



공학박사 학위논문

Quantifying Electrode Heterogeneity for Diagnosing the Degradation of Lithium Ion Batteries

전극의 불균일도 정량화를 통한 리튬 이온 배터리 열화 진단

2023년 8월

서울대학교 대학원 화학생물공학부 김 민 수

Quantifying Electrode Heterogeneity for Diagnosing the Degradation of Lithium Ion Batteries

전극의 불균일도 정량화를 통한 리튬 이온 배터리 열화 진단

지도 교수 최장욱

이 논문을 공학박사 학위논문으로 제출함 2023년 7월

서울대학교 대학원 화학생물공학부 김 민 수

김민수의 공학박사 학위논문을 인준함 2023년 6월

위 육	원 장	성영은	(인)
부위	원장	최장욱	(인)
위	원	이규태	(인)
위	원	김 기 재	(인)
위	원	문 준 영	(인)

Abstract

Electric vehicles (EVs) are imposing ever-challenging standards on the lifetime and safety of lithium-ion batteries (LIBs). Diagnosing the status of lithium-ion batteries is the critical step toward the electric vehicle era. Cell diagnosis is always required throughout batteries' whole life from the manufacturing stage, even after the end of life for reusing. This dissertation searched the quantifiable chemical indicators that monitor the internal status of a cell based on the understanding for chemical mechanism.

Firstly, at the post-manufacturing stage, cell inspection and classification of lithium ion batteries are the compulsory step for the transition to the electric vehicle era requiring high standard of safety and reliability. To meet high standard, it is important to sort out defective cells at the source before cells are loaded on EVs containing hundreds to thousands of cells. Consequently, it is important to diagnose the internal status and grade cells' performance at the stage of post-manufacturing. Heterogeneity indicator, or the electrochemical signal in differential voltage profile, is introduced as a key tool for cell inspection and classification. Specifically, the indicator is associated with the 'heterogenous' status inside cells such as uniform arrangement of electrodes, which affect uniformity of lithiation in a graphite anode. Importantly, the heterogeneous cells tended to exhibit lower cycle performance, which enables the heterogeneity indicator at the initial cycle to

iii

predict cycle life of cells and to classify cells for assembling modules. In practice, the module containing the consistent cells sorted by the heterogeneity indictor improved cycle performance than that of inconsistent cells. The chemical indicators such as heterogeneity indicator can contribute to ensure highly reliable and safe module by inspecting and sorting cells at the post-manufacturing stage.

Secondly, during operation of EVs, real-time non-destructive highly desired. monitoring of battery cell degradation is Unfortunately, high-nickel layered oxides, the preferred LIB cathodes for EVs, undergo performance degradation originating from micro-crack formation during cycling. Entropymetry is introduced as a real-time analytic tool for monitoring the evolution of microcracks in these cathodes along the state of charge. The entropy change of the layered cathode is associated with the lattice configuration and reflects the structural heterogeneity relevant to the evolution of these micro-cracks. The structural heterogeneity was correlated with peak broadening in *in-situ* X-ray diffractometry while varying the experimental conditions that affect crack formation such as the upper cut-off voltage during charging and the Ni-content of the active material. Entropymetry, proposed here as a nondestructive diagnostic tool, can contribute greatly to the safe and reliable operation of LIBs for EVs.

In summary, we introduced the chemical indicators that reflect the status inside batteries; the heterogeneity indicator for graphite anodes and entropymetry for Ni-rich cathodes. Both of the indicators were quantified as the peak height in differential voltage profile and

iv

the peak height in entropy change profile, which are attributed to the chemical phenomena inside a cell. At last, the chemical indicators were demonstrated as useful tools for monitoring and inspecting the inside of cells, with the ultimate goal of improving the safety and reliability of LIBs.

Keywords : Lithium ion batteries, battery diagnosis, heterogeneity, cell inspection, cell classification, entropymetry Student Number : 2020-37781

Table of Contents

1. Introduction 1
1.1. Transition to the electric vehicle era 1
1.2. Battery diagnostics based on chemical understanding 2
1.3. The chemical indicators identifying heterogeneity inside a
cell 4
1.4. References 5
2. Lifetime prediction of lithium ion batteries by using the
heterogeneity of graphite anodes
2.1. Introduction
2.2. Result and discussion1 2
2.2.1. Heterogeneity of Gr anodes 1 2
2.2.2. $\Delta Peak_{S2}$ as a key descriptor for electrode heterogeneity
2.2.3. Lifetime prediction of LFP/Gr cells by correlating with
⊿Peak _{S2}
2.2.4. Peak _{S2} as a tool of cell inspection
2.3 Conclusion
2.4 Experimental procedures
2.5 References
3. Entropymetry for detecting micro-cracks in high-nickel
layered oxide cathodes 4 8
3.1. Introduction

초	록	8	2
4. C	Conclusion	8	0
	3.5. References	7	5
	3.4. Experimental procedures	7	1
	3.3. Conclusion	7	1
	oxides	6	9
	3.2.5. Generalization across the family of high-Ni layered		
	3.2.4. Detection of micro-cracks from ΔS profiles	6	4
	3.2.3. Structural heterogeneity by micro-crack formation	5	8
	3.2.2. Structural changes of NCM811 along with the SOC	5	6
	3.2.1. Interpretation of ΔS profiles	5	2
	3.2. Result and discussion	5	2

List of Tables

List of Figures

Figure 1.1 Cumulative EV sales and EV market share. Battery, plug-
in hybrid and hydrogen fuel-cell EVs are all included 1
Figure 1. 2 Cell diagnosis and management of LIBs at each step in the
life cycle of LIBs
Figure 1. 3 Heterogeneity from particle, electrode to cell level in a
LIB
Figure 2. 1 Heterogeneity of Gr anodes and relation to voltage
profiles. Scheme showing the relation between spatial homogeneity
of lithiation in the Gr anode and voltage profile1 3
Figure 2. 2 Voltage and corresponding DV profiles of an LFP/Gr
cylindrical cell as a function of the capacity during charge consisting
of different stages1 4
Figure 2. 3 DV profiles against the capacity under different cycling
conditions 1 5
Figure 2. 4 $\Delta Peak_{S2}$ and $\Delta Peak_{S4}$ vs. SOH for four different cycling
conditions 1 6
Figure 2. 5 $\Delta Peak_{S4}$ is defined. Same voltage and DV profiles of the
LFP/Gr cylindrical cell shown in Figure 2. 2 1 7
Figure 2. 6 DV vs. capacity profiles during discharge under different
cycling conditions17
Figure 2. 7 SEM and optical (center) images of the Gr anodes of a
fresh unrolled LFP/Gr cell
Figure 2.8 SEM and optical (center) images of the Gr anodes of an
LFP/Gr cell cycled at 1C@ 25 ° C until SOH80 was reached1 9

Figure 2. 9 SEM and optical (center) images of the Gr anodes of				
LFP/Gr cell cycled at 2C@ 25 $^\circ$ C until SOH80 was reached 2 0				
Figure 2. 10 TOF-SIMS results of the Gr anodes in the LFP/Gr cells				
before cycling (SOH100), and after cycling at $1C@25\ ^\circ$ C and				
$2\text{C}@25\ ^\circ$ C until SOH80 was reached2 1				
Figure 2. 11 DMC solvent used for washing the jellyrolls of LFP/Gr				
cells: before cycling and after cycling (SOH80) at 1C@25 $^\circ$ C and				
2C@25 ° C 2 2				
Figure 2. 12 Correlation between electrode heterogeneity and cycle				
life				
Figure 2. 13 Correlation between electrode heterogeneity and				
electrode arrangement of LFP/Gr cylindrical cells				
Figure 2. 14 Vertical cross-sectional XRM images of the				
homogeneous and heterogeneous LFP/Gr cylindrical cells				
Figure 2. 15 MCC method for calculation of the roundness about the				
enlarged void at the core of the jellyrolls in the homogeneous and				
heterogeneous cells				
Figure 2. 16 Correlation between the life cycle and $Peak_{S2}$ intensity				
Figure 2. 17 Cycle life vs. $\Delta Peak_{S2}$ intensity plot with correlation				
coefficient of 0.75				
Figure 2. 18 Comparison of RMSE values during 1000 iterations				
between the dummy regressor and $Peak_{S2}$ intensity, $Peak_{S4}$ intensity,				
1^{st} <i>IR</i> , 1^{st} <i>Q</i> , and Var ($\angle Q_{100-10}(V)$)				
Figure 2. 19 Correlation of cycle life with $Peak_{S4}$ intensity, 1^{st} <i>IR</i> , 1^{st}				
Q , and Var ($\Delta Q_{100-10}(V)$)				

Figure 2. 20 Peak_{s2}-based diagnosis for module assembly. Using Peak_{S2} for the high-quality inspection of as-manufactured cells for Figure 2. 21 Module construction according to cell classification Figure 2. 22 Capacity distributions of six cells in each module group classified based on similar capacity and middle Peak_{S2}. IR distributions of six cells in each module group classified based on Figure 2. 23 Deviation of Peak_{S2} intensity vs. deviation of capacity decay of individual cells in different modules. Box plots for capacity **Figure 3.1** ΔS (black) and $dQ dV^{-1}$ (blue) profiles of NCM811 along the open circuit voltage (OCV) landscape. Schematic diagrams of entropy (S) and entropy change (ΔS) with different degrees of Figure 3. 2 Comparison of calculated and measured ΔS of NCM811 as **Figure 3. 3** Evolution of the *in-situ* XRD profiles around the (003) and (110) peaks during the first charging of NCM811 after precycling.

Figure 3. 4 Cross-sectional SEM images of NCM811 particles after precycle and at 101^{th} cycle at 60 ° C with upper cut-off of 4.1 V and 4.3 V. The scale of the white bar is 5 μ m. Magnified *in-situ* XRD profiles near (003) peaks at OCVs of 4.15 V, 4.2 V, and 4.25 V. 5 9 Figure 3. 5 Voltage profiles at the 2nd and 100th cycles for NCM811

1. Introduction

1.1. Transition to the electric vehicle era

As the climate change emerge as one of the most important agendas, the whole world has tried to reduce carbon emission.¹ The electrical vehicles (EVs) are one effort to reduce carbon emission from internal combustion engines.² In fact, regulations on internal combustion engines was being reinforced around the world and the supply of EVs is increasing. In detail, the market share of EVs is expected to increase up to 80% with cumulative EVs sales exceeding 1800 million by 2060 (Figure 1. 1).³



Figure 1.1 Cumulative EV sales and EV market share. Battery, plugin hybrid and hydrogen fuel-cell EVs are all included. Adapted from Cano et al.³

1.2. Battery diagnostics based on chemical understanding

Battery diagnosis and management will become more and more important as lots of EV drivers demand high reliability and safety for their EVs. In practice, cell diagnosis is inseparable from the entire life cycle of a battery form manufacturing to disposal (Figure 1. 2):

1) At the post-manufactured stage, cell inspection should screen out faulty cells.^{4, 5}

2) After inspection, cells are assembled into module and packs. At this stage, normal cells also need to be classified based on their performance.^{6, 7}

3) Once mounted on an EV, battery manage systems (BMSs) monitor and manage the batteries.^{8, 9}

4) After the end of life, batteries of EVs can be recycled into energy storage systems requiring lower power.^{10, 11}

However, it is still not enough to fully monitor and manage the health state of batteries. To do this, it is highly important to understand the internal status of the battery because all phenomena attribute to some physiochemical or electrochemical mechanism. Therefore, tremendous analyzes have been conducted to understand the chemical mechanism.¹² The shape and structure of the materials in a cell could be observed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM).¹³ And the surface of materials could be investigated by X-ray photoelectron

(XPS),¹⁴ time-of-flight secondary ion spectroscopy mass (TOF-SIMS),¹⁵ spectrometry energy dispersive *X*-rav spectroscopy (EDX).¹⁶ Also, electrolyte could be assessed through Raman spectroscopy,¹⁷ gas chromatography (GC).¹⁸ However, all of the above techniques helpful in understanding the chemical mechanism, but require cell disassembly. On the other hand, some techniques such as ultrasonic,¹⁹ X-ray,⁴ and thermography⁵ could identify the internal status of a cell without disassembly, but they require separate devices and are difficult to measure. Therefore, for practical use, it is ideal to investigate the internal status of a cell with current, voltage, and temperature that were already accessible or easily measurable.



Figure 1. 2 Cell diagnosis and management of LIBs at each step in the life cycle of LIBs.

Besides the aforementioned requisites, it can be used as a diagnostic tool only when it is possible to quantify a chemical phenomenon that indicates a specific state inside the cell. This is because cell inspection and BMS must numerically judge the state of the cell. Therefore, battery chemists need to identify the chemical indicators that quantify the internal status of a cell. The inspection tools and BMSs for LIBs would become accurate and sophisticated by utilizing diverse chemical indicators. Furthermore, identifying better chemical indicators could improve the reliability of EVs and advance the EV era.

1.3. The chemical indicators identifying heterogeneity inside a cell

Heterogeneity exists everywhere in battery systems, from the nanoscale to the macroscale (Figure 1. 3).⁸ In dynamic state such as charging, the concentration of Li ions would be uneven all over the place, from a particle of active materials to electrodes.²⁰ In static state, in addition, differences in pressure or temperature across the cell might cause spatially different distributions of lithium ions.²¹ Therefore, the condition inside a cell would affect the distribution of Li concentration. For example, the damaged region in active materials would retard the flow of Li ions.²² Also, local variation of temperature or pressure in a cell could induce different kinetics of Li ions.²³ In this light, the heterogeneity inside a cell could monitor the comprehensive status inside a cell. In detail, in this dissertation, the

structural change of the high-nickel cathode materials was monitored by entropy change. And the degree of uniformity on the graphite (Gr) electrode was assessed by the specific peak intensity in the differential voltage (DV) profile during charge. It is sure that the introduced chemical indicators, or the entropy change and the peak intensity in DV profile, would improve reliability and safety of EVs and the overall supply system of LIBs.



Figure 1. 3 Heterogeneity from particle, electrode to cell level in a LIB. (A) Adapted from Tian et al.²¹ (B) Ho et al.²⁴ (C) Senyshyn et al.²⁵

1.4. References

1. Gallego-Álvarez, I.; Segura, L.; Martínez-Ferrero, J., Carbon emission reduction: the impact on the financial and operational performance of international companies. *Journal of Cleaner Production* **2015**, *103*, 149–159.

