ABSTRACT: The performance and safety of lithium-ion batteries are plagued by several diverse, nonlinear aging mechanisms influenced by the electrochemical thermal interactions at the electrodes, usage history, and operating conditions. Understanding and deconvoluting the fundamental reaction mechanisms responsible for electrode degradation are key for developing technologies in Li-ion battery diagnostics and prognostics. Hence, there exists a need for high-precision operando techniques to investigate and characterize distinct electrode degradation modes over a gamut of operational variability. Cells embedded with a stable, nonpolarizable reference electrode offer an in situ and operando tool to decouple the complex electrochemical interplay between the electrode pair by measuring individual electrode responses simultaneously with the cell response in the time and frequency domains. This perspective comprehensively looks at 3-electrode (3ε) analytics as a versatile toolbox, highlighting recent techniques and parameters developed with an emphasis on degradation diagnostics and control strategies that is expected to drive the futuristic design of battery management systems.

1. INTRODUCTION

Lithium-ion batteries (LIBs) have become ubiquitous in the modern world with their ever-increasing range of applications in consumer electronics, wearable, electric vehicles, and grid storage. As we move toward high-power applications, identifying degradation and failure is crucial to improve energy efficiency and avoid potentially hazardous safety incidents. Major challenges in failure diagnostics of batteries include diverse aging mechanisms, nonlinear degradation modes, and electrode crosstalk.1

Degradation of batteries is a complex phenomenon influenced by electrochemical, thermal, and mechanical properties of the system, the history of usage (drive cycle), and external factors such as pressure or ambient temperature. Investigating the mechanistic underpinnings of degradation is essential to design engineering solutions for fast charging, reducing operational risks, and maximizing battery life.2,4

Electrode crosstalk plays a crucial role in the lifetime prediction of LIBs as electrode performances are interdependent where electrochemical reactions in one electrode can negatively impact the other electrode having a synergistic effect on aging and cell failure.5 Hence, there exists a need to characterize electrodes concurrently during operation to address capacity fade mechanisms to improve performance and safety and advance prognostics. Moreover, reference electrodes offer the perfect platform to characterize the anode and cathode simultaneously during operation, thereby helping decouple individual electrode contributions and pathways to cell failure. Furthermore, 3-electrode cells with an embedded reference provide nondestructive operando data which can be extended to any battery chemistry and form factor. In this perspective article, we look at the reference electrodes beyond their measurement capability as an analytics toolbox where they can be used for advanced diagnostics and control of LIBs.

Received: October 3, 2021
Accepted: November 17, 2021
Published: December 2, 2021
2. SCOPE OF THREE-ELECTRODE CELL ARCHITECTURE AS AN OPERANDO ANALYTICS TOOLBOX

2.1. Operando Measurement. Incorporating a reference electrode in a cell facilitates operando monitoring and characterization of individual electrodes in the cell at any given condition from charge/discharge cycling and electrochemical impedance spectroscopy. Typical reference electrodes used in LIBs are metallic lithium, lithium alloys (Li−Sn, Li−Al, Li−Au), and the two-phase materials lithium titanium oxide (LTO) and lithium iron phosphate (LFP). The location, orientation, and the geometry of the reference electrode play a vital role in the impedance measurement of the electrodes owing to contact resistance and artifacts arising from the misalignment of electrodes in the three-electrode setup. Irrespective of the choice of material used, the reference electrode must have the following properties to be considered reliable: (1) stable, reproducible potential, (2) chemical and electrochemical stability with time and temperature, (3) compact design which enables ease of insertion, and (4) artifact free configuration to enable transferability of results. Even after careful design, most reference electrodes start experiencing a drift in the measured potential after a finite amount of time due to the formation of a passivation layer on the electrode surface after a couple of months in long-term cycling or aging at high temperatures. Different methods have been used to tackle the drift in the measured reference potential such as surface engineering and pretreatment of the reference electrode or introducing a calibration cycle after every 10 cycles.

