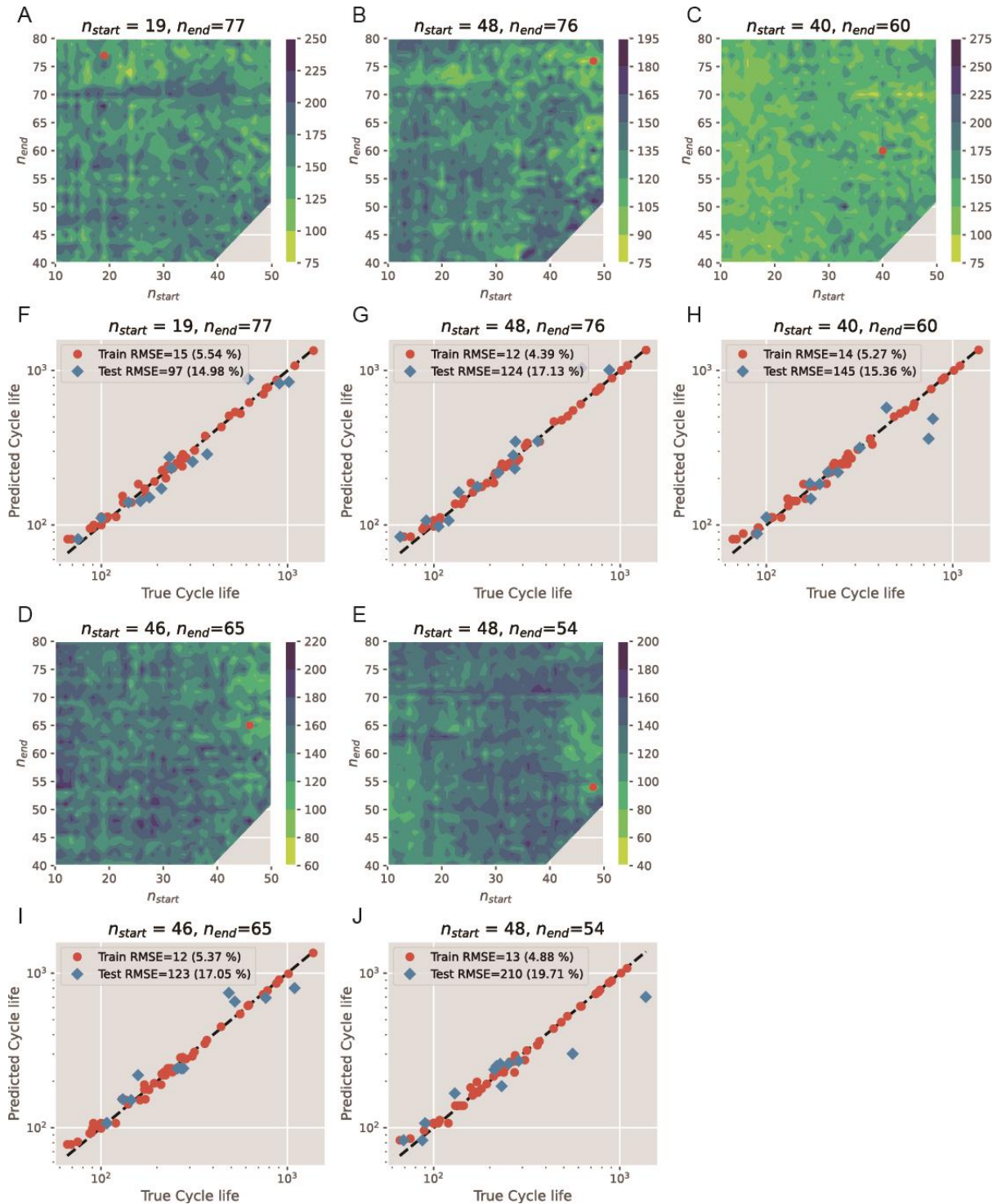


Supplemental Figure S7. GPR regression model cross validation.

