# Classification of High-Ni NCA/Gr-Si Commercial Cells before Rapid Capacity Drop by Diagnosing the Heterogeneous Degradation

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## **Supporting Information**

### Supplementary Note 1. Cycling and reference performance test

Commercial NCA/Gr-Si cells (INR21700-50G, Samsung SDI) were utilized to obtain the cycling dataset in pristine and degraded states. As Co and Al reduce cation mixing (Li<sup>+</sup>/Ni<sup>2+</sup>) and mitigate the residual Li compound formation on the cathode surface, they improve rate capability for layered oxide cathodes.<sup>1-3</sup> Due to its high energy density and cycling stability, NCA cathode in combination with graphite-silicon anode has recently been considered a good candidate material for next-generation LiBs. Thus, it is also required to develop diagnostic methods for efficient management, so the corresponding model cell was selected for an aging experiment. This model cell employed the cathode with a high-Ni NCA composition (Ni: Co: Al = 0.792: 0.148: 0.06, measured by ICP-OES) to achieve high energy density. The nominal capacity (Qnom) of model cell suggested by the manufacturer specification is 4.9Ah. The cells were aged under desired operating conditions by using a cycler (CC 05-20, WONIK PNE) and a climatic chamber (LTO450-A-20, DAESUNG E&T). In order to monitor the degradation of cells during the first operation, the

reference performance test (RPT) was conducted every week at room temperature ( $25^{\circ}C$ ) after the 4-hour rest for the purpose of thermal equilibrium. The voltage curve under the 0.1C charging process of cells was acquired from RPT and was supposed to be the OCV for the non-destructive analysis. In order to evaluate the SoH level in each RPT, the capacity was measured at a CC discharge scheme with a current of 0.5C from the fully charged SoC after a 0.1C CC-CV charge scheme. All the measurements included a rest period of 4 hours. The aging period of the first operation lasted for 16 weeks, and cells with similar SoH were selected to examine the subsequent cycle performance.

#### Supplementary Note 2. Non-destructive analysis of degradation

The data processing in this study was performed using the Pandas, Numpy, and Scipy packages in Python. The DV and IC curves were smoothed through the moving average filter with a window size of 10 for the comparison of feature values under the relieved noise. The peak height in the DV curve was calculated by subtracting the second local minimum from the second local maximum. Likewise, the peak height in the IC curve was calculated by subtracting the third local minimum from the fourth local maximum. The 0.1C charging voltage curve was normalized by setting the 3.0V to 4.2V range as a 0–100% SoC for an equivalent comparison of each case based on the SoC–OCV curve. The deformation patterns of the SoC-OCV curve were categorized in terms of the curvature deformation (Case A) and the curve lifting (Cases B and C). The curvature deformation stood out around 4.1V, which was also observed at the decrease of the fourth peak height in the IC curve. The curve lifting was called the voltage increase characteristically revealed in a wide range of 3.5V to 3.8V from the SoC-OCV curve. The two factors were combined by antagonistic interaction when establishing the health indicator in order to suggest the factor that dominantly contributed to the capacity loss. To examine the different degradation paths of cases, the impedance was analyzed after being measured by the EIS (SP-150e, BioLogic) at 50% of the SoC level. Nyquist plots were interpreted with electrical elements including the R<sub>ohm</sub>, R<sub>SEI</sub>, R<sub>ct</sub>, and Z<sub>w</sub> by adopting the second-order Randles circuit as an equivalent circuit model.<sup>4</sup> The R<sub>ct</sub> could be increased as the high-Ni cathode degraded,<sup>5,6</sup> whereas it was reported that the R<sub>ct</sub> decreased

during the occurrence of lithium plating on the anode surface.<sup>7</sup> Thus, the growth of  $R_{ct}$  was utilized for the comparison of cathode degradation.