2. Canals Casals, L.; Martinez-Laserna, E.; Amante García, B.; Nieto, N., Sustainability analysis of the electric vehicle use in Europe for CO2 emissions reduction. *Journal of Cleaner Production* **2016**, *127*, 425-437.

3. Cano, Z. P.; Banham, D.; Ye, S. Y.; Hintennach, A.; Lu, J.; Fowler, M.; Chen, Z. W., Batteries and fuel cells for emerging electric vehicle markets. *Nature Energy* **2018**, *3* (4), 279–289. 4. Masuch, S.; Gümbel, P.; Kaden, N.; Dröder, K. Applications and Development of X-ray Inspection Techniques in Battery Cell Production *Processes* [Online], 2023.

5. Sharp, N.; O'Regan, P.; Adams, D.; Caruthers, J.; David, A.; Suchomel,
M., Lithium-ion battery electrode inspection using pulse thermography. *Ndt*& E International 2014, 64, 41-51.

 Li, W.; Chen, S. Q.; Peng, X. B.; Xiao, M.; Gao, L.; Garg, A.; Bao, N.
 S., A Comprehensive Approach for the Clustering of Similar-Performance Cells for the Design of a Lithium-Ion Battery Module for Electric Vehicles. *Engineering* 2019, 5 (4), 795-802.

7. Wang, Q.; Cheng, X. Z.; Wang, J. In *A new algorithm for a fast testing and sorting system applied to battery clustering*, 2017 6th International Conference on Clean Electrical Power (ICCEP), 27–29 June 2017; 2017; pp 397–402.

8. Wang, Y. J.; Tian, J. Q.; Sun, Z. D.; Wang, L.; Xu, R. L.; Li, M. C.; Chen, Z. H., A comprehensive review of battery modeling and state estimation approaches for advanced battery management systems. *Renew Sust Energ Rev* 2020, *131*, 110015.

9. Shen, M.; Gao, Q., A review on battery management system from the modeling efforts to its multiapplication and integration. *International Journal of Energy Research* **2019**, *43* (10), 5042–5075.

10. Liao, Q. Q.; Mu, M. M.; Zhao, S. Q.; Zhang, L. Z.; Jiang, T.; Ye, J. L.; Shen, X. W.; Zhou, G. D., Performance assessment and classification of retired, lithium ion battery from electric vehicles for energy storage. *International Journal of Hydrogen Energy* **2017**, *42* (30), 18817–18823.

11. Zhou, Z. K.; Duan, D.; Kang, Y. Z.; Shang, Y. L.; Cui, N. X.; Chang, L.; Zhang, C. H., An efficient screening method for retired lithium –ion batteries based on support vector machine. *Journal of Cleaner Production* **2020**, *267*, 121882.

12. Waldmann, T.; Iturrondobeitia, A.; Kasper, M.; Ghanbari, N.; Aguesse,
F.; Bekaert, E.; Daniel, L.; Genies, S.; Gordon, I. J.; Löble, M. W.; De Vito,
E.; Wohlfahrt-Mehrens, M., Review—Post-Mortem Analysis of Aged
Lithium-Ion Batteries: Disassembly Methodology and Physico-Chemical

Analysis Techniques. *Journal of The Electrochemical Society* **2016**, *163* (10), A2149-A2164.

McDowell, M. T.; Lee, S. W.; Harris, J. T.; Korgel, B. A.; Wang, C.;
 Nix, W. D.; Cui, Y., In Situ TEM of Two-Phase Lithiation of Amorphous
 Silicon Nanospheres. *Nano Letters* 2013, *13* (2), 758-764.

Blyth, R. I. R.; Buqa, H.; Netzer, F. P.; Ramsey, M. G.; Besenhard, J.
O.; Golob, P.; Winter, M., XPS studies of graphite electrode materials for lithium ion batteries. *Applied Surface Science* 2000, *167* (1-2), 99-106.

15. Ota, H.; Akai, T.; Namita, H.; Yamaguchi, S.; Nomura, M., XAFS and TOF-SIMS analysis of SEI layers on electrodes. *Journal of Power Sources* **2003**, *119*, 567–571.

 Sarkar, A.; Velasco, L.; Wang, D.; Wang, Q.; Talasila, G.; de Biasi, L.;
 Kubel, C.; Brezesinski, T.; Bhattacharya, S. S.; Hahn, H.; Breitung, B., High entropy oxides for reversible energy storage. *Nat. Commun.* 2018, *9* (1), 3400.

17. Ruther, R. E.; Callender, A. F.; Zhou, H.; Martha, S. K.; Nanda, J., Raman Microscopy of Lithium–Manganese–Rich Transition Metal Oxide Cathodes. *Journal of The Electrochemical Society* **2014**, *162* (1), A98– A102.

18. Gachot, G.; Ribiere, P.; Mathiron, D.; Grugeon, S.; Armand, M.; Leriche, J. B.; Pilard, S.; Laruelle, S., Gas chromatography/mass spectrometry as a suitable tool for the Li-ion battery electrolyte degradation mechanisms study. *Anal Chem* **2011**, *83* (2), 478-85.

19. Zappen, H.; Fuchs, G.; Gitis, A.; Sauer, D. U., In-Operando Impedance Spectroscopy and Ultrasonic Measurements during High-Temperature Abuse Experiments on Lithium-Ion Batteries. *Batteries* **2020**, *6* (2), 25.

20. Klink, S.; Schuhmann, W.; La Mantia, F., Vertical Distribution of Overpotentials and Irreversible Charge Losses in Lithium Ion Battery Electrodes. *ChemSusChem* **2014**, *7* (8), 2159–2166.

Tian, C. X.; Xu, Y. H.; Nordlund, D.; Lin, F.; Liu, J.; Sun, Z. H.; Liu, Y.
J.; Doeff, M., Charge Heterogeneity and Surface Chemistry in Polycrystalline Cathode Materials. *Joule* 2018, 2 (3), 464-477.

22. Wang, J.; Kim, H.; Hyun, H.; Jo, S.; Han, J.; Ko, D.; Seo, S.; Kim, J.; Kong, H.; Lim, J., Probing and Resolving the Heterogeneous Degradation of Nickel-Rich Layered Oxide Cathodes across Multi-Length Scales. *Small Methods* **2020**, *4* (10), 2000551.

23. Robinson, J. B.; Darr, J. A.; Eastwood, D. S.; Hinds, G.; Lee, P. D.; Shearing, P. R.; Taiwo, O. O.; Brett, D. J. L., Non-uniform temperature distribution in Li-ion batteries during discharge – A combined thermal imaging, X-ray micro-tomography and electrochemical impedance approach. *J Power Sources* **2014**, *252*, 51–57.

24. Ho, A. S.; Parkinson, D. Y.; Finegan, D. P.; Trask, S. E.; Jansen, A. N.; Tong, W.; Balsara, N. P., 3D Detection of Lithiation and Lithium Plating in Graphite Anodes during Fast Charging. *ACS Nano* **2021**, *15* (6), 10480–10487.

25. Senyshyn, A.; Muhlbauer, M. J.; Dolotko, O.; Hofmann, M.; Ehrenberg,
H., Homogeneity of lithium distribution in cylinder-type Li-ion batteries. *Sci. Rep.* 2015, 5 (1), 18380.

8

2. Lifetime prediction of lithium ion batteries by using the heterogeneity of graphite anodes

2.1. Introduction

The accelerated transition to electric vehicles (EVs) in the mobility sector is driving the production of enormous numbers of battery cells. Each EV contains hundreds to thousands of cells depending on the type of cell.^{1, 2, 3} Warranting the safe and durable cycling of these cells with high reliability requires the internal status of each lithium ion battery (LIB) cell to be diagnosed and graded at the post-manufacturing stage and during cycling.^{4, 5, 6} In the current battery value chain, cell makers inspect the quality of manufactured cells by evaluating the capacity, direct current internal resistance (DCIR), drop in the open circuit voltage (OCV), etc.^{7,8} The internal features of a battery cell can also be examined by using tools such as acoustic spectroscopy,^{9, 10} X-ray computed tomography,^{11, 12} and fiber Bragg grating (FBG) sensing.¹³ The former electrochemical analyses provide superficial information regarding the state of health (SOH) of a cell, whereas the majority of the latter techniques are destructive (requiring the cell to be opened) or require redundant steps and additional equipment. At present, cell makers usually rely on electrochemical methods, particularly in the formation cycle, to make the "go or no go" decision for individual cells before releasing them.

Among the diverse electrochemical diagnostic tools. differential voltage analysis (DVA) is one of the most attractive; although the differential voltage (DV) can be simply calculated from the normal potential vs. the capacity profile, it offers useful information related to the state of the electrode such as the loss of lithium inventory (LLI) and loss of active material (LAM).^{14, 15, 16, 17} Specifically, Sauer et al. reported that DVA can inform the homogeneity of a graphite (Gr) anode in a LiFePO₄ (LFP)/Gr cell,¹⁴ in such a way that the sharpness of the peak on the DV profile reflects the homogeneity of lithium (Li) ion intercalation behavior in the Gr anode. Using a similar rationale, a separate study revealed that the inhomogeneous distribution of Li in the Gr anodes in 18650-type cylindrical cells resulted from the geometrical dimensions of the cylinder in use.¹⁸ Sauer's group also experimentally verified that the spatially inhomogeneous degradation of the Gr anode in a $Li[Ni_xMn_yCo_z]O_2$ (NMC)/Gr pouch cell could be reflected in its DV profiles.¹⁹ However, to the best of our knowledge, the cell-to-cell variation at the post-manufacturing stage and the resulting differences in the lifetime have not yet been quantitatively evaluated using any chemical descriptor including the reaction homogeneity.

Advanced diagnosis should preferably take the state of a cell in the manufacturing stage or early cycling period into account.^{20, 21} The internal resistance (*IR*) is one of the most widely used parameters for monitoring the degradation of a LIB cell.^{8, 22, 23} Although the evolution of the *IR* largely corresponds with the capacity fade during cycling,²³ inspection of the *IR* alone may not

1 0

offer sufficient accuracy for predicting the upcoming cycle life.²⁴ Stefanopoulou et al. reported that the resistance at low SOC can be used to predict the cycle life of a cell by grasping the state of the solid electrolyte interphase (SEI), which is closely linked to the protocol of the formation cycle.²⁵ However, this approach has clear limitations because it is not usually applicable to cells that undergo the same or similar formation cycles, but cycle under different conditions. On the other hand, Chueh and Braatz et al. developed a method that successfully predicted the cycle life of LFP/Gr cells by utilizing the change in the voltage profile between the 10th and 100th cycles.²⁴ Despite statistical verification with a substantial number of cells, the given data-based analysis relies on the electrochemical data from a certain number of initial cycles and is therefore not applicable to cells at an early stage of cycling. In addition, the reported analysis may not reflect the cycling conditions, which could be different from those during the initial 100 cycles or another cycling range that could similarly serve as a prediction standard.

In this work, we predicted the cycle life of commercial LFP/Gr cylindrical cells by using the reaction heterogeneity during the charge process, as reflected in the DV profiles. This approach is valid throughout the entire duration of cycling, even including the formation cycle, without the need to implement additional analytical or mathematical processing. Particularly, the change in the peak intensity on the DV profiles quantitatively reflects the heterogeneity of Li ion intercalation into the graphite anode, which is closely correlated with the cycle life. This analysis yielded highly reliable statistics (i.e., Pearson correlation coefficient (ρ) of 0.82) between the identified heterogeneity descriptor (the peak on the DV profile) and cycle life for 77 LFP/Gr cells. Notably, most physical characterizations available to date would not enable the heterogeneity of LIB electrodes to be captured sufficiently to reliably predict the cycle life of the corresponding cells with high accuracy. Moreover, the heterogeneity analysis proposed in this study can be used even at the formation cycle so that it could serve as a sophisticated inspection tool with regard to the manufacturing quality of cells under test. In the same context, this methodology could also be used to build a highly reliable battery module by examining and sorting individual cells at the post-manufacturing stage.

2.2. Result and discussion

2.2.1. Heterogeneity of Gr anodes

A LIB cell tends to exhibit heterogeneous behaviors in terms of Li ion diffusion and storage, which to some extent is the result of irregular electrode environments with respect to the temperature, pressure, or the presence of an electric field. These heterogeneous behaviors could also originate from imperfect manufacturing processes such as nonuniform electrode coating and calendaring. The nonuniform Li ion flux and storage under these environmental conditions during operation, additional to manufacturing discrepancies, lead to irregular interfacial degradation and therefore accelerate capacity decay.^{26, 27} Figure 2. 1A and 2. 1B depict the lithiation process in the Gr anodes in a jellyroll with homogeneous and heterogeneous distributions of Li ion storage, respectively, in relation to the so-called staging effect. Specifically, these figures capture stage II of the Gr anodes at which Li ions (green spheres) occupy every other layer. At this stage II, Li ion occupation could be either regular (Figure 2. 1A) or (relatively) irregular (Figure 2. 1B)



Figure 2. 1 Heterogeneity of Gr anodes and relation to voltage profiles. Scheme showing the relation between spatial homogeneity of lithiation in the Gr anode and voltage profile: (A) homogeneous and (B) heterogeneous lithiation near stage II. Corresponding voltage profiles of different regions in the Gr electrodes (bottom). (C) Voltage profiles of the cells with spatially homogeneous and heterogeneous Gr anodes at stage II.

over Gr electrodes depending on the various electrode states and operating conditions. This distinct effect of the heterogeneity in this stage during lithiation must be reflected in the potential profiles (shown below the illustrations in Figure 2. 1A and 2. 1B). The heterogeneous lithiation at different locations in the electrode is represented by the potential profiles with some variations in the peak shape and a peak shift, which lead to one collective profile with a gentle slope between the two voltage plateaus (Figure 2. 1C). Based on this logic, a cell with greater heterogeneity in its lithiation distribution would have a less steep slope around the stage transition. Figure 2. 2 displays the voltage (top) and $dV dQ^{-1}$ profiles (bottom) of an LFP/Gr cell. Based on the rationale that the slope of the voltage profile near a stage transition reflects the spatial heterogeneity of lithiation, the gap between the valley and the peak in stage II on the



Figure 2. 2 Voltage (top) and corresponding DV (bottom) profiles of an LFP/Gr cylindrical cell as a function of the capacity during charge consisting of different stages.