(A-E) GPR contour map of the validation set's RMSE from 5-fold train-validation, with the red circular dot representing the best RMSE for each fold, respectively.

(F-J) Parity plot of the model performance – fold 0 to 4 from left to right, with the MAPE given inside the brackets in the legend.

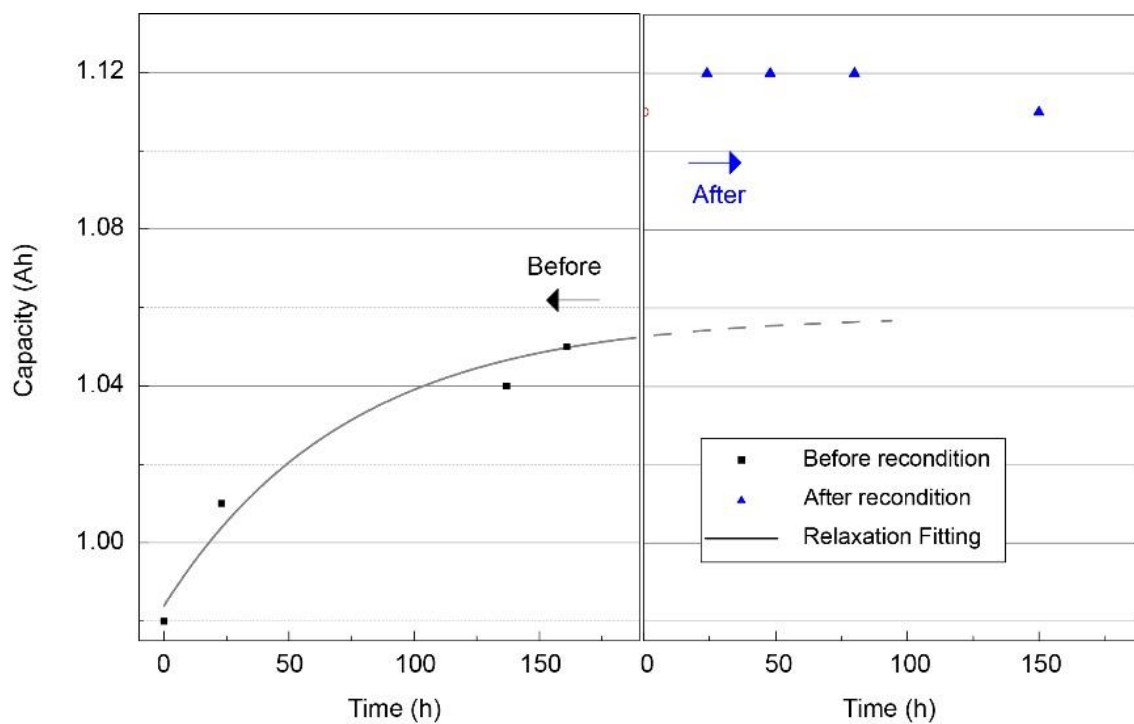
GBR Model Cross Validation



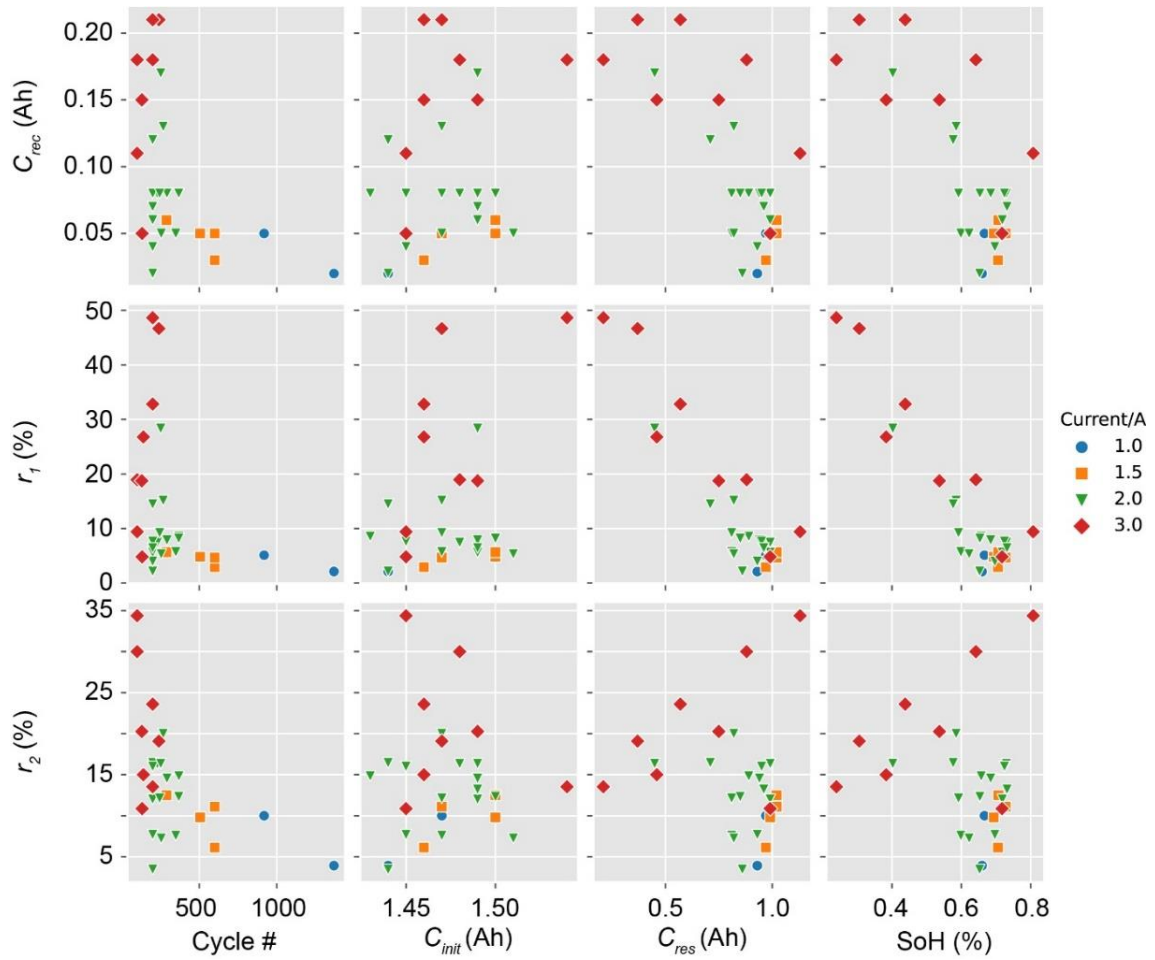
Supplemental Figure S8. GBR regression model cross validation.