This section briefly explores the measurement capability of a three-electrode cell. Figure 1a shows the schematic representation of reference electrode in a cell and its applicability in different form factors. Figure 1b shows the types of measurements feasible using an embedded reference in a full cell in time domain and frequency domain.

2.1.1. Synchronous Electrode Potential Measurement. Despite the complexities in the design and construction, three-electrode cells with an embedded reference remain as the simplest and most inexpensive in situ, operando tool to monitor and decouple individual electrode mechanisms. Figure 1 shows the schematic of a three-electrode cell which can be built in any form factor to simultaneously measure the electrode potentials during cell operation. Deconvolution of electrode potential from the cell voltage enhances our understanding of overpotential contributions from each electrode at any given point of cell cycling.

2.1.2. Decoupling Electrode Impedance Contributions from Cell Impedance. Electrochemical impedance spectroscopy
copy is an in situ measurement technique that provides insights into electrochemical processes occurring at different time scales and helps characterize electrodes through noninvasive means. Impedance measurement of full cells gives the superimposed impedance response of the cathode and the anode, which makes it difficult to deconvolute electrode level processes for meaningful interpretation of the data. Using half-cells or symmetric cells to measure individual electrode impedance is destructive and would require teardown of cells and harvest electrodes at multiple points of operation and aging resulting in an increased number of test cells, test time, and complexity. This process is error-prone and can affect the reproducibility of the results. However, impedance measurement using the reference electrode allows us to non-destructively examine various electrode processes for meaningful interpretation of the data. Tracking the impedance evolution of the electrodes with state of charge, cyclic aging, storage, and abuse conditions paves the way to nondestructively identify and deconvolute different aging mechanisms occurring at the anode and cathode.¹¹,¹⁹–²⁶

2.2. Operando Analytics Using Three-Electrode Cells. Three-electrode cells are traditionally used for operando monitoring and measurement of individual electrode potentials and impedances in the cell. However, a lot more information can be derived from the electrode potential measurement which can lead to predictive diagnostics of cell failure modes by studying the electrode level reaction mechanisms and their interdependence with the rate of aging. The analytical capability of the three-electrode setup is often overlooked due to the dearth of studies using three-electrode-based diagnostics that extend beyond electrode potential and impedance measurement. Figure 2 shows the scope of the operational landscape including nominal operating conditions, abuse conditions, and operational extremes that can be characterized using the state-of-electrode information from three-electrode measurement and the subsequent analytics developed to study electrode reaction mechanisms. This section explores various parameters that have been proposed by earlier studies to examine electrode degradation at different operating conditions using reference electrodes.

2.2.1. Electrode Resistances. Cells cycled with a rest period after charge/discharge have a relaxation potential gradient...
during the rest period. When the potential difference is normalized by the current before the rest period, the relaxation resistance of the electrode can be estimated using eq 1 in Table 1. The calculated relaxation resistance is a combination of ohmic, charge transfer, and concentration polarization resistances in the electrode/cell. The relaxation resistance of the full cell is approximately proportional to the internal resistance and closely follows the pattern of the capacity fade curve.

High-frequency resistance of electrodes can be measured using eq 2 in Table 1 by applying a current pulse of period ranging from 1 ms to 5 s depending upon the precision of the measuring instrument. The high-frequency resistance is a function of electrode/electrolyte interface kinetics at the electrode and is often approximated to the electrode passivation layer resistance. Tracing the changes in the electrode resistances helps uncover the limiting electrode and electrode mechanisms that predominantly contribute to aging. Examining the evolution of electrode aging mechanisms aids in the design of operational regimes and battery management systems to prevent or delay cell failure.