 $dV dQ^{-1}$ profile, denoted $\Delta Peak_{S2}$ (green arrow), was established as a descriptor to represent the heterogeneity of lithiation in the Gr anode.^{14, 19, 28}

LFP/Gr cells were monitored under four different conditions $(1C@25 \circ C, 2C@25 \circ C, 1C@45 \circ C, and 1C@10 \circ C)$ until their state of health (SOH) reached 80% to confirm the relation between the heterogeneity of the Gr anode and the value of $\Delta Peak_{S2}$ (Figure 2. 3). For reference, the SOH in this study was solely used to represent the capacity retention:

$$SOH(n) = \frac{Q(n)}{Q_{BOL}} \times 100$$



Figure 2. 3 DV profiles against the capacity under different cycling conditions: (A) 1C@25 °C, (B) 2C@25 °C, (C) 1C@45 °C, and (D) 1C@10 °C. The legends refer to the SOH (%).

where Q_{BOL} and Q(n) are the capacity at the beginning of life (BOL) and the n^{th} cycle, respectively. Depending on the changes in the value of $\Delta Peak_{S2}$, the 1C@45 °C and 1C@25 °C conditions are classified as "homogeneous" degradation and the 1C@10 °C and 2C@25 °C conditions as "heterogeneous" degradation. These results imply that a low temperature and high C-rate tend to more significantly induce heterogeneity of the Gr electrode (Figure 2. 4). $\Delta Peak_{S4}$, a heterogeneity descriptor related to stage IV (Figure 2.5), also varied consistently among the cells that underwent



Figure 2. 4(A) ΔPeak_{S2} and (B) ΔPeak_{S4} vs. SOH for four different cycling conditions: 1C@25 °C, 2C@25 °C, 1C@45 °C, and 1C@10 °C.



Figure 2.5 ΔPeak_{S4} is defined. Same voltage (top) and DV (bottom) profiles of the LFP/Gr cylindrical cell shown in Figure 2. 2.

homogeneous and heterogeneous degradation (Figure 2. 4). Remarkably, the series of results in Figure 2. 4A convey an important message that, even at the same SOH (the same capacity retained), the heterogeneity of the electrode could differ such that the degradation trend in subsequent cycles could be different. Once again, the key operating conditions have a deterministic effect on the evolution of the heterogeneity. We considered applying the same



Figure 2. 6 DV vs. capacity profiles during discharge under different cycling conditions: (A) 1C@25 °C and (B) 2C@25 °C.

methodology to the discharge profiles (Figure 2. 6). Although the peaks of the DV profiles during discharge allow the cell evolution to be distinguished at different C-rates, the discharge profiles are not as suitable as their charge counterparts in diagnosing the state of a cell because the amount of Li ions intercalated in the Gr could affect the Δ Peak_{S2} intensity.²⁹

The degradation of the Gr anodes was confirmed by disassembling the cylindrical cells. The Gr anode in the fresh cell had a clean, Li-



Figure 2. 7 SEM and optical (center) images of the Gr anodes of a fresh unrolled LFP/Gr cell. "Inside" and "outside" refer to the side facing inward and outward in the jellyroll, respectively. "Case" and "core" refer to the part near the can case and the core of the jellyroll, respectively. The numbers in the SEM images correspond to the spots indicated in the optical image in the center.

free surface and intact Gr particles in the scanning electron microscopy (SEM) images (Figure 2. 7). For reference, the optical image of the electrode in the center of Figure 2. 7 displays both the inside and outside of the graphite anode (double-sided Gr coated on the current collector). In this image, the area toward the left-hand side corresponds to the end closest to the can case, and the area toward the right-hand side is closer to the core of the jellyroll. The



Figure 2. 8 SEM and optical (center) images of the Gr anodes of an LFP/Gr cell cycled at 1C@ 25 °C until SOH80 was reached. "Inside" and "outside" refer to the side facing inward and outward in the jellyroll, respectively. "Case" and "core" refer to the part near the can case and the core of the jellyroll, respectively. The numbers in the SEM images correspond to the spots indicated in the optical image in the center.

images in Figure 2. 8 and 2. 9 are laid out in the same fashion. When imaged at SOH80, the Gr anode cycled at 1C@25 °C had an overall clean surface, but intensive Li plating was observed near spot 4 (Figure 2. 8). In contrast, at the same SOH80, the Gr anode cycled at 2C@25 °C had more extensive surface damage across the entire electrode. Moreover, SEM images at higher magnification (Figure 2. 9) revealed the surface to be covered with reaction by-products.



Figure 2. 9 SEM and optical (center) images of the Gr anodes of LFP/Gr cell cycled at 2C@ 25 °C until SOH80 was reached. "Inside" and "outside" refer to the side facing inward and outward in the jellyroll, respectively. "Case" and "core" refer to the part near the can case and the core of the jellyroll, respectively. The numbers in the SEM images correspond to the spots indicated in the optical image in the center.

The overall electrode scale indicated that the surface of the Gr anode cycled at 2C@25 °C was more severely degraded, which must be linked to heterogeneous (de)lithiation through its Gr anode. The locally severe Li plating of the particular jellyroll at 1C@25 °C is attributed to its natural inhomogeneity as well as the larger charging capacity at 1C compared to 2C. In particular, the larger charging capacity could promote severe Li plating once the cell ages. Furthermore, the outside of the anode is known to be more vulnerable to Li plating. This is because the area of the facing cathode is larger than that of the anode owing to the curvature of the jellyroll, providing a higher likelihood for Li ions to be locally concentrated.³⁰ On the



Figure 2. 10 TOF-SIMS results of the Gr anodes in the LFP/Gr cells (A) before cycling (SOH100), and after cycling at (B) 1C@25 °C and (C) 2C@25 °C until SOH80 was reached.

other hand, according to time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis (Figure 2.10), larger quantities of LiF_2^{-2} and C_2HO^- were detected for the Gr anode cycled at 2C@25 °C compared to the anode cycled at 1C@25 °C. These two fragments are decomposition products of the LiPF₆ salt and electrolyte solvents. respectively. The more significant decomposition of the electrolyte reflects increased interfacial polarization as the C-rate is increased. For the same reason, the color of the dimethyl carbonate (DMC) solvent used to wash the jellyrolls changed according to the cycling conditions (Figure 2. 11). The DMC used to wash the fresh Gr anode and the aged Gr that underwent cycling until SOH80 at 1C@25 °C appeared to be transparent. In contrast, the DMC that was used to wash the Gr anode cycled until SOH80 at 2C@25 °C turned yellowish as a result of its more unstable SEI formation, which is rooted in its more heterogeneous (dis) charging reaction.



Figure 2. 11 DMC solvent used for washing the jellyrolls of LFP/Gr cells: (A) before cycling and after cycling (SOH80) at (B) 1C@25 °C and (C) 2C@25 °C.
2.2.2. $\Delta Peak_{S2}$ as a key descriptor for electrode heterogeneity

To examine the possibility of using $\Delta \text{Peak}_{\text{S2}}$ as a key descriptor of cell degradation, multiple LFP/Gr commercial cells were operated for one cycle and their first charging profiles were analyzed by focusing on $\Delta \text{Peak}_{\text{S2}}$. For example, two cells were identified as homogeneous and heterogeneous cells based on their large and small values of $\Delta \text{Peak}_{\text{S2}}$, respectively, as displayed in Figure 2. 12A. The cycle life of these two cells corresponded with their anode heterogeneity in that the homogeneous and heterogeneous cells retained 80% of their initial capacities for 373 and 193 cycles, respectively (Figure 2. 12B). The heterogeneity of the Gr anode in the heterogeneous cell presumably gave rise to relatively more nonuniform reactions resulting from locally concentrated current and heat distributions³¹, which shortened its cycle life. Hence, the



Figure 2. 12 Correlation between electrode heterogeneity and cycle life. (A) DV profiles of homogeneous and heterogeneous cells, and (B) their corresponding cycle life when measured at 1C for both charge and discharge at room temperature.

correlation between $\Delta Peak_{S2}$ and the cycle life informs that $\Delta Peak_{S2}$ on the DV profile could be an indicator of the quality of asmanufactured cells.

The heterogeneity of Gr electrodes that led to the distinct cyclability was indeed reflected in the electrode arrangements in the



Figure 2. 13 Correlation between electrode heterogeneity and electrode arrangement of LFP/Gr cylindrical cells. (A) Side cross-sectional XRM images of the homogenous and heterogenous cells (left). Enlarged views of the upper sides of electrodes in the jellyrolls (right). Top cross-sectional XRM images of the (B) homogeneous and (D) heterogeneous cells. All scale bars in this figure are 1 mm. (C) Enlarged central voids of the jellyrolls containing the homogeneous and heterogeneous cells to compare the roundness of the voids.

jellyrolls. Examination of a cross-section of the cell from the side using X-ray microscopy (XRM) (Figure 2. 13A and 2. 14) captured the copper (Cu) and aluminum (Al) current collectors as thin bright and thick dark lines, respectively, as indicated with the orange and sky-blue markings. The Gr anode and LFP cathode, respectively, were coated on both sides of the Cu and Al current collectors, and the greater thickness of the cathodes originated from the thicker coating of LFP than Gr. The lines connecting the edges of the anodes and cathodes are presented below the XRM images in orange and sky-blue color, respectively. The current collectors in these two



Figure 2. 14 Vertical cross-sectional XRM images of the (A) homogeneous and (B) heterogeneous LFP/Gr cylindrical cells.

cells had two highly distinct arrangements (Figure 2. 13A, right). The homogeneous cell exhibited an even alignment with a uniform anode overhang (the marginal area of the anode because of its larger size than that of the facing cathodes). By contrast, the anodes and cathodes of the heterogeneous cell were misaligned such that the edges of some cathodes extended beyond the upper ends of the surrounding anodes ("cathode overhang," the opposite of anode overhang), as indicated by the red arrows in the magnified figure. Cathode overhang is highly detrimental to the cyclability and safety of a cell as Li can be plated on the upper edge area of the Gr anode due to oversupply of Li from the protruding cathode, giving rise to short circuits.

The top view cross-sectional XRM images were captured across the cylindrical cells to assess the roundness of the jellyrolls (Figure 2. 13B and 13D). The jellyroll of the homogeneous cell had undistorted circular shape whereas the shape of the an heterogeneous cell's was more ellipsoidal. The shapes of the core holes of these two jellyrolls also reflected their respective rolled structures (shown in blue and magenta), in Figure 2. 13C. The roundness of the core holes was quantitatively evaluated by employing the maximum circumscribed circle (MCC) method through which the inner and outer radii (R_{in} and R_{out}) were attained (Figure 2. 15).³² The roundness error $(R_{out} - R_{in})$ of the homogeneous cell was 0.21 mm and that of the heterogeneous cell was three times as large (0.64 mm). Important to note is that the heterogeneity assessment involving $\Delta Peak_{s2}$ can be a useful tool to inspect the state of the electrode coating and assembly and predict the lifetime of the corresponding cell.



Figure 2. 15 MCC method for calculation of the roundness about the enlarged void at the core of the jellyrolls in the (A) homogeneous and (B) heterogeneous cells.

2.2.3. Lifetime prediction of LFP/Gr cells by correlating with $\Delta Peak_{S2}$

A total of 77 LFP/Gr cylindrical cells were cycled under the unified condition of 1C@25 °C to further probe the correlation between $\Delta Peak_{S2}$ and the cycle life (Figure 2. 16A). The cycle life was defined as the number of cycles required to reach SOH80. The SOH was monitored by measuring the capacity at 0.2C@25 °C every 100 cycles. Although all the cells were cycled under the same conditions, their respective cycle lives spanned a wide range from 151 to 567 cycles, revealing the variation in the quality of the manufactured cells. The dV dQ⁻¹ profiles of the corresponding cells are displayed in Figure 2. 16B. As is evident from the cycle life vs. Peak_{S2} scatter plot (Figure 2. 16C), these two parameters had a high Pearson correlation coefficient of 0.82 for the 77 cells. Note that the Peak_{S2} intensity was used in this analysis instead of the Δ Peak_{S2} intensity because of the fluctuation in the valley near 0.4 Ah, which is attributed to the limited resolution of voltage detection when the voltage plateaued at the transition from stage III to stage II. The Pearson correlation coefficient of the Δ Peak_{S2} intensity was 0.75 (Figure 2. 17). This implies that it must be possible to use the



Figure 2. 16 Correlation between the life cycle and Peak_{S2} intensity. (A) Cycling retention profiles and (B) differential voltage profiles of 77 LFP/Gr cells under an equivalent cycling condition of 1C charging and 1C discharging. (C) Correlation between Peak_{S2} intensity and cycle life with the Pearson correlation coefficient of 0.82. The colors of dots and lines in all plots are graded according to the cycle life and are indicated on the color scale bar in (A).



Figure 2. 17 Cycle life vs. $\Delta Peak_{S2}$ intensity plot with correlation coefficient of 0.75.

aforementioned correlation to predict the cycle life of asmanufactured cells. We used cross-validation to corroborate the reliability of the proposed prediction approach based on Peak_{S2}, as one of the most widely used methods to estimate the prediction error.³³ The univariate lifetime prediction model based on the Peak_{S2} intensity yielded the lowest mean percent error (MPE) of 13.5% and a root mean square error (RMSE) of 51 cycles for the test dataset (Table 2. 1 and Figure 2. 18). The MPE test error for the Peak_{S2} intensity was less than half of the error obtained by the dummy regressor, which was set as the baseline because it is simply based on the mean of the training dataset without any features. On the contrary, the predictive models using other parameters such as the Peak_{S4} intensity, the 1st *IR*, and the 1st capacity (*Q*) did not improve the predictive performance and produced test errors similar to those of the dummy regressor (Table 2. 1 and Figure 2. 19). On the one

	RMSE (cycles)		MPE (%)	
	Train	Test	Train	Test
Dummy regressor	92	93	28.2 (5.5)	28.5 (4.8)
Peak _{S2} intensity	52	51	13.6 (0.7)	13.5 (2.4)
Peak _{S4} intensity	81	81	22.8 (1.1)	22.8 (3.9)
1 st IR	93	94	28.3 (1.2)	28.5 (4.7)
$1^{st} Q$	94	94	28.4 (1.3)	28.6 (4.9)
Var $(\varDelta Q_{100-10}(V))$	60	60	15.6 (1.0)	15.6 (2.8)

Table 2. 1 Prediction errors of the lifetime prediction models. Training and testing errors of the lifetime prediction models using different parameters from the dataset of 77 LFP/Gr cells. The error values of the dummy regressor without any features serve as a baseline. The values in parentheses are the standard deviations.

hand, the prediction model with the variance of ΔQ_{100-10} (V) (capacity gap between the voltage profiles at the 100th and 10th cycles), the descriptor reported by Severson et al., achieved a test error of 15.6% for our dataset.²⁴ Thus, it produced a significantly smaller prediction error than the dummy regressor, but larger than the one based on the Peak_{S2} intensity. From a practical viewpoint, our method based on the Peak_{S2} intensity is attractive as it requires only the voltage profile in the first cycle. Apparently, the change in the Peak_{S2} intensity over cycling allows the heterogeneity of the Gr anode and thus the cell degradation to be monitored.