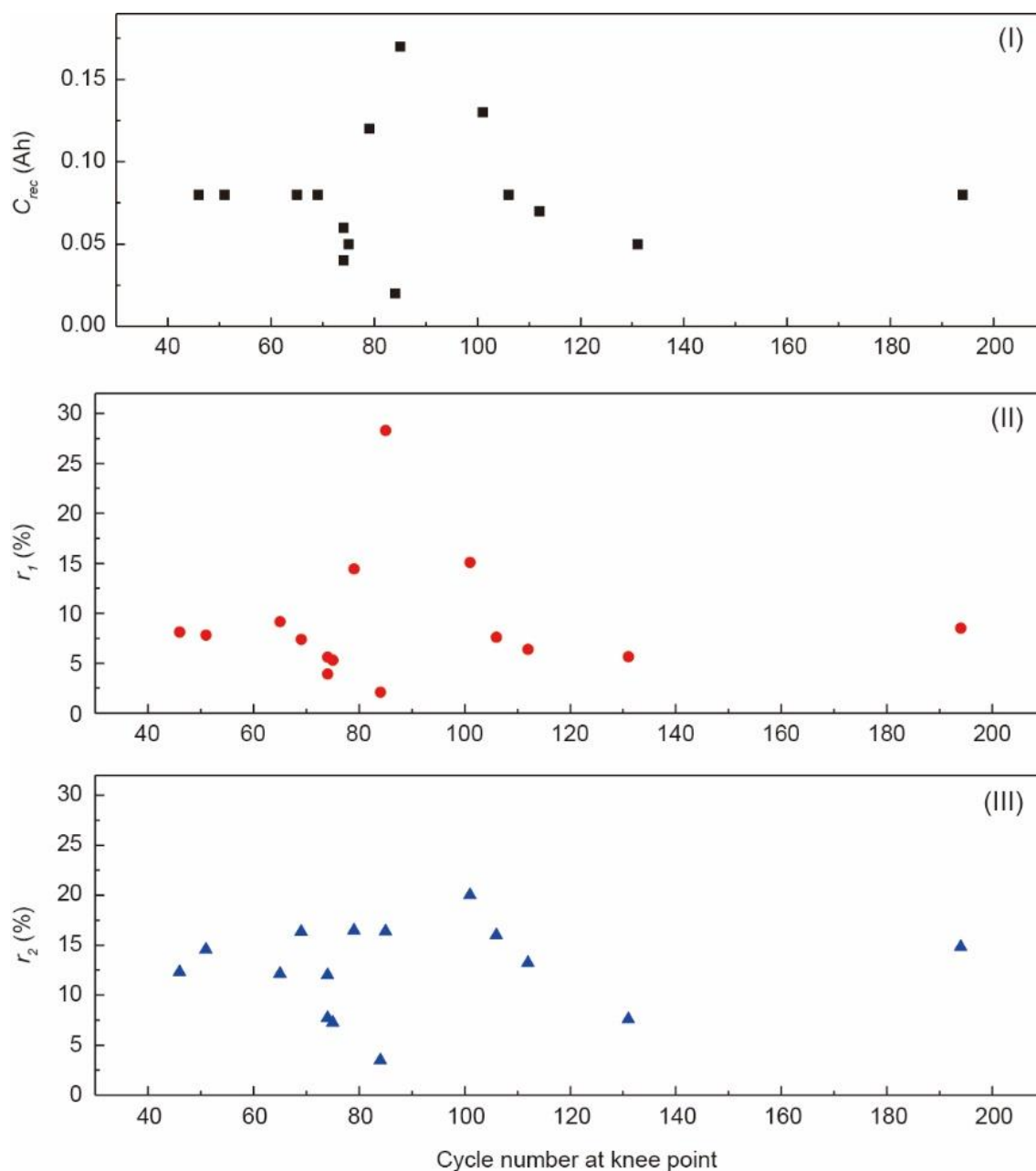
(A-E) GBR contour map of the validation set's RMSE from 5-fold train-validation, with the red circular dot representing the best RMSE for each fold, respectively.

(F-J) Parity plot of the model performance – fold 0 to 4 from left to right, with the MAPE given inside the brackets in the legend.