2.2. Lithium Plating. Lithium plating is an anode centric degradation process in LIBs where lithium ions are metallically deposited on the anode surface instead of intercalating through the electrode. The lithium plating process is triggered by the mismatch between the rate of ion influx to the anode and the rate at which lithium ions can be accommodated into the graphite interlayers. This mismatch is often triggered at high current densities, low temperatures, and high states of charge of the anode and is accompanied by negative anode potential during lithium deposition. The deposited lithium can detach from the electrode during discharge forming "dead lithium" which can lead to a loss of cyclable lithium ions. Plated lithium readily reacts with electrolyte resulting in electrolyte decomposition to form a passivation layer which further strains the ion transport in the system. Understanding lithium plating is crucial to design effective strategies for fast charging and low-temperature operation. Reference electrodes are used to detect lithium plating using the anode potential measurement as it is thermodynamically favorable to plate lithium when anode potential becomes negative.

Relevant parameters to quantify the duration, rate, and intensity of lithium plating derived from the anode potential measurement shown in eqs 3–5 in Table 1 were defined and developed in earlier studies. The plating period is the total duration when lithium plating is occurring at the electrode which can be measured as the time interval where the anode potential remains negative. Plating power and energy corresponding to the average power and energy consumed by the anode during lithium plating regime, i.e., plating period. Quantitative investigation of plating using the developed parameters has shown that plating is a nonlinear, discontinuous, stochastic phenomenon whose intensity is determined by a complex interplay of the charging current and the heat generated during liithiation.

Studies have shown plating energy influences the morphology of the plated lithium and the subsequent cell failure. Estimation of plating energy along with the Coulombic efficiency helps in identifying the reversibility of the plated lithium and irreversible capacity loss from the loss of cyclable lithium ions. Tracking the plating parameters with cycling helps in comprehending the quantitative evolution of the plating process with continuously changing electrode and interface properties with aging.

2.2.3. Abuse Mechanisms. 2.2.3.1. Overdischarge. Overdischarge is an abuse condition where the cell is discharged beyond the recommended voltage window and can result in SEI decomposition and dissolution of the copper current collector in the anode. The dissolved copper can grow dendritically toward the cathode creating metallic copper bridges and internal short circuits which can ultimately lead to safety incidents. This phenomenon can occur to cells in battery packs when the pack is not well-balanced or when one or some of the cells in the pack fails or fail earlier than the rest. Individual electrode potential measurements using reference electrodes have shed light on the ranges of cell discharge voltage corresponding to different electrochemical mechanisms such as deintercalation, SEI decomposition, and copper dissolution which result in varying degrees of capacity fading and cell failure. After severe overdischarge, the cell undergoes a point of reverse potential where the anode potential becomes greater than the cathode potential due to conductivity loss in anode and copper deposition on the cathode resulting in net negative full cell voltage. This mechanism is elucidated by individual electrode potential measurements and is used as an inflection point between slight and severe overdischarge regimes.

2.2.3.2. Overcharge. Overcharging involves charging a cell beyond its full capacity which can result in various side reactions that generate heat and may lead to thermal runaway. Side reactions include metallic lithium plating at the anode, structural disintegration of cathode particles, exothermic decomposition of electrolyte, and gassing resulting in irreversible capacity loss and safety incidents. Overcharge can occur in battery packs as a result of variation of cell-to-cell capacities resulting in charging certain cells to a state of charge (SOC) higher than 100%. Electrode impedance analysis of overcharged commercial LiFePO4 cells from three-electrode configurations shows that the breakdown and reformation of the interface at the cathode contributes to an increase in the cell impedance and the impending cell failure. Understanding the degradation pathways of overcharge conditions using