## Supplementary Note 3. Cell disassembly & postmortem analysis

The degraded cells disassembled in a dry-room environment. Each electrode was rinsed with DMC solvent for the half-cell test and the observation of surface morphology. The cathode and anode samples for the half-cell test were collected from the core region of each electrode to monitor the degraded states. The 2032-coin cell was assembled by containing the 14-pi-size working electrode (NCA cathode or Gr-Si anode punched from the INR21700-50G cell), 16-pi-size lithium metal, a 19-pi-size separator (CELGARD<sup>®</sup>, 2320, 20µm thickness PP/PE/PP membrane with 39% porosity), and a 70-ml electrolyte of 1.0M LiPF<sub>6</sub> in EC/DMC=1/2(v/v)+2%VC (Sigma-Aldrich). The half-cell test was conducted by using the cell cycler (WBCS 3000, WonATech) in a climatic chamber (LI-IL250, LKLabKorea). The morphologies of anodes before and after the second operation were observed through SEM-EDS analysis from the Cold Field Emission Scanning Electron Microscope (HITACHI, S-4800). While there was no notable deformation in Case A before second operation, the anodes in Cases B and C showed the deformed surface, including the expansion or pulverization of Si compound. It could be possible that the trapped lithium accumulates in anode materials under specific operating conditions due to Li<sup>+</sup> crosstalk between Si and graphite or a two-way diffusion mechanism.<sup>8,9</sup> The deformed morphology might result in increasing the pressure on adjacent particles and clogging the pore, which would hinder the lithiation process. After the second operation, the graphite anode materials of Cases B and C were widely covered by impurities with oxygen components, which were not likely to come from silicon oxide compounds considering the distribution of Si components in EDS. It has been reported that lithium deposition can occur without an internal short circuit.<sup>10</sup> In the meantime, inactive lithium can be made during plating by quickly forming SEI, which blocks the electrically conductive network.<sup>11</sup> Thus, it is considered that the sluggish lithiation of the degraded anode caused the lithium deposition, and the violent side reactions occurred during rapid capacity drops in Cases B and C. The stress distribution on graphite materials between the core and the skin region of the anode was investigated by the Raman spectroscope (WITec, alpha300R) with laser settings of 532 nm and 1 mW power. The results of SEM-EDS and Raman spectroscopy were obtained using the equipment of UNIST Central Research Facilities (UCRF).

#### Supplementary Note 4. Feature extraction & processing

In order to automatically determine the characteristic points on the IC curve with a smoothing process, the Lorentzian function-based fitting method was employed using the nonlinear least squares algorithm in the Scipy package of Python.<sup>12</sup> The characteristic points of a pristine state were measured from the mean value of 100 cells in their pristine state. Based on these points of pristine state, features from degraded cells were extracted following the suggested equations to represent the curvature deformation and curve lifting factors. The Gompertz model consists of the asymptote ( $\theta_1$ ), x-axis displacement ( $\theta_2$ ), and growth rate ( $\theta_3$ ) as parameters that determine the activation function for feature processing. This study employed the parameter values as  $\theta_1 = 2$ ,  $\theta_2 = 3$ , and  $\theta_3 = 0.632$ .



**Fig. S1** Inspection by non-destructive analysis in the pristine state: Each case has an overlapped (a) voltage curve, (b) DV curve, and (c) IC curve, showing that they were in uniform states before operation.



**Fig. S2** Comparison of the cycle performance (under 1C/1.25C DOD100% at  $45^{\circ}$ C) between reference cells and degraded cells. Case A followed the capacity loss of reference cells, but Cases B and C showed rapid capacity drops.



**Fig. S3** Inspection by non-destructive analysis after the first operation: (a) Different shapes of voltage curves despite similar capacity levels. (b) Comparison of features on the second peak of the DV curve that showed a decreasing tendency in the order of severe capacity loss during the second operation. (c) Comparison of features on the fourth peak of the IC curve that showed a decreasing tendency in the order of mild capacity loss during the second operation.



**Fig. S4** Resistance growth after the first operation: (a) Nyquist plots of each case from EIS measurement. (b) Equivalent circuit model based on the second order Randles circuit for the quantification of each element in the Nyquist plot. (c) The result table of quantified elements with a significant growth of  $R_{ct}$  in Case A but less growth of  $R_{ct}$  in Cases B and C.



**Fig. S5** Electrode half-cell test to approach the voltage curve deformation of the aged cell: (a) Cathode voltage curves in each case sequentially showing the capacity loss, and (b) cathode IC curves with the variation of peak height in the H2-H3 phase exhibiting the loss of cathode active materials. (c) Anode voltage curves in each case without distinct capacity loss, and (d) the anode IC curves with little deformation.



**Fig. S6** Each electrode and separator after disassembly: (a) Case A with ordinary exteriors before and after the second operation. (b) Case B with anode exfoliation at the core region after the rapid capacity drop in the second operation. (c) Case C with anode exfoliation in the overall region after the most severe capacity drop in the second operation.