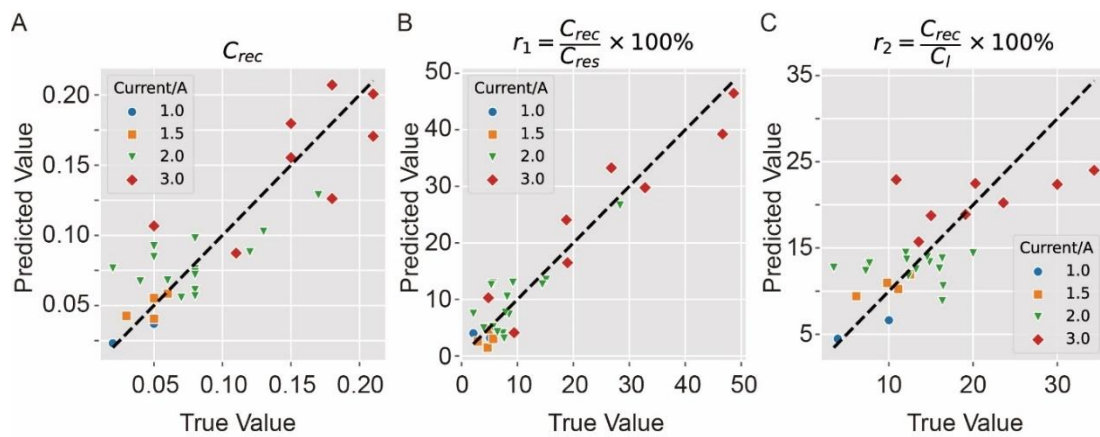


Supplemental Figure S9. Capacity changes of a cycled cell before and after reconditioning during open circuit voltage (OCV) storage. The fitted curve of rest before reconditioning follows $y = 1.058(1 - 0.07e^{-x/75.702})$.





Supplemental Figure S11. Correlations of cycle number at knee point with (I) recovered capacity (C_{rec}), (II) recovery rate (r_1) and (III) recovery rate (r_2) for the cells cycled at 2.0 A.