Figure 2. 18 Comparison of RMSE values during 1000 iterations between the dummy regressor and (A) Peak_{S2} intensity, (B) Peak_{S4} intensity, (C) 1st *IR*, (D) 1st *Q*, and (E) Var (ΔQ_{100-10} (V)).



Figure 2. 19 Correlation of cycle life with (A) Peak_{S4} intensity, (B) 1^{st} *IR*, (C) 1^{st} *Q*, and (D) Var (ΔQ_{100-10} (V)).

2.2.4. Peak_{S2} as a tool of cell inspection

The ability to accurately inspect individual cells can be most useful for building a high-performance module that entails integrating cells. The quality of as-manufactured cells could be assessed based on various parameters such as the Peak_{S2} intensity, OCV drop, capacity, internal resistance (*IR*), etc. (Figure 2. 20), of which the Peak_{S2} intensity would be the most powerful as it directly relates to the heterogeneity of the reaction involving Li ions. The



Figure 2. 20 $Peak_{S2}$ -based diagnosis for module assembly. Using $Peak_{S2}$ for the high-quality inspection of as-manufactured cells for the assembly of cells into a module.

Peak_{S2}-based inspection allows as-manufactured cells to be classified into normal (healthy) and faulty ones with respect to their expected lifespan based on the proven correlation between the two parameters from a statistically reliable number of cells. The proposed inspection process therefore enables faulty cells to be screened out. As the performance of a module is determined by the performance of its constituent cells, it is critically important to assemble a collection of cells with consistent performance. Faulty cells decay more rapidly and reach the charging cut-off voltage earlier, thereby limiting the capacity of the entire module in each cycle. The exclusion of underperforming cells would largely eliminate cell-to-cell variation in the module to prevent the cycling performance of the module from deteriorating. The problem caused by faulty cells is usually overcome by incorporating a balancing algorithm in battery management systems (BMSs), but this BMS-based remedy obviously has limited ability to restore the imbalance once faulty cells are included in the module.^{34, 35} The capability to identify faulty cells at the asmanufactured stage addresses this shortcoming and would be beneficial for quality control prior to module assembly.

To prove this capability, we experimentally evaluated the effect of the cycle life of cells on that of the entire module. The aforementioned 77 cells were classified into three groups based on the Peak_{S2} intensity (Figure 2. 21A): low (0.18 \sim 0.20), middle (0.20) ~ 0.22), and high (0.22 ~ 0.24). This grouping provides a useful correlation with the cycle life. We constructed 5 modules comprising 6 cells each, with each module consisting of cells selected for their particular properties with respect to the different parameters of interest (Figure 2. 21B); module 1: low Peak_{S2}, module 2: middle Peak_{S2}, module 3: high Peak_{S2}, module 4: controlled 1st cycle capacity $(1^{st} Q)$, and module 5: controlled 1^{st} cycle *IR*. Apart from modules 1-3, the properties of the cells included in modules 4 and 5, respectively, were such that either $1^{st} Q$ or $1^{st} IR$ is similar to that of module 2 but the value of Peak_{s2} spans the entire range of low, middle, and high values of the Peaks2 intensity. This arrangement enabled us to verify the univariate effect of Peaks2 as a sorting factor by excluding the effect of 1^{st} Q or 1^{st} IR. Our approach is based on the rationale that modules consisting of cells with controlled properties in terms of these parameters would be able to offer more stable cell balancing and therefore more sustainable cyclability. The actual values of the individual cells in these modules are plotted in Figure 2.

3 4



Figure 2. 21 Module construction according to cell classification based on the Peak_{S2} intensity. (A) Box plots of cycle life vs. Peak_{S2} intensity for three different groups of cells classified by the Peak_{S2} intensity. (B) Construction of five different modules consisting of six cells based on different standards (peak_{S2} intensity, 1st *IR*, and 1st *Q*). (C) Cycling performance of different modules constructed as in (B).

22 and listed in Table 2. 2.

Tests of the cycle life of these modules indicated that the overall trend followed that of the Peak_{S2} intensity of individual cells fairly well (Figure 2. 21C). The cycle life decreased in the sequence: module 3 (high Peak_{S2}), module 2 (middle Peak_{S2}), module 4 (controlled 1st Q), module 5 (controlled 1st IR), and module 1 (low Peak_{S2}). Remarkably, the cycle life of modules 4 and 5 was inferior to that of module 2 even though their average Peak_{S2} intensities, thus

their average expected cycle life, were almost the same as that of module 2, which reconfirms the importance of consistent performance of individual cells in a module. In addition, the deviation in the capacity decay of individual cells after cycling (until reaching SOH70) was more significant for modules 4 and 5 compared to modules 1–3 (Figure 2. 23). This is closely linked to the fact that the difference in the heterogeneity of the cells within a module widens the range of degradation among the cells during cycling. Moreover, more extensive deviation triggers the shortening of the cycle life of the corresponding module because the performance of a module is mostly limited by the worst performing cells. The more alarming



Figure 2. 22 (A) Capacity distributions of six cells in each module group classified based on similar capacity (orange) and middle Peak_{S2} (purple). (B) *IR* distributions of six cells in each module group classified based on similar *IR* (green) and middle Peak_{S2} (purple).

	middle Peak _{S2}	controlled $1^{st} Q$	controlled 1 st IR
<i>Q</i> avg. (Ah)	0.987	0.987	_
Q std. (Ah)	0.0102	0.0105	-
$IR \text{ avg.} $ (Ω)	0.162	_	0.162
IR std.	0.0051	_	0.0049

Table 2. 2 Average and standard deviation of capacity and *IR* for the cells selected for the middle Peak_{S2}, similar 1^{st} *IR*, and similar 1^{st} *Q* modules.

reality is that the imbalance of cells in a module induces over(dis)charging of those cells with lower capacities, which is known to increase the possibility of fire.³⁶ To summarize, the quantitative classification of as-manufactured cells based on the reaction heterogeneity represents a remarkable benefit for warranting the performance quality of cells as well as that of the modules composed of the given cells.



Figure 2. 23 (A) Deviation of $Peak_{S2}$ intensity vs. deviation of capacity decay of individual cells in different modules. (B) Box plots for capacity decay of individual cells in different modules.

2.3 Conclusion

An unparalleled number of battery cells will be loaded on EVs as we enter the era of mobility transition. The accurate diagnosis of asmanufactured cells would therefore undoubtedly be a useful technology to warrant reliable battery operation to customers. Based on the rationale that cell diagnosis should capture the key features of the charge-discharge reaction in a cell, we focused on the lithiation heterogeneity of the Gr anode, because cell degradation is usually accompanied by the progression of spatially heterogeneous reactions. In this study, the Peaks2 intensity was identified as the descriptor that reflects the lithiation heterogeneity of the Gr anode. The heterogeneity of the Gr anode is well correlated with the cycle life of LFP/Gr commercial cells with high statistical reliability and can therefore be used to predict the lifetime of random individual cells. Based on the given logic, the $Peak_{S2}$ analysis can be used to identify and remove faulty cells at the as-manufacturing stage. We foresee the possibility of embedding various chemical descriptors that reflect the cell state from (electro) chemical viewpoints, including the Peaks2 intensity, in diagnostic algorithms to advance BMSs.

2.4 Experimental procedures

Cycling of cells and modules

The dataset related to battery cycling was generated from 77 commercial LFP/Gr cells (IFR18500, China). The cells have the

nominal capacity of 1 Ah and the nominal voltage of 3.2 V. All the cells were cycled with an identical cycling protocol (1C, 2.5–3.9 V) using a battery cycler (WBCS 3000, WonATech, South Korea) in a chamber (IL-11, JEIO TECH, South Korea) at 25 °C. Every cell was subjected to the reference performance test (RPT) every 100 cycles. The RPT test started with three consecutive cycles at 0.2C (0.2 A) to evaluate the capacity, followed by DVA and DCIR measurements. For the DCIR test, the voltage was raised to 3.35 V (=SOC50) at 0.2C. Then, the pulse series of 0.1C, 0.5C, and 1C charge-discharge were applied for 10 s in width with 10 min intervals. To assess the aging, each cell was cycled at 1C (1 A) in the range of 2.5 V to 3.9 V, and the capacity was checked at 0.2C every 100 cycles. The cycle life was referred to as the number of cycles required to reach SOH80, which was estimated by polynomial regression using the capacity measured every 100 cycles. The modules were cycled by connecting 6 cells in parallel by nickel plate welding. The modules were galvanostatically cycled at 1C (6 A) with a capacity check at 0.2C (1.2 A) every 100 cycles. The cycle life of the modules was defined and analyzed in the same manner as that of the cells.

Testing various parameters as descriptors of capacity decay

All parameters except for $\Delta Q_{100-10}(V)$ were evaluated from the initial three cycles in the first RPT protocol before cycling. The parameters (Peak_{S2} and Peak_{S4} intensity) related to the dV dQ⁻¹ profile used the data in the third cycle of the first RPT. The Δ Peak_{S2} intensity corresponds to the difference between the ridge near 0.6 Ah and the valley near 0.4 Ah in the transition to stage II. The Peak_{S2}

39

intensity is the absolute value at the ridge. The ΔPeak_{S4} intensity corresponds to the difference between the ridge near 0.1 Ah and the valley near 0.15 Ah in stage IV. The 1st DCIR was extracted from the DCIR test in the first RPT. In the DCIR test, (dis)charging pulses of 0.1C, 0.5C, and 1C were applied, and the current-voltage plot was drawn, where the slope corresponded to the resistance. The 1st *Q* is the discharge capacity of the third cycle in the first RPT. The variance of $\Delta Q_{100-10}(V)$ is the variance of the capacity difference between the 10th and 100th cycles in the voltage vs. discharge capacity curve.²⁴

Characterization

The vertical – and cross-sectional images of the cylindrical cells were obtained using high-resolution 3D XRM (Xradia 620 Versa, Carl Zeiss, USA). The MCC method was used to evaluate roundness.³² The center was determined by the smallest circumscribed circle which passes through protruding points of the original profile. Then, the inscribed circle was drawn based on the center of the minimum circumscribed circle. The out-of-roundness the difference between the radius of the inscribed and is circumscribed circles. The by-products on the surface of Gr anodes before and after cycling were analyzed by depth profiling with TOF-SIMS (TOF.SIMS 5, ION-TOF, Germany) using negative polarity. The primary source was Bi_3^+ with 30 keV and 0.7 pA, and the etching source was Cs⁺ with 500 eV and 40 nA. The analysis and etching areas were sized 100 \times 100 μ m² and 300 \times 300 μ m², respectively. The XRM and TOF-SIMS analyses were performed at the National

4 0

Center for Inter-university Research Facilities (NCIRF) of Seoul National University (SNU). The surface of Gr anodes before and after cycling was visualized by using a field-emission scanning electron microscope (SUPRA 55VP, Carl Zeiss, Germany) at the National Instrumentation Center for Environmental Management (NICEM) of SNU.

Statistical analysis and lifetime prediction model

The mean and standard deviation of each variable for the dataset of 77 LFP/Gr cells are listed in Table 2. 3. ρ was used to describe the degree and direction of linearity between the two variables. $|\rho| > 0.8$ was usually considered to have a strong correlation.³⁷ ρ is statistically significant when both variables follow a normal distribution.³⁸ Boxand-whisker plots (Figure 2. 21A) were drawn to present the cycle life of the groups divided based on the Peak_{S2} intensity. The interquartile range (IQR) in the box plots was from the 25th percentile to 75th percentile with the median as the dashed horizontal line. The

Variables	Mean	Std.	
Cycle life	295.4	92.0	
Peak _{S2} intensity (V Ah ⁻¹)	0.211	0.014	
Peak _{S4} intensity (V Ah ⁻¹)	0.310	0.033	
1^{st} DCIR (\mathcal{Q})	0.169	0.010	
1 st capacity (Ah)	0.989	0.008	
Var (⊿Q ₁₀₀₋₁₀ (V))	0.0005	0.0003	

Table 2. 3 Mean and standard deviations of each variable for thedataset of 77 LFP/Gr cells.

length of the whisker was defined as 1.5 times the IQR.

K-fold cross-validation was employed for calculating prediction errors to avoid data overfitting and create a generalized model.³⁹ Before the cross-validation, 20% of the dataset was split and used as the test set. K = 5 was used for all univariate models, which means that the remaining data was equally divided into 5 parts, of which 4 subsets became the training set and the remaining subset became the validation set. Then, the model was trained using the training set and the model performance was verified by the validation set. Considering that all the subsets could be a validation set, the performance of the model for processing the training set was calculated as the average of all cases. Finally, the performance of the model on the test set was calculated. All the above processes were performed for 1000 random dataset splits using shuffling.

Ridge regression was used as a univariate linear regression model to minimize overfitting through regularization.⁴⁰ The formula is:

$$\beta_{\text{ridge}}$$
: argmin $\left[\sum_{i=1}^{n} \left(y_i - \beta_0 - \sum_{j=1}^{p} \beta_j x_{ij}\right)^2 + \lambda \sum_{j=1}^{p} \beta_j^2\right]$

where β is a coefficient of the model, *n* is the number of samples, *x* is a feature vector of the model, *p* is the number of features and λ is a regularization parameter. By optimizing λ , a linear regression model with balanced bias and variance could be obtained. At each iteration of the cross-validation, the optimal λ was found using GridsearchCV.

The performance of the model was evaluated using the RMSE

and MAPE. RMSE is intuitive because it maintains units of the data and MAPE is convenient to compare various types of data because it uses ratio values. The formulas are:

RMSE =
$$\sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2}$$

MAPE (%) = $100 \times \frac{1}{n} \sum_{i=1}^{n} \left| \frac{y_i - \hat{y}_i}{y_i} \right|$

where *n* is the number of samples, *y* is the observed value, and \hat{y} is the predicted value.

Data analysis and machine learning modeling were processed in Python with the Pandas, NumPy, and scikit-learn packages.

2.5 References

Cano, Z. P.; Banham, D.; Ye, S. Y.; Hintennach, A.; Lu, J.; Fowler, M.;
 Chen, Z. W., Batteries and fuel cells for emerging electric vehicle markets.
 Nat Energy 2018, *3* (4), 279–289.