Table 1. Quantitative Parameters to Investigate Electrode Degradation and Lithium Plating Using Three-Electrode Measurements

| Parameter                     | Equation                                      |
|-------------------------------|-----------------------------------------------|
| relaxation resistance         | \( \frac{V_{\text{fL}} - V_{\text{NIL}}}{I_{\text{FL}}} \) |
| high-frequency resistance     | \( \frac{\Delta V_{\text{pulse, electrode}}}{I_{\text{pulse}}} \) |
| plating period                | \( t_{\text{plating}} = \int_{0}^{t_{\text{FL}}} dt \) |
| plating energy                | \( E_{\text{plating}} = C \int_{t_{1}}^{t_{2}} |V_{\text{Anode}}| dt \) |
| plating power                 | \( P_{\text{plating}} = \frac{E_{\text{plating}}}{t_{\text{plating}}} \) |

| Variables | Description |
|-----------|-------------|
| \( V_{\text{fL}} \) | Voltage at full load |
| \( V_{\text{NIL}} \) | Voltage at no load |
| \( I_{\text{FL}} \) | Full load current |
| \( t_{\text{FL}} \) | Duration when lithium plating is occurring at the electrode |
| \( \Delta V_{\text{pulse, electrode}} \) | Potential difference during pulse |

ACS Omega 2021, 6, 33284–33292
three-electrode analytics allows us to estimate the maximum allowable limits of the overcharge to avoid irreversible performance loss and thermal runaway.

2.2.4. Aging and Capacity Loss Delineation. Battery performance and cycle life depend upon several aging mechanisms such as loss of lithium inventory from the lithium plating, SEI growth, and electrolyte decomposition and loss of active material from particle fracture. The recurring wear and tear of the electrodes result in inevitable caging of the cell from the complex interplay of degradation mechanisms such as SEI growth, electrolyte decompositions, particle fracture and isolation, transition metal dissolution, lithium plating, and structural disordering.42,43 Regardless of the mechanism, any degradation translates to a loss of lithium inventory and loss of active material in the electrodes resulting in capacity fading. Earlier studies have used destructive testing of cells to harvest the active material in the electrodes and decouple the losses at different stages of capacity fading.30 However, a method29 was developed using three-electrode measurements in pouch cells to identify and decouple irreversible capacity loss and irretrievable capacity loss stems from the disproportionate increase in the electrode resistances which renders a part of the available capacity at the electrode uncyclable. The irretrievable capacity quantitatively depicts the limiting electrode and greatly simplifies the quantitative evaluation of electrode aging mechanisms. The electrode potential mapping at low rates can also be used in differential voltage and incremental capacity analysis to identify the phase transitions responsible for the capacity fade.44−46 In addition to identifying the limiting electrode, the span of charge/discharge associated with the capacity fade can be detected. Research on temperature-induced aging and lithium plating has used incremental capacity analysis and found that the reduced phase transition of stage ii−iii lithiated graphite corresponds to a majority of the capacity fading in the cell.30 Interface kinetics, electrode overpotentials, and degradation modes caused by operational defects from aging of the cells can be tracked precisely using the three-electrode configuration and can be used to quantitatively evaluate the capacity loss mechanisms with aging.

2.2.5. Beyond Lithium-Ion. The applicability of three-electrode analytics extends beyond lithium-ion to lithium and sodium metal batteries, solid-state batteries.49−52 Given the high specific capacity, sustainability, and low cost, Na−Sn batteries are promising next-generation batteries. However, Sn electrodes are plagued by large volume expansion, fractures, pulverization leading to a loss of active material and the electrochemical performance with cycling. Additionally, unstable solid electrolyte interphase (SEI) formation in Na metal due to intensive side reactions gradually forms a thicker layer and increases the overall cell impedance. The insulating thick SEI layer disrupts the flux uniformity, causing uneven plating and ramified dendritic growth, eventually killing the cell. However, most of the time, cell malfunctions before the dendrites can cause short circuits; thus, it is necessary to understand the continuous SEI growth and impedance accumulation.
Effects of both Na metal and Sn electrode—electrolyte interphases are usually unavoidable. A three-electrode Na−Sn cell with a sodium reference electrode was cycled to monitor the cell’s voltage by charging and discharging at a 0.1 C rate, and the voltage profile can be seen in Figure 3b. The electrolyte is based on NaClO4 in PC. The results showed an early higher specific capacity indicated by longer sodiation/desodiation time followed by an elevated capacity decline. Traditionally, it is believed that alloying electrode such as Sn with more extensive mechanical degradation is the main culprit behind the diminishing cell performance. However, the counter electrode (Na metal) plays a critical role in causing the electrochemical instability of the cell. Figure 3c shows the voltage profiles of the Na plating/stripping process. It shows a steadily increasing overpotential value. This increment in voltage hysteresis can be attributed to the reduction of the electroactive surface area, decreasing the electrochemical reaction rate, and deteriorating the charge transfer kinetics. Consequently, the charge transfer resistance and polarization at the interface in the Na metal are increased with cycling.