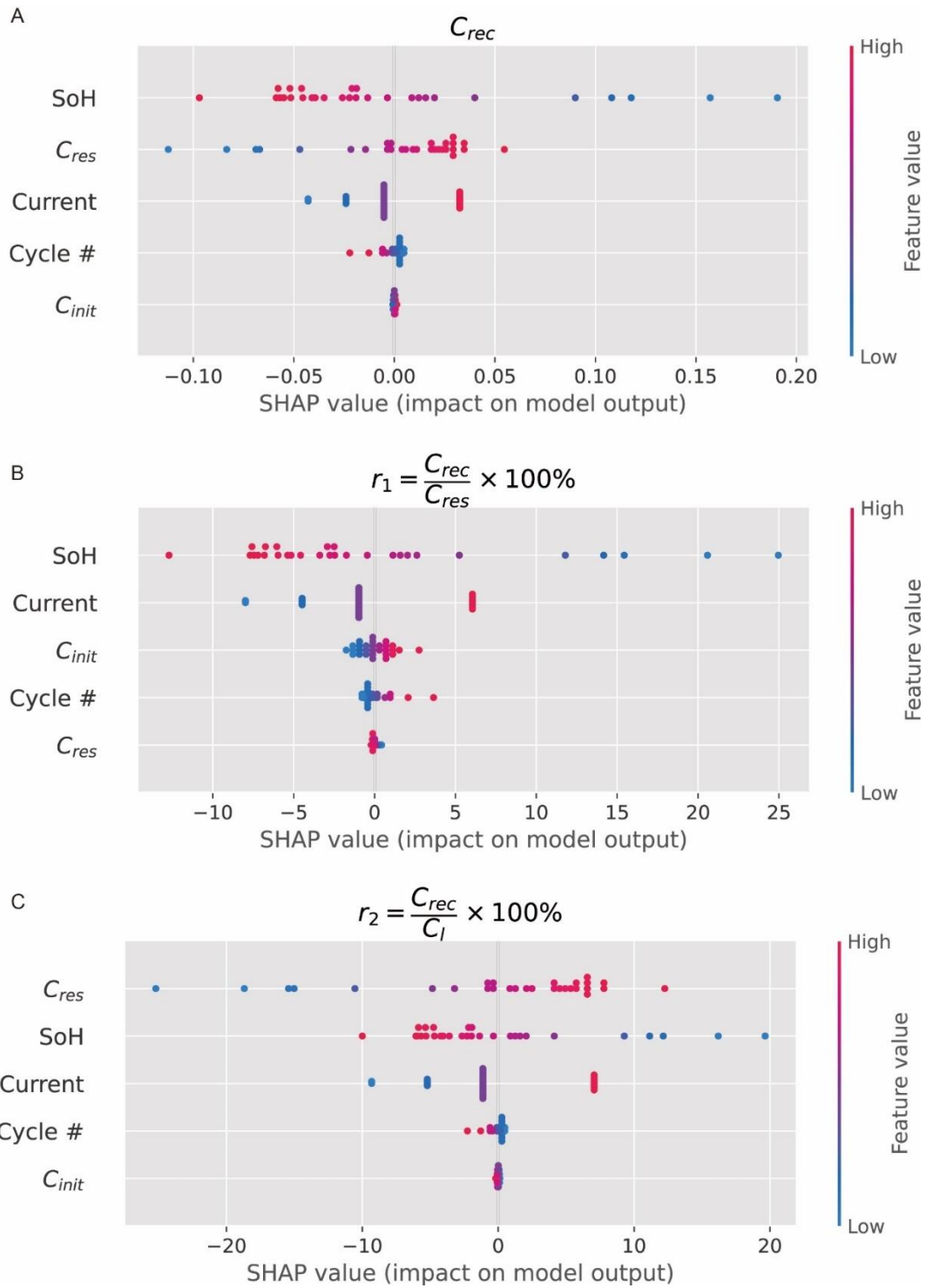


Supplemental Figure S12. Linear regression modeling of recovery rates with respect to SoH, residual capacity C_{res} , initial capacity C_{init} , cycle number, and cycling current.

(A) Recovered capacity (C_{rec}).

(B) recovery rate r_1 .

(C) recovery rate r_2 .



Supplemental Figure S13. SHAP analysis of the recovery metrics.

(A) C_{rec} with respect to cell's history and end of cycle state, i.e. cycle number (Cycle #), initial capacity (C_{init}), residual capacity (C_{res}), state of health (SoH) and current (Current).

(B) r_1 with respect to cell's history and end of cycle state, i.e. cycle number (Cycle #), initial capacity (C_{init}), residual capacity (C_{res}), state of health (SoH) and current (Current).

(C) r_2 with respect to cell's history and end of cycle state, i.e. cycle number (Cycle #), initial capacity (C_{init}), residual capacity (C_{res}), state of health (SoH) and current (Current).

2. Supplemental Tables

Supplemental Table S1. Cell cycling information and capacity recovery after reconditioning treatments.

C_i , C_{res} , C_{aft} and C_{rec} represent initial capacity, residual capacity, capacity after reconditioning and

recovered capacity, respectively. r_1 and r_2 are recovery rates defined as $r_1 = \frac{C_{rec}}{C_{res}} \times 100\%$ and $r_2 =$

$\frac{C_{rec}}{C_i} \times 100\%$.