2. Tran, M.; Banister, D.; Bishop, J. D. K.; McCulloch, M. D., Realizing the electric-vehicle revolution. *Nat Clim Change* **2012**, *2* (5), 328-333.

3. Schuster, S. F.; Brand, M. J.; Berg, P.; Gleissenberger, M.; Jossen, A., Lithium-ion cell-to-cell variation during battery electric vehicle operation. *J Power Sources* **2015**, *297*, 242–251.

4. Chen, W. D.; Liang, J.; Yang, Z. H.; Li, G., A Review of Lithium–Ion Battery for Electric Vehicle Applications and Beyond. *Energy Procedia* **2019**, *158*, 4363–4368.

5. Kenney, B.; Darcovich, K.; MacNeil, D. D.; Davidson, I. J., Modelling the impact of variations in electrode manufacturing on lithium-ion battery modules. *J Power Sources* **2012**, *213*, 391–401.

6. Feng, F.; Hu, X. S.; Hu, L.; Hu, F. L.; Li, Y.; Zhang, L., Propagation mechanisms and diagnosis of parameter inconsistency within Li–Ion battery packs. *Renew. Sustain. Energy Rev.* **2019**, *112*, 102–113.

Ryll, K.; Hoffmann, L.; Landrath, O.; Lienesch, F.; Kurrat, M., Key
 Figure Based Incoming Inspection of Lithium-Ion Battery Cells. *Batteries* 2021, 7 (1), 9.

8. Kim, J. H.; Lee, S. J.; Lee, J. M.; Cho, B. H., A new direct current internal resistance and state of charge relationship for the Li-ion battery pulse power estimation. *The 7th Internatonal Conference on Power Electronics* **2007**, 1173–1178.

 Bommier, C.; Chang, W.; Lu, Y. F.; Yeung, J.; Davies, G.; Mohr, R.;
 Williams, M.; Steingart, D., In Operando Acoustic Detection of Lithium Metal
 Plating in Commercial LiCoO2/Graphite Pouch Cells. *Cell Rep Phys Sci* 2020, *1* (4), 100035.

 Zappen, H.; Fuchs, G.; Gitis, A.; Sauer, D. U., In-Operando Impedance Spectroscopy and Ultrasonic Measurements during High-Temperature Abuse Experiments on Lithium-Ion Batteries. *Batteries* 2020, 6 (2), 25.

Deng, Z.; Lin, X.; Huang, Z. Y.; Meng, J. T.; Zhong, Y.; Ma, G. T.;
 Zhou, Y.; Shen, Y.; Ding, H.; Huang, Y. H., Recent Progress on Advanced
 Imaging Techniques for Lithium-Ion Batteries. *Adv Energy Mater* 2021, *11* (2), 2000806.

12. Robinson, J. B.; Darr, J. A.; Eastwood, D. S.; Hinds, G.; Lee, P. D.; Shearing, P. R.; Taiwo, O. O.; Brett, D. J. L., Non-uniform temperature distribution in Li-ion batteries during discharge – A combined thermal imaging, X-ray micro-tomography and electrochemical impedance approach. *J Power Sources* **2014**, *252*, 51–57.

Huang, J. Q.; Blanquer, L. A.; Bonefacino, J.; Logan, E. R.; Dalla Corte,
 D. A.; Delacourt, C.; Gallant, B. M.; Boles, S. T.; Dahn, J. R.; Tam, H. Y.;
 Tarascon, J. M., Operando decoding of chemical and thermal events in
 commercial Na(Li)-ion cells via optical sensors. *Nat Energy* 2020, *5* (9),
 674-683.

14. Lewerenz, M.; Marongiu, A.; Warnecke, A.; Sauer, D. U., Differential

voltage analysis as a tool for analyzing inhomogeneous aging: A case study for LiFePO4|Graphite cylindrical cells. *J Power Sources* **2017**, *368*, 57–67.

Pastor-Fernández, C.; Uddin, K.; Chouchelamane, G. H.; Widanage,
 W. D.; Marco, J., A Comparison between Electrochemical Impedance
 Spectroscopy and Incremental Capacity-Differential Voltage as Li-ion
 Diagnostic Techniques to Identify and Quantify the Effects of Degradation
 Modes within Battery Management Systems. *J Power Sources* 2017, *360*, 301-318.

16. Zhu, J. G.; Darma, M. S. D.; Knapp, M.; Sorensen, D. R.; Heere, M.; Fang, Q. H.; Wang, X. Y.; Dai, H. F.; Mereacre, L.; Senyshyn, A.; Wei, X. Z.; Ehrenberg, H., Investigation of lithium-ion battery degradation mechanisms by combining differential voltage analysis and alternating current impedance. *J Power Sources* **2020**, *448*, 227575.

17. Keil, P.; Jossen, A., Calendar Aging of NCA Lithium-Ion Batteries Investigated by Differential Voltage Analysis and Coulomb Tracking. *J. Electrochem. Soc.* **2016**, *164* (1), A6066-A6074.

Senyshyn, A.; Muhlbauer, M. J.; Dolotko, O.; Hofmann, M.; Ehrenberg,
H., Homogeneity of lithium distribution in cylinder-type Li-ion batteries. *Sci. Rep.* 2015, 5 (1), 18380.

Sieg, J.; Storch, M.; Fath, J.; Nuhic, A.; Bandlow, J.; Spier, B.; Sauer,
D. U., Local degradation and differential voltage analysis of aged lithiumion pouch cells. *J Energy Storage* 2020, *30*, 101582.

20. Strange, C.; dos Reis, G., Prediction of future capacity and internal resistance of Li-ion cells from one cycle of input data. *Energy and AI* **2021**, *5*, 100097.

21. Baumhöfer, T.; Brühl, M.; Rothgang, S.; Sauer, D. U., Production caused variation in capacity aging trend and correlation to initial cell performance. *J Power Sources* **2014**, *247*, 332–338.

22. Guha, A.; Patra, A., State of Health Estimation of Lithium-Ion Batteries Using Capacity Fade and Internal Resistance Growth Models. *Ieee T Transp Electr* **2018**, *4* (1), 135–146.

23. Chen, L.; Lü, Z.; Lin, W.; Li, J.; Pan, H., A new state-of-health estimation method for lithium-ion batteries through the intrinsic

relationship between ohmic internal resistance and capacity. *Measurement* **2018**, *116*, 586–595.

Severson, K. A.; Attia, P. M.; Jin, N.; Perkins, N.; Jiang, B.; Yang, Z.;
Chen, M. H.; Aykol, M.; Herring, P. K.; Fraggedakis, D.; Bazan, M. Z.; Harris,
S. J.; Chueh, W. C.; Braatz, R. D., Data-driven prediction of battery cycle
life before capacity degradation. *Nat Energy* 2019, 4 (5), 383-391.

25. Weng, A.; Mohtat, P.; Attia, P. M.; Sulzer, V.; Lee, S.; Less, G.; Stefanopoulou, A., Predicting the impact of formation protocols on battery lifetime immediately after manufacturing. *Joule* **2021**, *5* (11), 2971–2992.

26. Li, R.; Ren, D.; Wang, S.; Xie, Y.; Hou, Z.; Lu, L.; Ouyang, M., Nondestructive local degradation detection in large format lithium-ion battery cells using reversible strain heterogeneity. *J Energy Storage* **2021**, *40*, 102788.

27. Bach, T. C.; Schuster, S. F.; Fleder, E.; Müller, J.; Brand, M. J.; Lorrmann, H.; Jossen, A.; Sextl, G., Nonlinear aging of cylindrical lithiumion cells linked to heterogeneous compression. *J Energy Storage* **2016**, *5*, 212–223.

28. Lewerenz, M.; Sauer, D. U., Evaluation of cyclic aging tests of prismatic automotive LiNiMnCoO2–Graphite cells considering influence of homogeneity and anode overhang. *J Energy Storage* **2018**, *18*, 421–434.

29. Kato, H.; Kobayashi, Y.; Miyashiro, H., Differential voltage curve analysis of a lithium-ion battery during discharge. *J Power Sources* **2018**, *398*, 49-54.

30. Ren, X.; Li, Z.; Tian, W.; Zheng, Y.; Sun, J.; An, L.; Wang, F.; Wen, L.; Wang, X.; Wang, L.; Liang, G., Enhanced cycling performance of cylindrical lithium-ion battery with high areal capacity electrodes via non-uniform load. *Ionics* **2020**, *26* (2), 691-702.

31. Liu, Y. Y.; Zhu, Y. Y.; Cui, Y., Challenges and opportunities towards fast-charging battery materials. *Nat Energy* **2019**, *4* (7), 540–550.

32. Sui, W. T.; Zhang, D., Four Methods for Roundness Evaluation. *Phys. Procedia* **2012**, *24*, 2159–2164.

33. Arlot, S.; Celisse, A., A survey of cross-validation procedures for model selection. *Stat. Surv.* **2010**, *4* (none), 40–79, 40.

34. Wang, X. Y.; Fang, Q. H.; Dai, H. F.; Chen, Q. J.; Wei, X. Z., Investigation on Cell Performance and Inconsistency Evolution of Series and Parallel Lithium-Ion Battery Modules. *Energy Technol-Ger* **2021**, *9* (7), 2100072.

Hua, Y.; Zhou, S. D.; Cui, H. G.; Liu, X. H.; Zhang, C.; Xu, X. W.; Ling,
H. P.; Yang, S. C., A comprehensive review on inconsistency and equalization technology of lithium-ion battery for electric vehicles. *Int J Energ Res* 2020, 44 (14), 11059-11087.

36. Zhang, Z. Y.; Zhang, L. Z.; Hu, L.; Huang, C. X., Active cell balancing of lithium-ion battery pack based on average state of charge. *Int J Energ Res* **2020**, *44* (4), 2535-2548.

37. Zou, K. H.; Tuncali, K.; Silverman, S. G., Correlation and simple linear regression. *Radiology* **2003**, *227* (3), 617–22.

 Akoglu, H., User's guide to correlation coefficients. *Turk. J. Emerg. Med.* 2018, *18* (3), 91–93.

Ghojogh, B.; Crowley, M., The theory behind overfitting, cross validation, regularization, bagging, and boosting: tutorial. *arXiv.1905.12787* 2019.

40. Hastie, T., Ridge Regularization: An Essential Concept in Data Science. *Technometrics* **2020**, *62* (4), 426–433.

3. Entropymetry for detecting micro-cracks in high-nickel layered oxide cathodes

3.1. Introduction

As electric vehicles (EVs) are increasingly finding their way into our everyday lives, the demand for monitoring the battery state with focus on safety and performance has strengthened.¹⁻³ Even if a battery cell is manufactured without defects, it tends to degrade with cycling and time. More challenging is that the degradation behavior is difficult to predict because the available parameters (i.e., the current, voltage, capacity, and temperature) and combinations thereof do not accurately reflect the state of the cell. For example, cells that repeatedly undergo fast charging or are exposed to high temperature usually exhibit shorter lifetimes,^{4, 5} but it is nontrivial to forecast when and how the capacity decay starts and evolves. Thus, from the outside, it is difficult to diagnose the health and safety of a cell and this is the very limitation of current battery management systems (BMSs).³ By contrast, examination of the interior of a cell at the material level is a well-known approach to identify the degradation mechanism. For example, high-nickel (Ni) layered cathode materials, the most popular family of cathode materials for EV applications, are known to degrade by parasitic side reactions on their surface involving transition metal (TM) dissolution in conjunction with Li-Ni cation mixing. However, methods capable of capturing the

degradation states of these materials and interfaces in a nondestructive manner are presently unavailable.

The aforementioned degradation of layered oxide cathodes engages in the structural destruction. The details of crystallographic changes during such destruction have been studied in detail using diverse analytical tools including *X*-ray diffraction (XRD) and transmission electron microscopy (TEM).⁶⁻⁸ However, these methods are destructive; cycling needs to be terminated to allow the cell to be opened. Therefore, the development of non-destructive ways for analyzing the structure of layered cathode materials during cycling is desirable. Along this direction, entropy could be an appropriate parameter because it relates to the crystallographic ordering of the given layered oxide structure.^{9, 10}

Entropy is the state function associated with the degree of randomness of a system.¹¹ With respect to inorganic materials, the entropy represents the disordering of atoms in the corresponding crystal lattice. Thus, the arrangement of Li ions in the layered host structure could be correlated to the entropy in such a way that configurational entropy refers to the number of possible arrangements of Li ion occupancies and vacancies in the lattice structure.^{12, 13} In this regard, Boltzmann's entropy is described by the following formula:

$$S = k_B \cdot \ln W \tag{3-1}$$

where $k_{\rm B}$ is the Boltzmann constant and W is the number of possible microstates. In the case of the layered cathode material, W

corresponds to the number of arrangements of Li ion occupancies and vacancies.

Applying this logic, if the entropy change (ΔS) of a layered cathode material could be measured during cycling, the structural change responsible for inducing performance degradation could be non-destructively monitored. For a battery cell, ΔS could be assessed by measuring the change in the open-circuit voltage (OCV) with respect to the temperature change based on the following series of equations. The derivation of ΔS starts with the following relation involving the Gibbs free energy (ΔG):

$$\Delta G(x) = - nFE(x) \tag{3-2}$$

where n is the charge number of the carrier ion (n=1 for the Li ion), F is the Faraday constant, and E is the OCV. The Gibbs free energy and OCV are both functions of x, the stoichiometry of the Li ion in the formula of the cathode material. The free energy relates to the enthalpy change (ΔH) and entropy change (ΔS):

$$\Delta G(x) = \Delta H(x) - T\Delta S(x) \tag{3-3}$$

Combining equations (2) and (3) yields the following relation between the entropy change and OCV:

$$\Delta S(x) = F(\frac{\mathrm{d}E(x)}{\mathrm{d}T}) \tag{3-4}$$

This equation indicates that ΔS can be obtained by measuring the OCV upon sweeping the temperatures at each state of charge (SOC)

of the cell. $^{14-16}$

The usefulness of entropymetry was demonstrated for LiCoO2 by monitoring the structural configuration at different SOCs over cycling, and the effect of adding Ni as a dopant was elucidated in the same context.⁹ In the present work, we further expand the territory of entropymetry to cover popular high-Ni layered cathode materials, particularly focusing on their structural destruction as represented by the formation of micro-cracks. The family of high-Ni layered cathodes has played a pivotal role in increasing the energy density of a cell and thus extending the mileage of EVs.^{17, 18} However, the high Ni content leads to anisotropic elongation along the c-axis,⁸ which creates micro-cracks. The formation of these cracks has a fatal effect on the cycle life because the electrolyte can penetrate the cracks and trigger side reactions that increase the interfacial resistance.¹⁹ Importantly, the formation of these cracks and the resulting structural heterogeneity would change ΔS ,^{20, 21} indicating that entropymetry could be an appropriate non-destructive tool to monitor the formation of cracks in high-Ni cathode materials and therefore assess the health of the corresponding cell. By employing various cycling conditions as well as *in-situ* XRD, we indeed verify that entropymetry can mirror the structural degradation of highnickel layered oxide cathodes.