As schematically illustrated in Figure 3d, sodium metal and tin electrodes suffer from different types of structural degradation during the sodiation process; it is also beneficial to diagnose and distinguish the individual electrode performance in operando. Insertion of a sodium strip reference, which can be easily pressed onto a thin Cu-wire, enables an easier assembly of the coin cell, shown in Figure 3e. Desodiation in tin electrodes occurs in multiple intermediate reaction steps, as evidenced by the plateaus (red curve) in Figure 3f. However, an interesting trend can be observed for voltage—time profiles of sodium metal during the plating process. As the transition from the Na$_x$Sn to Sn occurs in three steps, the dealloyed Na deposits in the Na metal follow the same pattern of overpotential. Examining the potential of the Na metal electrode independently using the reference electrode shows the interplay of the sodium electrode degradation with the phase transitions in the tin electrode which can be controlled by regulating the charge cutoff potential of the cell improving the morphological integrity and performance of the electrodes.

### 2.3. Operando Control Using Three-Electrode Configuration

Reference electrodes have played a crucial role in fast charging diagnostics and the study of lithium plating using anode potential measurements. Lithium plating becomes thermodynamically possible when the anode potential becomes negative with respect to Li/Li$^+$ due to the high ion flux or severe diffusivity limitations during high-rate and low-temperature charging. By limiting the anode potential to positive values, the propensity to plate metallic lithium on the anode can be eliminated during charging. A charging strategy based on maintaining a positive anode potential developed by Barsukov et al.\textsuperscript{52} at Texas Instruments was tested using a three-electrode cell. The anode potential was controlled in conjunction with the cell voltage to control the charge current in the reconstructed commercial pouch cell with reference electrode at a subzero temperature of $−5$ °C at a 1 C rate.\textsuperscript{28} The cell charged without controlling the anode potential exhibits copious amounts of lithium plating and failed in 12 cycles. The cell charged with the anode potential control using reference exhibited no visible lithium plating and had an extended cycle life of 87 cycles. Further analysis of electrode resistances revealed that the cells with lithium plating exhibited an accelerated anode resistance rise which resulted in increasing the internal resistance of the cell causing swift cell failure. The increasing anode resistance also adversely affected the reversibility of the plated lithium resulting in irreversible loss of lithium inventory and rapid capacity fading. The cells charged with anode control exhibit stable anode resistance throughout cycling indicating minimal damage at the anode resulting in improved performance and lifetime. Figure 4 shows the comparison of the default charging and reference controlled plating free charging. By eliminating lithium plating using reference control, the plating induced degradation processes such as dead lithium formation, secondary SEI growth, and electrolyte consumption resulting in delayed cell failure. Based on the results, a battery management system (BMS) designed to charge by maintaining constant anode impedance was developed and tested.\textsuperscript{29} The BMS uses only full cell measurements such as voltage and temperature to estimate the anode impedance using the physics-based model.