**Fig. S7** Morphology of each cell anode from SEM-EDS analysis (red – C, orange – Si, green – O, yellow – F, cyan – P): (a) Anode morphologies in Case A without distinct deformation during entire operations. (b) Anode morphologies in Case B with pulverized Si compound clogging the porous structure before the second operation and with mossy-like lithium plating after the second operation. (c) Anode morphologies in Case C with the expanded Si compound before the second operation and with mossy-like lithium plating after the second operation.



**Fig. S8** Illustration of feature extraction. Curvature deformation in the H2-H3 phase (around 4.1V) and curve lifting factors in the low voltage range (around 3.5-3.8V) would be extracted by using the features based on the characteristic points on the IC curve (bottom).



**Fig. S9** Diagnosis by the DV curve analysis: The comparison of a feature on the second DV peak ( $\Delta$ h within the dashed lines) at (a) SoH 94% and (b) SoH 91% levels. (c) Plot of feature values that cause confusion for the classification of degradation paths due to the poor resolution.



**Fig. S10** Coulombic efficiency (CE) during the rate capability test: (a) The comparison of CE between  $C_{max}$  and  $D_{max}$  cases collected at SoH 94% (average CE for  $C_{max, 94}$  vs.  $D_{max, 94}$  / 0.3C: 99.86% vs. 99.91%; 0.5C: 99.93% vs. 99.96%; 0.7C: 99.93% vs. 99.96%; 1.0C: 99.84% vs. 99.90%; 0.5C duration: 99.90% vs. 99.95%). (b) The comparison of CE between  $C_{max}$  and  $D_{max}$  cases collected at SoH 91% (average CE for  $C_{max, 91}$  vs.  $D_{max, 91}$  / 0.3C: 99.81% vs. 99.93%; 0.5C: 99.76% vs. 100.1%; 0.7C: 99.68% vs. 100.06%; 1.0C: 98.93% vs. 100.01%; 0.5C duration: 99.64% vs. 100.09%).



**Fig. S11** The result of the rate capability test from the energy (Wh) perspective: (a) Wh-capacity and (b) energy efficiency (EE, Wh<sub>dis</sub>/Wh<sub>ch</sub>) of C<sub>max</sub> and D<sub>max</sub> cases collected at SoH 94% (average EE for C<sub>max, 94</sub> vs. D<sub>max, 94</sub> / 0.3C: 94.19% vs. 94.05%; 0.5C: 92.32% vs. 92.21%; 0.7C: 90.17% vs. 90.15%; 1.0C: 87.18% vs. 87.45%; 0.5C duration: 91.97% vs. 91.98%). (c) Wh-capacity and (d) EE of C<sub>max</sub> and D<sub>max</sub> cases collected at SoH 91% (average EE for C<sub>max, 91</sub> vs. D<sub>max, 91</sub> / 0.3C: 93.57% vs 93.12%; 0.5C: 91.29% vs. 91.14%; 0.7C: 88.79% vs. 88.86%; 1.0C: 84.69% vs. 86.0%; 0.5C duration: 89.92% vs. 90.94%).

# **a** Pristine



**Fig. S12** The observation of electrode surface variations from cells of the  $C_{max}$  case: The electrode surface without the lithium deposition in (a) Pristine and (b) after 60 cycles. The local lithium deposition in the core region (c) after 75 cycles and its aggravation (d) after failure.

Category	Specification
Manufacturer	SAMSUNG SDI
Model	INR 21700-50G
Dimensions	21.14 x 70.38 mm
Weight	68.8 g
Nominal capacity	4.9Ah
	(Charge: 0.33C, 4.2V, 0.025C cut-off @ RT / Discharge: 0.2C, 2.5V cut-off @ RT)
Nominal voltage	3.63V
Max charge current	1C (4.9A)
Max discharge current	2C (9.8A) for continuous / 3C (14.7A) not for continuous
Operating Temperature	0 to 45 °C for charge / -20 to 60 °C for discharge
(Cell surface)	
Cycle life	80% (3.92Ah) after 1000 cycles
	@ RT, 0.33C, 4.2V 0.05C CCCV cut-off for charge and 1C,

 Table. S1 Manufacturer specification of commercial cell adopted for aging experiment.

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