3.2. Result and discussion

3.2.1. Interpretation of ΔS profiles

Among the family of high-Ni layered cathodes, we evaluated LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) of which the Ni-content is sufficiently large to induce micro-cracks.⁸ We first note that the entropy change experienced by layered cathode materials is mainly related to configurational entropy rather than vibrational or electronic entropy. This is in accordance with Fultz and Yazami's earlier report that the vibrational and electronic entropy contribute insubstantially during the operation of LiCoO₂.²² Figure 3. 1A shows the ΔS and dQ dV⁻¹ profiles of precycled NCM811 as a function of the OCV while charging during its first cycle. Interestingly, in the regions shaded pale green where the dQ dV⁻¹ profile exhibits peaks, the ΔS profile declines monotonically with a slope reversal in between the shaded colored regions. This correlation seems reasonable because the peaks of the $dQ dV^1$ profile usually are associated with electrochemical reactions accompanied by structural changes that alter the lattice arrangements significantly.²³

To understand the profile shape by particularly focusing on the region demarcated by the orange box in Figure 3. 1A, three different *S* profiles were simulated with respect to the energy state (Figure 3. 1B): no separation (black), mild separation (green), and discrete separation (grey). The "no separation" behavior corresponds to the monotonic Li (de)intercalation in the absence of drastic entropy



Figure 3. 1 (A) ΔS (black) and $dQ dV^{-1}$ (blue) profiles of NCM811 along the open circuit voltage (OCV) landscape. (B) Schematic diagrams of entropy (*S*) and entropy change (ΔS) with different degrees of energy state separation in the OCV landscape.

change, whereas the two split convex profiles (mild and discrete separations) indicate the presence of a restricted phase at the midpoint, dividing the *S* landscape into front and rear parts.^{12, 13, 24} The degree of separation between the two states depends on the extent to which the mid-phase condition is restricted. For example, if the mid-phase is completely restricted ($S_{mid} = 0$), the front and rear states are discretely separated (see "discrete separation" in Figure

3. 1B). Each Li site has its own energy state at which a Li ion can be (de)intercalated, and the energy of this site is determined based on the lattice environment offered by the host structure. In this regard, each peak on the $dQ dV^{-1}$ profile (blue curve in Figure 3. 1A) can be considered to be the potential at which Li ions are stored at sites with the equivalent energy states. Because the profile of S typically becomes convex when Li ions fill sites of the equivalent energy state, the apex of the convex profile of S corresponds with each peak on the $dQ dV^{-1}$ profile. In this way, the two pale green regions in Figure 3. 1B represent two different energy states, which manifest themselves as independent convex parabolas on the S profile. These two convex parabolas are then converted into two separate monotonically declining curves on the ΔS profile. At the same time, the mid-point between the two parabolas in the S profile translates into a slope reversal around the mid-point of the ΔS profile. Thus, the slope reversal on the ΔS profile, in turn, can be correlated with the presence of a restricted phase in the S landscape. Moreover, the more entropically restricted the mid-phase is, the steeper the reversed slope becomes near the mid-point (grey curve in Figure 3. 1B). With this logic, the relatively gentle slope reversal in the middle region in Figure 3. 1A (red arrow in the orange box) indicates mild separation with respect to S. In addition, we calculated the ΔS profile of NCM811 along the SOC by assuming that each peak on the $dQ dV^{-1}$ profile corresponds to an equivalent energy state of Li sites (see details in Figure 3. 2). The calculated ΔS profile corresponds well with the measured ΔS profile, which validates our reasoning above. This interpretation of ΔS in relation to changes in the cathode structure is well aligned with that of previous studies on LiMn₂O₄.^{13,}



Figure 3. 2 (A) Comparison of calculated and measured ΔS of NCM811 as a function of the voltage. (B) Peak deconvolution of the $dQ dV^{-1}$ plot recorded during charging, which was used to calculate ΔS . Supposing that each peak represents Li sites with equivalent energy, ΔS can be calculated by following equation 3–6.

Entropy of mixing =
$$-R (x_1 \ln x_1 + x_2 \ln x_2)$$
 (3-5)
 x_i = The mole fraction of component *i*

$$\Delta S = -R \frac{d[\sum_{x=1}^{n} \{P_{\text{Li}'x}(V) * \ln P_{\text{Li}'x}(V) + P_{\text{Vac}'x}(V) * \ln P_{\text{Vac}'x}(V)\}]}{dV}$$
(3-6)

 $P_{\text{Li'}x}(V)$ = Possibility of the vacancies being occupied with Li ions with the equivalent energy (x) at the corresponding voltage

=

Integrated area to the corresponding voltage (*V*) in the peak with the equivalent energy (*x*) Total integrated area of the peak with the equivalent energy (*x*)

 $P_{\text{Vac'}x}(V)$ = Possibility of the vacancies being unoccupied with Li ions with the equivalent energy (x) at the corresponding voltage = 1 -

Integrated area to the corresponding voltage (*V*) in the peak with the equivalent energy (*x*) Total integrated area of the peak with the equivalent energy (*x*)

3.2.2. Structural changes of NCM811 along with the SOC

We conducted *in-situ* XRD analysis to observe the structural change of NCM811 during charging with the aim of correlating these changes with its entropy change. Figure 3. 3A shows the evolution of in-situ XRD peaks corresponding to the *c*-lattice (003) and *a*lattice (110) during charging.⁸ The changes in these lattice parameters were calculated from the XRD results and are presented in the upper part of Figure 3. 3B. The c-lattice parameter increases gradually as the potential scans to around 4 V, but decreases abruptly at around 4.2 V. By contrast, the a-lattice parameter decreases continuously in the same potential range. When charging commences, the distance between the oxygen layers increases as Li ions are extracted because of the diminished screening effect of Li ions. As charging progresses, however, the negative charges on the oxygen atoms decrease because the TM 3d and O 2p orbitals overlap to a certain extent, thereby lowering the interslab repulsion and causing the oxygen layers to collapse at high SOC levels.²³ Apart from the changes in the lattice parameters, peak broadening also provides information related to the crystalline size and microstrain of the material.²⁵ The broadening of the (003) peak also changes drastically near 4.2 V and this is discussed in detail in the following section.

In fact, the lattice parameters of most Ni-rich NCM layered



Figure 3. 3 (A) Evolution of the in-situ XRD profiles around the (003) and (110) peaks during the first charging of NCM811 after precycling. The red profiles were obtained at the voltages noted on the left. (B) Changes (top) in the c- and a-lattice parameters along with the OCV and their derivatives (bottom). D represents d- spacing.

cathodes undergo similar changes;^{8, 26} particularly, with increasing nickel content (notably ≥ 0.8), the H2 \rightarrow H3 phase transition occurs more dominantly near 4.2 V and the corresponding decrease in the intensity of the *c*-lattice peak becomes more prominent,²³ introducing local strain at the grain boundaries.²⁷ Notably, the scale of the *c*-lattice change (~ 0.6 Å) is much larger than that of the *a*lattice (~ 0.06 Å), as is evident from the differential *d*-spacing curves with respect to the voltage (dDd V⁻¹, D = d-spacing) in Figure 3. 3B. Therefore, consistent with the literature,^{19, 26, 28, 29} the anisotropic expansion/contraction near 4.2 V and the resulting abrupt change in the *c*-lattice parameter must be the main culprit responsible for the formation of cracks between and within Ni-rich NCM particles.

3.2.3. Structural heterogeneity by micro-crack formation

Figure 3. 4A–C shows cross-sectional images of secondary particles of the NCM811 cathode at different cycling states. Here, the precycle refers to the state after two formation cycles, whereas the other two images show the cathode after 100 cycles at 60 °C with upper cut-off potentials of 4.1 V and 4.3 V, respectively. The cycling performance and voltage profiles of these different conditions are presented in Figure 3. 5. After the precycle, the particle did not appear to contain any micro-cracks at all (Figure 3. 4) whereas after


Figure 3. 4 Cross-sectional SEM images of NCM811 particles (A) after precycle and at 101th cycle at 60 ° C with upper cut-off of (B) 4.1 V and (C) 4.3 V. The scale of the white bar is 5 μ m. Magnified *in-situ* XRD profiles near (003) peaks at OCVs of (D) 4.15 V, (E) 4.2 V, and (F) 4.25 V.

100 cycles with upper cut-off voltages of 4.1 V and 4.3 V, the particles displayed cracks of various magnitudes (Figure 3. 4B and 3. 4C). A comparison of the two particles after 100 cycles revealed that crack formation at the microscale was more severe when the cathode was charged to 4.3 V (Figure 3. 4C), reconfirming that cracks are dominantly formed at higher voltages.^{30, 31}



Figure 3. 5 Voltage profiles at the 2^{nd} and 100^{th} cycles for NCM811 half-cells with cut-off voltages of (A) 4.1 V and (B) 4.3 V with 1C/1C (charge/discharge) at 60 °C.

For high-Ni NCM cathodes, heterogenous lithiation is a wellaccepted phenomenon as lithiation takes place throughout many primary particles with different sizes and levels of contact with the electrolyte. Doeff et al.³² confirmed the occurrence of heterogenous lithiation in polycrystalline cathode materials by observing the distribution of the oxidation states of Ni in a secondary particle using X-ray absorption near-edge structure (XANES) analysis to create a 2D map. In contrast to the intuition that heterogenous lithiation in a secondary particle could occur mainly because of the kinetic limitation of Li ion diffusion through the secondary particle, the heterogenous SOC in a secondary particle remains even after an extended period of rest. Chueh et al. explained that the heterogenous SOC across primary particles (even after a long rest) could arise to relieve the heterogeneous stress field among the primary particles in a polycrystalline secondary particle.²¹ In the same context, Liu et al. revealed the occurrence of inhomogeneities between the surface and bulk with respect to the oxidation state during cycling. In particular, high-voltage operation is known to play a role in inducing local disorder and strain from which micro-cracks evolve.²⁰

Within a primary particle, intragranular cracks could also be generated in relation to heterogeneous (de)lithiation along the c-lattice.³³ These intragranular cracks can be triggered by the formation of dislocations or transition to the rock salt phase, both of which give rise to tensile stress and consequently uneven (de)intercalation of Li ions. A crack usually evolves from the premature stage to the more discrete, permanent stage as tensile stress is accumulated, and it also tends to propagate through a granule.^{6, 34} Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) analyses portray a consistent scenario with regard to microstructural evolution (Figure 3. 6). Upon scanning from the bulk region to an intragranular crack (white arrow in Figure 3. 6A), the oxidation state of Ni decreases



Figure 3. 6 (A) STEM image and (B) EELS analysis of NCM811 particles after 100 cycles at 60 °C with upper cut-off of 4.3 V. EELS was scanned along the direction indicated by the white arrow in (A).

(Figure 3. 6B), which is indicative of the formation of the rock salt phase in the vicinity of the crack. Hence, an intragranular phase transition constitutes evidence of the atomic heterogeneity of a cycled NCM811 particle involving crack formation.⁶

Figure 3. 4D-F show the magnified in-situ XRD peaks of NCM811 after the precycle and at the 101th cycle at 60 °C with upper cut-off potentials of 4.1 V and 4.3 V, respectively. The reason for focusing on the profiles when the potential passed through $4.2~\mathrm{V}$ in each case is the drastic phase transition known to occur around this potential. Peak broadening or separation at 4.2 V could occur via the following mechanisms. First, the NCM family undergoes an $H2 \rightarrow H3$ phase transition at ~ 4.2 V although the degree of the phase transition is known to vary depending on the Ni content.⁸ Second, multiple peaks could appear in reflection of a heterogenous SOC within a secondary particle.³⁵ In these particles, rapid and anisotropic contraction of randomly oriented primary particles also causes the strain and extent of lithiation to vary.²¹ In this manner, the formation of intra- and intergranular cracks would accelerate heterogenous (de)lithiation accompanied with peak broadening around ~ 4.2 V during charging. Doeff and Liu et al.³⁶ also reported that cracks hinder the facile diffusion of Li ions into particles such that the local difference in ionic diffusivity among primary particles causes different SOCs in a secondary particle.

The peak broadening was evaluated quantitatively by measuring the integral breadth, defined as the integral area of the peaks over the intensity of the highest peak, at OCVs of 4.15, 4.2, and 4.25 V to compare the peak broadening for different cycling conditions during charging. For the precycled electrode, the (003) peak shifts to a higher 2-theta value without peak separation (Figure 3. 4D), which means that the phase separation between H2 and H3 is impeded.^{33, 37} Nonetheless, owing to the presence of the energy barrier between the two phases, the integral breadth slightly increases at 4.2 V (the potential at which the H2 \rightarrow H3 phase transition is known to occur), as compared to that at 4.15 V and 4.25 V. However, the cycled NCM811 electrodes showed peak separations and broader peaks at 4.2 V (Figure 3. 4E and 3. 4F). Between the two different cutoff conditions, the electrode with the cut-off of 4.3 V had broader peaks (Figure 3. 4F) than that with the cut-off of 4.1 V (Figure 3. 4E). This observation can be understood in a way that the phase separation between H2 and H3 becomes more significant during cycling with the higher cutoff voltage in the microscopic environment in which crack formation accelerates uneven (de)lithiation along the c-lattice layers. Additionally, intergranular cracks themselves give rise to a heterogenous SOC between primary particles. In the same vein, the degree of shift with respect to the c-lattice parameter from 4.15 V to 4.25 V increases from Figure 3. 4D to Figure 3. 4F: 0.36 Å after the precycle, 0.45 Å after 100 cycles with a cut-off of 4.1 V, and 0.52 Å after 100 cycles with a cut-off of 4.3 V. These results imply that the broader distribution of d-spacing of the c-lattice layers directly stems from the layers splitting into lithiated and delithiated ones, which results in the emergence of dual XRD peaks for the (003) plane. Overall, the micro-cracks would affect the lithiation heterogeneity throughout all the particles, and this property can be captured by measuring the peak broadening using in-situ XRD at ~4.2 V.