Cell ID	Current/ A	Cycle #	$(C_i+C_{res})/$ Ah	$C_{res}/$ Ah	$C_{aft}/$ Ah	$C_{rec}/$ Ah	$r_1/\%$	$r_2/\%$
72	1.0	918	1.47	0.97	1.03	0.05	5.10	10.00
73	1.0	1368	1.44	0.93	0.97	0.02	2.11	3.92
Cella	1.5	600	1.46	0.97	1.06	0.03	2.91	6.12
CellG	1.5	506	1.50	0.99	1.09	0.05	4.81	9.80
CellJ	1.5	600	1.47	1.02	1.12	0.05	4.67	11.11
CellT	1.5	289	1.50	1.02	1.12	0.06	5.66	12.50
Cellf	2.0	200	1.49	0.99	1.13	0.06	5.61	12.00
Cellg2	2.0	369	1.43	0.89	1.02	0.08	8.51	14.81
Cellh2	2.0	230	1.48	0.99	1.16	0.08	7.41	16.33
Cellj2	2.0	292	1.49	0.94	1.10	0.08	7.84	14.55
Cellk2	2.0	268	1.47	0.82	0.99	0.13	15.12	20.00
Celll2	2.0	200	1.44	0.71	0.95	0.12	14.46	16.44
Cellm	2.0	200	1.45	0.95	1.13	0.08	7.62	16.00
Cello	2.0	245	1.47	0.81	0.95	0.08	9.20	12.12
Cellp2	2.0	368	1.50	0.85	1.06	0.08	8.16	12.31
Cellq2	2.0	252	1.49	0.45	0.77	0.17	28.33	16.35
Cellr2	2.0	349	1.47	0.81	0.93	0.05	5.68	7.58
Cells2	2.0	255	1.51	0.82	0.99	0.05	5.32	7.25
Cellu2	2.0	200	1.44	0.86	0.96	0.02	2.13	3.45
Cell81	2.0	200	1.49	0.96	1.16	0.07	6.42	13.21
Cell82	2.0	200	1.45	0.93	1.05	0.04	3.96	7.69
Cell15	3.0	100	1.48	0.88	1.13	0.18	18.95	30.00
Cell16	3.0	100	1.45	1.13	1.28	0.11	9.40	34.38
CellC10	3.0	240	1.47	0.37	0.66	0.21	46.67	19.09
CellC11	3.0	132	1.45	0.99	1.09	0.05	4.81	10.87
CellC12	3.0	200	1.46	0.57	0.85	0.21	32.81	23.60
CellC14	3.0	200	1.54	0.21	0.55	0.18	48.65	13.53
CellC16	3.0	140	1.46	0.46	0.71	0.15	26.79	15.00
CellC7	3.0	130	1.49	0.75	0.95	0.15	18.75	20.27