3.2.4. Detection of micro-cracks from ΔS profiles

Figure 3. 7 displays the cycling performance of four cells operated for different cycling periods or under different conditions: 50 or 100 cycles at 60 °C with cut-off potentials of 4.1 or 4.3 V. These series of data verify that the cyclability of NCM811 is highly sensitive to the cut-off voltage when cycled at high temperature. To correlate the cycling performance with the degree of crack formation, we plotted the integral breadths for these cells after 50 or 100 cycles (Figure 3. 7). The integral breadths of all the cells remain in the narrow range when the operating potential is below 4.1 V. However,



Figure 3. 7 Cycling performance of four NCM811 cells for 50 or 100 cycles at 60 ° C with cut-off potentials of 4.1 or 4.3 V, respectively.

the integral breadth profiles increased rapidly around 4.2 V for all of the cells, but they increased distinctly with that of the cell operated for 100 cycles with a cut-off of 4.3 V having increased most significantly. In the same line as the aforementioned description, the increase in the integral breadth is attributed to the H2 \rightarrow H3 phase



Figure 3. 8 (A) Changes in the integral breadth (integrated intensity/maximum intensity of the highest peak) based on analyses of the *in-situ* XRD peaks. (B) Entropy changes *vs.* OCV. The error bars at 4.2 V correspond to the range of minimum and maximum values obtained from four different cells measured under the same conditions.

transition. The increase is thus associated with heterogenous lithiation induced by micro-cracks, suggesting that the cell with a cut-off of 4.3 V experienced crack formation most considerably for 100 cycles. Importantly, the changing trend observed for the integral breadth profiles bears a remarkable resemblance to that of the ΔS profiles (Figure 3. 8), particularly near 4.2 V. The cell operated for 100 cycles with a cut-off of 4.3 V exhibited the greatest decrease in ΔS . This correlation between the integral breadth and ΔS can be understood on the basis of the rationale that heterogeneous lithiation



Figure 3. 9 Multiple measurements of ΔS for the half-cells of NCM811 after (A) 50 cycles with cut-off of 4.1 V, (B) 50 cycles with cut-off of 4.3 V, (C) 100 cycles with cut-off of 4.1 V and (D) 100 cycles with cut-off of 4.3 V at 60 ° C.

over different particles to broaden the (003) peak is directly linked to the behavior of ΔS as the heterogeneity represents the complexity in the atomic configuration in the lattice. Specifically, as the microstructures of particles become heterogeneous, the number of available microstates at the given SOC decreases, with the result that ΔS is lowered accordingly. The ΔS measurements were quite reproducible over multiple cells for identical cycling conditions (Figure 3. 9). The lattice distortion accompanying the phase transition above 4.2 V hinders Li diffusion between primary particles, which further accelerates the heterogenous (de)lithiation. The rapid decline in the Li ion diffusivity above 4.2 V was confirmed by analyses using the galvanostatic intermittent titration technique (GITT) (Figure 3. 10).³⁸

As depicted in Figure 3. 11, the energy states of the Li sites are more or less equivalent in the original state as the local lattice



Figure 3. 10 Relative diffusivity *vs.* SOC for NCM811 cathode as measured via GITT analysis after 100 cycles at 60 °C with different cut-off voltages.



Figure 3. 11 Schematic comparison between homogeneous and heterogeneous lithiation of an NCM811 particle before and after degradation. As the number of micro-cracks and extent of surface degradation increase, heterogeneous lithiation preferably occurs, which causes the configurational entropy to decrease.

environments of the Li sites are largely identical. However, the formation of cracks perturbs the original uniform energy states of the Li sites such that, at a given SOC, the number of possible microstates decreases; that is, the configurational entropy is lowered. Projecting the impact of the local lattice environment on individual Li ions in the process of diffusion, those Li ions in the original state have equivalent energy barriers for diffusion to homogeneously lithiate a particle. In contrast, in the case of a cracked particle, Li ions experience different energy barriers for diffusion at a given state of charging, whereupon heterogeneous lithiation is promoted. All in all, as a result of the increasing formation of cracks, heterogeneous environments constitute the core of uneven lithiation and could explain why entropymetry can serve as a tool for detecting cracks in Ni-rich layered oxide cathodes.

3.2.5. Generalization across the family of high-Ni layered oxides

Other than the NCM811 cathodes, entropymetry was applied to NCM622 and LiNiO₂ (Figure 3. 12) to see the versatility of this technique with respect to the detection of crack formation arising from high-Ni compositions. For this test, half-cells containing both



Figure 3. 12 Cross-sectional SEM images of (A) NCM622 and (B) LiNiO₂ particles after 100 cycles at 60 °C with upper cut-off of 4.3 V. The scale of the white bar is 5 µm. (C) Cycling performance of half-cells with NCM622 and LiNiO₂ cathodes at 60 °C with cut-off potential of 4.3 V. (D) Entropy changes along OCV for the NCM622 and LiNiO₂ cells before and after cycling.

NCM622 and LiNiO₂ were cycled at 60 °C with the cut-off potential of 4.3 V. As displayed in Figure 3. 12C, the capacity of the NCM622 cell gradually decreased for 100 cycles, whereas that of the LiNiO₂ cell steeply declined even within 25 cycles. The more severe capacity fading of the LiNiO₂ cell is ascribed to the aforementioned mechanism that, the higher the Ni content of the NCM cathode, the greater is the amount of shrinkage along the c-axis above 4.1 V.⁸ This axial strain induces severe crack propagation and a rapid decline in capacity. An SEM analysis visualized the lesser extent of crack formation in secondary particles of NCM622 after 100 cycles than those of LiNiO₂ after only 25 cycles (Figure 3. 12A and 3. 12B). To confirm the correlation between the degree of crack formation and the change in the entropy metry profile, the entropy changes of NCM622 and LiNiO₂ were measured before and after cycling. Precycled LiNiO₂ exhibited the signature trough at 4.2 V (the pale green region in Figure 3. 12D), which downshifted after 25 cycles, and is consistent with the trend observed for NCM811 in Figure 3. 8B. By contrast, the change in the entropy of NCM622 after 100 cycles with a cut-off of 4.3 V was far less prominent in the signature region compared to both LiNiO₂ after 25 cycles and NCM811 after 100 cycles, indicating that the heterogeneity in its structure was less advanced. The comparative results between these two cathodes with their different Ni contents reconfirm that entropymetry is a useful tool for evaluating the extent to which micro-cracks have developed.

3.3. Conclusion

In summary, we demonstrated the effectiveness of entropymetry as a non-destructive analytical tool for diagnosing the formation and evolution of micro-cracks in high-Ni layered cathodes, which is closely related to their cycle life. Entropymetry detects microcracks by utilizing the structural heterogeneity as the main parameter because the formation and propagation of micro-cracks changes the number of microstates of Li ion occupancy/vacancy and thus the configurational entropy. We foresee the advancement of BMS technology by taking into consideration the key chemical reactions in a cell and the structural changes in the electrodes, and expect entropymetry to play a critical role in the development of this technology.

3.4. Experimental procedures

Electrochemical tests

The cathodes were fabricated by first preparing a slurry by dispersing the active material (NCM622 or 811, LiNiO₂), poly(vinylidene fluoride) (PVDF, Kynar), and super P (TIMCAL) in N-methyl-pyrrolidone (NMP) with a mass ratio of 83 : 10 : 7. The slurry was cast on aluminum foil and dried at 70 °C for 12 h under vacuum. The mass loading of the active material was 1.5 mg cm⁻².

Coin cells were prepared in an Ar-filled glove box by assembling a polypropylene separator (Celgard 2400), the cathode (working electrode), and Li metal foil (counter/reference electrode). Lithium hexafluorophosphate (LiPF₆, 1M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC : DMC = 1 : 1 vol%, PANAX E-TEC) was used as the electrolyte. For cycling tests, the galvanostatic mode was adopted in the potential window of 3.0-4.3 V vs. Li/Li⁺ using a battery cycler (PEBC05-0.01, PNE solution). Cycling was carried out in constant current (CC) mode of 1C followed by constant voltage (CV) mode with a cut-off of 0.5C for charging, and CC mode of 1C for discharging. Before cycling, every cell underwent pre-cycling at 0.1C for 2 cycles to form a stable solid electrolyte interphase (SEI) layer.

Characterization of materials

In-situ XRD patterns were acquired at the Analysis Center for Research Advancement (KARA) of Korea Advanced Institute of Science and Technology (KAIST) using an X-ray diffractometer (R-AXIS IV, Rigaku Corp.) and on beamline 1D of the Pohang Accelerator Laboratory (PAL) using a MAR345 image plate detector. A 2032-type coin cell with a 1.5 mm hole at the center was used for the transmission of X-rays and the hole was sealed with Mylar film (6 μ m, PREMIER lab supply) and 4460 adhesive epoxy (Duralco). The coin cell was scanned at 0.06 C for 30 min and rested for 15 min, and these steps were repeated for the entire charging period. The beam exposure time was 5 min in the 15 min-rest step and the beam source was Cu K α . The 2D images were converted to diffraction patterns by using RIGAKU Display. Cross-sectional images of the electrodes were obtained by field-emission scanning electron microscopy and a focused ion beam (FE-SEM/FIB, Helios G4, Thermo Fisher Scientific). The atomic morphology was visualized by Cs-corrected scanning transmission electron microscopy (Cs-STEM, JEM-ARM200F, JEOL Ltd). The FE-SEM, FIB, and Cs-TEM analyses were performed at the National Center for Interuniversity Research Facilities (NCIRF) of Seoul National University.

Entropy measurements

The ΔS measurements were conducted by remotely controlling the operation temperature of a cell by using an incubator (IL-11, JEIO TECH). The voltage and SOC were monitored and adjusted by using a battery cycler (PEBC05-0.01, PNE solution). To extract ΔS , the variation in the OCV was monitored at each SOC while the temperature was changed. The temperature was first set to 30 °C for 120 min and then lowered to 20 °C for 60 min and again raised to 30 °C. The OCV measurements at the different temperatures were repeated at the next SOC, which was reached by applying 0.06C for 30 min. The last OCV point during charge was 4.5 V. To ensure accurate ΔS measurements, a baseline correction was applied to the OCV profile; a virtual baseline was created (blue dotted line in Figure 3. 13) by connecting the two OCV points at 2 h and 3.3 h, which correspond to the exact OCV values measured at 30 °C just before the temperature was lowered to 20 °C and again immediately after maintaining the temperature at this level for 60 min. The reproducibility of this methodology was confirmed by conducting

73



Figure 3. 13 Measurement of the entropy changes of batteries by monitoring variations in the OCV upon temperature variations. measurements on multiple identical cells (Figure 3. 14).



Figure 3. 14 Verification of the reproducibility of ΔS measurements for different cells containing precycled NCM811 cathodes.

3.5. References

 Severson, K. A.; Attia, P. M.; Jin, N.; Perkins, N.; Jiang, B.; Yang, Z.; Chen, M. H.; Aykol, M.; Herring, P. K.; Fraggedakis, D.; Bazan, M. Z.; Harris, S. J.; Chueh, W. C.; Braatz, R. D., Data-driven prediction of battery cycle life before capacity degradation. *Nat Energy* **2019**, *4* (5), 383-391.

Huang, J. Q.; Blanquer, L. A.; Bonefacino, J.; Logan, E. R.; Dalla Corte,
 D. A.; Delacourt, C.; Gallant, B. M.; Boles, S. T.; Dahn, J. R.; Tam, H. Y.;
 Tarascon, J. M., Operando decoding of chemical and thermal events in commercial Na(Li)-ion cells via optical sensors. *Nat Energy* 2020, *5* (9), 674-683.

3. Lu, L. G.; Han, X. B.; Li, J. Q.; Hua, J. F.; Ouyang, M. G., A review on the key issues for lithium-ion battery management in electric vehicles. *J Power Sources* **2013**, *226*, 272–288.

Ma, S.; Jiang, M. D.; Tao, P.; Song, C. Y.; Wu, J. B.; Wang, J.; Deng,
T.; Shang, W., Temperature effect and thermal impact in lithium-ion batteries: A review. *Prog. Nat. Sci.* 2018, *28* (6), 653-666.

5. Fleischhammer, M.; Waldmann, T.; Bisle, G.; Hogg, B. I.; Wohlfahrt– Mehrens, M., Interaction of cyclic ageing at high–rate and low temperatures and safety in lithium–ion batteries. *J Power Sources* **2015**, *274*, 432–439.

6. Lin, Q. Y.; Guan, W. H.; Zhou, J. B.; Meng, J.; Huang, W.; Chen, T.; Gao, Q.; Wei, X.; Zeng, Y. W.; Li, J. X.; Zhang, Z., Ni-Li anti-site defect induced intragranular cracking in Ni-rich layer-structured cathode. *Nano Energy* **2020**, *76*, 105021.

7. Nam, K. W.; Bak, S. M.; Hu, E. Y.; Yu, X. Q.; Zhou, Y. N.; Wang, X. J.; Wu, L. J.; Zhu, Y. M.; Chung, K. Y.; Yang, X. Q., Combining In Situ Synchrotron X-Ray Diffraction and Absorption Techniques with Transmission Electron Microscopy to Study the Origin of Thermal Instability in Overcharged Cathode Materials for Lithium-Ion Batteries. *Adv Funct Mater* **2013**, *23* (8), 1047–1063.

8. Ryu, H. H.; Park, K. J.; Yoon, C. S.; Sun, Y. K., Capacity Fading of Ni-Rich Li[NixCoyMn1-x-y]O2 (0.6 $\leq x \leq 0.95$) Cathodes for High-

Energy-Density Lithium-Ion Batteries: Bulk or Surface Degradation? *Chem. Mater.* **2018**, *30* (3), 1155–1163.

9. Kim, H. J.; Park, Y.; Kwon, Y.; Shin, J.; Kim, Y. H.; Ahn, H. S.; Yazami, R.; Choi, J. W., Entropymetry for non-destructive structural analysis of LiCoO2 cathodes. *Energ Environ Sci* **2020**, *13* (1), 286–296.

 Yazami, R.; Reynier, Y.; Fultz, B., Entropymetry of Lithium Intercalation in Spinel Manganese Oxide: Effect of Lithium Stoichiometry. *ECS Trans.* 2006, 1 (26), 87–96.

 Lambert, F. L., Configurational entropy revisited. *J Chem Educ* 2007, 84 (9), 1548–1550.

12. Leiva, E. P. M.; Perassi, E.; Barraco, D., Shedding Light on the Entropy Change Found for the Transition Stage II→Stage I of Li-Ion Storage in Graphite. *J. Electrochem. Soc.* **2016**, *164* (1), A6154-A6157.

Kobayashi, Y.; Mita, Y.; Seki, S.; Ohno, Y.; Miyashiro, H.; Nakayama,
M.; Wakihara, M., Configurational Entropy of Lithium Manganese Oxide and
Related Materials, LiCryMn2-yO4 (y= 0, 0.3). *J. Electrochem. Soc.* 2008, 155 (1), A14.

14. Zhang, X. F.; Zhao, Y.; Patel, Y.; Zhang, T.; Liu, W. M.; Chen, M.; Offer, G. J.; Yan, Y., Potentiometric measurement of entropy change for lithium batteries. *Phys. Chem. Chem. Phys.* **2017**, *19* (15), 9833–9842.

Osswald, P. J.; del Rosario, M.; Garche, J.; Jossen, A.; Hoster, H. E.,
 Fast and Accurate Measurement of Entropy Profiles of Commercial
 Lithium-Ion Cells. *Electrochim Acta* 2015, *177*, 270–276.

16. Yazami, R., *Thermodynamics of Electrode Materials for Lithium–Ion Batteries*. 2009; p 67–102.

Liu, W.; Oh, P.; Liu, X.; Lee, M. J.; Cho, W.; Chae, S.; Kim, Y.; Cho,
 J., Nickel-rich layered lithium transition-metal oxide for high-energy
 lithium-ion batteries. *Angew. Chem. Int. Ed.* 2015, *54* (15), 4440-57.

 Kim, J.; Lee, H.; Cha, H.; Yoon, M.; Park, M.; Cho, J., Prospect and Reality of Ni-Rich Cathode for Commercialization. *Adv Energy Mater* 2018, 8 (6), 1702028.

Yin, S. Y.; Deng, W. T.; Chen, J.; Gao, X.; Zou, G. Q.; Hou, H. S.; Ji,
 X. B., Fundamental and solutions of microcrack in Ni-rich layered oxide

cathode materials of lithium-ion batteries. *Nano Energy* **2021**, *83*, 105854. 20. Mao, Y. W.; Wang, X. L.; Xia, S. H.; Zhang, K.; Wei, C. X.; Bak, S.; Shadike, Z.; Liu, X. J.; Yang, Y.; Xu, R.; Pianetta, P.; Ermon, S.; Stavitski, E.; Zhao, K. J.; Xu, Z. R.; Lin, F.; Yang, X. Q.; Hu, E. Y.; Liu, Y. J., High-Voltage Charging-Induced Strain, Heterogeneity, and Micro-Cracks in Secondary Particles of a Nickel-Rich Layered Cathode Material. *Adv Funct Mater* **2019**, *29* (18), 1900247.

21. Gent, W. E.; Li, Y.; Ahn, S.; Lim, J.; Liu, Y.; Wise, A. M.; Gopal, C. B.; Mueller, D. N.; Davis, R.; Weker, J. N.; Park, J. H.; Doo, S. K.; Chueh, W. C., Persistent State-of-Charge Heterogeneity in Relaxed, Partially Charged Li1- x Ni1/3 Co1/3 Mn1/3 O2 Secondary Particles. *Adv. Mater.* **2016**, *28* (31), 6631-8.

Reynier, Y.; Graetz, J.; Swan-Wood, T.; Rez, P.; Yazami, R.; Fultz,
B., Entropy ofLiintercalation inLixCoO2. *Phys. Rev. B* 2004, *70* (17), 174304.

23. Kondrakov, A. O.; Gesswein, H.; Galdina, K.; de Biasi, L.; Meded, V.; Filatova, E. O.; Schumacher, G.; Wenzel, W.; Hartmann, P.; Brezesinski, T.; Janek, J., Charge-Transfer-Induced Lattice Collapse in Ni-Rich NCM Cathode Materials during Delithiation. *J Phys Chem C* **2017**, *121* (44), 24381-24388.

24. Schlueter, S.; Genieser, R.; Richards, D.; Hoster, H. E.; Mercer, M. P., Quantifying structure dependent responses in Li–ion cells with excess Li spinel cathodes: matching voltage and entropy profiles through mean field models. *Phys. Chem. Chem. Phys.* **2018**, *20* (33), 21417–21429.

25. Lee, E. J.; Chen, Z.; Noh, H. J.; Nam, S. C.; Kang, S.; Kim, D. H.; Amine, K.; Sun, Y. K., Development of microstrain in aged lithium transition metal oxides. *Nano Lett.* **2014**, *14* (8), 4873–80.

26. Kim, J. H.; Ryu, H. H.; Kim, S. J.; Yoon, C. S.; Sun, Y. K., Degradation Mechanism of Highly Ni-Rich Li[NixCoyMn1-x-y]O2 Cathodes with x > 0.9. ACS Appl. Mater. Interfaces 2019, 11 (34), 30936-30942.

27. Ryu, H. H.; Park, G. T.; Yoon, C. S.; Sun, Y. K., Suppressing detrimental phase transitions via tungsten doping of LiNiO2 cathode for next-generation lithium-ion batteries. *J. Mater. Chem. A* **2019**, *7* (31),

18580-18588.

 Kondrakov, A. O.; Schmidt, A.; Xu, J.; Gesswein, H.; Monig, R.; Hartmann, P.; Sommer, H.; Brezesinski, T.; Janek, J., Anisotropic Lattice Strain and Mechanical Degradation of High- and Low-Nickel NCM Cathode Materials for Li-Ion Batteries. *J Phys Chem C* 2017, *121* (6), 3286-3294.
 Yoon, C. S.; Ryu, H. H.; Park, G. T.; Kim, J. H.; Kim, K. H.; Sun, Y. K., Extracting maximum capacity from Ni-rich Li[Ni0.95Co0.025Mn0.025]O2cathodes for high-energy-density lithiumion batteries. *J. Mater. Chem. A* 2018, *6* (9), 4126-4132.

30. Robert, R.; Novák, P., Structural Changes and Microstrain Generated on LiNi0.80Co0.15Al0.05O2during Cycling: Effects on the Electrochemical Performance. *J. Electrochem. Soc.* **2015**, *162* (9), A1823–A1828.

Cheng, X. P.; Li, Y. H.; Cao, T. C.; Wu, R.; Wang, M. M.; Liu, H.; Liu,
 X. Q.; Lu, J. X.; Zhang, Y. F., Real-Time Observation of Chemomechanical
 Breakdown in a Layered Nickel-Rich Oxide Cathode Realized by In Situ
 Scanning Electron Microscopy. Acs Energy Lett 2021, 6 (5), 1703-1710.

32. Tian, C. X.; Xu, Y. H.; Nordlund, D.; Lin, F.; Liu, J.; Sun, Z. H.; Liu, Y.
J.; Doeff, M., Charge Heterogeneity and Surface Chemistry in Polycrystalline Cathode Materials. *Joule* 2018, *2* (3), 464–477.

33. Lim, J. M.; Hwang, T.; Kim, D.; Park, M. S.; Cho, K.; Cho, M., Intrinsic Origins of Crack Generation in Ni-rich LiNi0.8Co0.1Mn0.1O2 Layered Oxide Cathode Material. *Sci. Rep.* **2017**, *7* (1), 39669.

34. Yan, P.; Zheng, J.; Gu, M.; Xiao, J.; Zhang, J. G.; Wang, C. M., Intragranular cracking as a critical barrier for high-voltage usage of layerstructured cathode for lithium-ion batteries. *Nat. Commun.* **2017**, *8* (1), 14101.

35. Qian, K.; Huang, B.; Liu, Y.; Wagemaker, M.; Liu, M.; Duan, H.; Liu, D.; He, Y. B.; Li, B.; Kang, F., Increase and discretization of the energy barrier for individual LiNixCoyMnyO2 (x + 2y =1) particles with the growth of a Li2CO3 surface film. *J. Mater. Chem. A* **2019**, *7* (20), 12723-12731.

Besli, M. M.; Xia, S. H.; Kuppan, S.; Huang, Y. Q.; Metzger, M.; Shukla,
A. K.; Schneider, G.; Hellstrom, S.; Christensen, J.; Doeff, M. M.; Liu, Y. J.,
Mesoscale Chemomechanical Interplay of the LiNi0.8Co0.15Al0.0502

Cathode in Solid-State Polymer Batteries. *Chem. Mater.* **2019,** *31* (2), 491-501.

Märker, K.; Reeves, P. J.; Xu, C.; Griffith, K. J.; Grey, C. P., Evolution of Structure and Lithium Dynamics in LiNi0.8Mn0.1Co0.102 (NMC811)
Cathodes during Electrochemical Cycling. *Chem. Mater.* 2019, *31* (7), 2545-2554.

38. Li, J.; Huang, J.; Li, H.; Kong, X.; Li, X.; Zhao, J., Insight into the Redox Reaction Heterogeneity within Secondary Particles of Nickel-Rich Layered Cathode Materials. *ACS Appl. Mater. Interfaces* **2021**, *13* (23), 27074-27084.

4. Conclusion

As coming the EV era, knowing the status of cells become important. Battery is based on electrochemical materials, understanding chemical mechanism is essential. And based on understanding chemical phenomena, we should quantify chemical phenomena by using accessible signals such as current, voltage, and temperature. In this dissertation, I introduced two chemical indicators that represent the status inside a cell. The first one was the peak intensity in the DV profile to monitor the heterogeneity of Gr anodes in a cell in relative to the uniformity of a cell. The images inside cells by XRM verified that the heterogeneity indicator matched to the status inside a cell such as arrangement of electrodes or the roundness of a jellyroll. furthermore, the introduced indicator could predict the cycle life of cells at the first cycle so that it could be utilized as inspection and classification tool at the postmanufacturing stage. And the second one was entropymetry to see the structural change of Ni-rich oxide cathodes such as microcrack degradation. It is possible because the entropy represents the arrangement of Li ions in the host structure of active materials. The structural deformation by microcracks could be assessed by the entropy change at ~ 4.2 V in Ni-rich oxide cathodes, which matched to the structural change measured by *in-situ* XRD. Battery diagnosis and management are highly important not only to improve the performance of batteries but also to ensure the safety and reliability of EVs. critical chemical indicators such as the heterogeneity indicator and entropymetry could act as tools for inspecting and managing the batteries.

초 록

전기 자동차(EV) 시대로 전환됨에 따라 리튬 이온 배터리(LIB)의 수명과 안전성에 대해 높은 기준을 요구하고 있습니다. 그 중에서도 LIB의 상태 진단은 EV 시대를 향한 중요한 기술입니다. 배터리 제조 직후부터 모듈 및 팩 조립, EV 운행 중, 수명이 다한 후 배터리 재사용 단계까지 배터리의 탄생부터 폐기까지 모든 단계에서 셀 진단 및 관리는 항상 필요합니다. 그래서 이 학위논문에서는 배터리 진단 및 관리를 위해 배터리 내부의 화학적 이해를 바탕으로 수치화 가능한 화학적 인자를 탐색하여 열화 진단 연구를 수행했습니다.

첫 번째로, 제조 직후 단계에서 LIB의 셀 검사 및 분류는 높은 수준의 안전성과 신뢰성이 요구되는 전기자동차 시대로의 전화을 위한 필수 단계입니다. EV는 수백 개에서 수천 개의 배터리 셀을 포함하기 때문에 수명과 안전성에 대한 높은 기준을 맞추기 위해서는 탑재 전 불량 셀을 선별하는 것이 중요합니다. 따라서 제조 직후 단계에서 셀 내부 상태 진단 및 셀의 성능 등급을 분류하는 것이 중요합니다. 이 논문에서는 셀 검사 및 분류를 위하 핵심 도구로써 전기화학적으로 측정 가능한 균일도 지표와 미분 전압 곡선의 피크 인자를 소개했습니다. 구체적으로, 균일도 지표는 전극의 배열과 같은 셀 내부의 '균일도' 상태와 관련이 있으며, 이는 흑연 음극 내의 리튬 이온 분포에 영향을 미칩니다. 중요한 것은 불균일한 셀이 낮은 사이클 성능을 나타내는 경향이 있어 초기 사이클에서 균일도 지표를 통해 셀의 수명을 예측하고 모듈 조립을 위한 셀을 분류할 수 있다는 것입니다. 실제로, 규일도 지표에 의해 분류된 비슷한 성능의 셐을 포함하는 모듈은 성능 편차가 큰 셀을 포함한 모듈보다 사이클 성능이 향상되었습니다. 균일도 지표와 같은 화학적 인자는 제조 직후 단계에서 배터리를 검사하고 선별함으로써 신뢰성이 높고 안전한 모듈을 보장하는데 기여할 수 있습니다.

8 2

두 번째로, EV 작동 중에 배터리 셀 열화에 대한 실시간 비파괴 모니터링이 매우 중요합니다. 불행하게도 EV용으로 선호되는 LIB 양극인 high-Ni 층상 산화물은 사이클 동안 미세 균열 형성으로 인해 성능 저하를 야기합니다. 이러한 양극에서 microcracks의 생성을 실시간 모니터링하는 분석 도구로 entropymetry라는 방법을 사용했습니다. 층상 양극의 엔트로피 변화는 격자 구성과 관련이 있으며 이러한 microcracks의 진화와 관련된 구조적 불균일도를 반영합니다. 구조적 불균일도 변화는 실시간 *X*-선 회절 곡선의 피크와의 상관관계를 통해 알 수 있었고, 이는 또한 엔트로피 변화와 매칭되어 엔트로피 변화가 구조적 변화를 반영함을 알 수 있었습니다. 여기서 비파괴 진단 도구로 제안된 entropymetry는 EV용 LIB의 안전한 작동과 높은 신뢰성에 크게 기여할 수 있습니다.

요약하자면 배터리 내부의 상태를 반영하는 화학적 인자인 1) 흑연 음극에 대한 균일도 지표와 2) high-Ni 양극에 대한 entropymetry를 차용하여 열화 진단에 활용했습니다. 두 지표 모두 셀 내부의 화학 현상에 기인하는, 미분 전압 곡선의 피크 높이와 엔트로피 변화 프로파일의 피크 높이로 정량화되었습니다. LIB의 안전성과 신뢰성 향상이라는 목표를 위해 셀 내부를 검사하고 관리하는 데 유용한 도구로써 화학적 인자를 탐색하고 실증하였습니다.

주요어 : 리튬 이온 배터리, 배터리 진단, 불균일도, 셀 검사, 셀 분류, entropymetry

학 번:2020-37781

8 3