Supplemental Table S2. Cell cycling and reconditioning protocols. The number of cycles 919 here refers to a particular cell cycled at 1A whose data are fit by the ECM used.

Operation	Protocol	#Rep
Cycling	1. 1A CC charge to 4V -> 2min rest 2. 1A CC discharge to 2.5V -> 2min rest	919
Checkup	1. 0.3A CC charge to 3.6V -> 2min rest 2. 0.3A CC discharge to 2V - 2min rest	2
Voltage hold	2A CC charge to 3.6V -> 3.6V hold for 3 days -> 10min rest	1
Voltage hold	2A CC discharge to 2V -> 2V hold for 3 days -> 10min rest	1
Checkup	3. 0.3A CC charge to 3.6V -> 10min rest 4. 0.3A CC discharge to 2V - 10min rest	2

Supplemental Table S3. The measured and simulated discharge capacity at the last complete cycle (#918) during cycling, the second cycle of the pre-reconditioning capacity checkup, and the second cycle of the post-reconditioning checkup.

	Cycle 918	Pre checkup	Post checkup
Experiment dis Q [Ah]	0.967	0.995	1.030
Simulation dis Q [Ah]	0.972	0.995	1.034

Supplemental Table S4. ECM parameters to be fit to experiment data with their prior ranges.

Parameter	Range
R_2^\pm	[10m Ω , 300m Ω]
$k = R_1^\pm/R_2^\pm$	[1, 8]
$k_e = R_e/R_2^\pm$	[500, 2000]
Q_{max}^-	[1.1Ah, 2.2Ah]
$r_{N/P} = Q_{max}^-/Q_{max}^+$	[1, 2]
$z_1^-(t_0)$	[1e-8, 0.3]
$z_1^+(t_0)$	[0.7, 1 - 1e-8]
$z_2^-(t_0)$	[1e-8, 0.3]
$z_2^+(t_0)$	[0.7, 1 - 1e-8]

3. Supplemental Method

ECM Fitting Procedure. The ECM of Figure 4(B) has nine unknown parameters as listed in Table S5, and with each set of parameter values, it can be time-integrated by `scipy.integrate.solve_ivp` in the SciPy library to obtain the voltage response to any imposed voltage or current protocol. To fit the parameters, we use the protocols listed in Table S3 chained in a sequence, except that we only simulate the last three cycles (cycle 917 to 919) of the cycling part to reduce simulation costs. The initial time t_0 is set to the beginning of these initial three cycles. The model voltage responses for cycle 918, the second pre-reconditioning checkup cycle, and the two post-reconditioning checkup cycles are compared to their experimental counterparts and the optimal parameters are to minimize the mean squared errors based on these voltage data. This nonlinear least-square problem is then solved by the global optimization algorithm of differential evolution implemented as `scipy.optimize.differential_evolution` in the SciPy library, with the parameters constrained to the ranges listed in Table S5 chosen according to prior physical knowledge of the cell and some preliminary trial-and-error parameter exploration. The obtained parameter values are listed in Table 2.