---

Figure 4. Schematic comparison of cell performance with and without operando anode potential control using three-electrode configuration. The cell without anode potential suffers from lithium plating and secondary parasitic mechanisms such as dead lithium and passivation layer formation from the deposited lithium resulting in earlier cell failure. The cell with anode potential control charging exhibitsthe efficient intercalation of graphite particles by eliminating lithium plating and exhibits superior performance and cycle life.
derived from operando impedance characterization of electrodes and successfully eliminated lithium plating during fast charging. This is a clear example of using three-electrode cells as an analytical toolbox where we identified the limiting electrode mechanism and isolated and eliminated the dominant degradation process using reference control for the development and validation of the battery management system.

3. LIMITATIONS OF THREE-ELECTRODE MEASUREMENTS

Embedding a reference electrode in commercial cells can be challenging and may alter the performance and safety of the cell as it conflicts with existing cell design. Small misalignment of the electrodes will result in significant error in the electrode potential measurements. Furthermore, nonuniform current distribution in the electrode and electrolyte may result in impedance artifacts which will affect the applicability of three-electrode cells in large format cells and solid state batteries. As we move toward solid state batteries, characterization of the interface properties becomes crucial and the need for multi-electrode setups arises. Four-electrode measurements have been used to study the dynamic evolution of the interface properties and parameter extraction as the four-electrode setups eliminate polarization resistances arising from non-equipotential interfaces.

4. CONCLUSION

Driven by the growing requirements for increased performance and safety of batteries, a strong need for understanding battery degradation and the development of predictive models prevails. However, battery prognostics through predictive modeling is often complicated by the multifaceted nature of battery degradation. While the recent surge in data-driven models using machine learning to identify cell failure and degradation has produced astonishing results, a large amount of training data in a variety of operating conditions is required for generalization and accuracy. Using physics to inform the machine learning models will result in robust predictions with fewer training data sets. The evolution of electrode impedance, thermodynamics, phase transitions, and the state of the electrode can be analytically studied through a three-electrode cell to understand the fundamental physics of electrode degradation and provide valuable insights to predictive modeling. Furthermore, the high-resolution electrode-pertinent data obtained from three-electrode cells is inherently capable of integrating the physics of reaction mechanisms into the machine learning models. In addition to the state of electrode diagnostics, the three-electrode cell can be used in control algorithms to isolate and eliminate electrode level degradation to spur the development of futuristic charging protocols even under operational extremes. Effective utilization of the three-electrode setup as an analytical toolbox offers a plethora of operando electrode level information regardless of the battery chemistry or form factor and will be a paradigm shift in the field of battery design and prognostics.

Authors

Sobana P. Rangarajan – School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, United States
Susmita Sarkar – School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, United States
Yevgen Barsukov – Texas Instruments Inc., Dallas, Texas 75243, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c05494

Notes

The authors declare no competing financial interest.

Biographies

Sobana P. Rangarajan is a doctoral candidate in the School of Mechanical Engineering at Purdue University. She received her B.E. in Electrical and Electronics Engineering from Anna University, India, and her Master’s in Renewable Energy from Academy of Innovative Scientific Research, India. Her research focuses on understanding and eliminating degradation mechanisms during fast charging of lithium batteries.

Susmita Sarkar is a Ph.D. candidate in the School of Mechanical Engineering at Purdue University-West Lafayette (USA). She received her M.S. in Mechanical Engineering from Missouri University of Science and Technology Rolla (USA). Her research interests are in the areas of optimization of electrolytes for next generation metal-based batteries.

Yevgen Barsukov is a TI fellow and the head of algorithm development in the battery management systems group at Texas Instruments Inc. Barsukov specializes in applying leading theoretical methods of battery analysis to improve the battery controlling technology used for fuel-gauging, health and safety information in notebooks, mobile phones, and other portable devices.

Partha P. Mukherjee is a University Faculty Scholar and Professor of Mechanical Engineering at Purdue University. His research focuses on mesoscale physics and analytics of transport, chemistry, microstructure, and interface interactions in energy storage and conversion. Mukherjee has published more than 150 journal articles on different energy storage chemistries (https://engineering.purdue.edu/ETS/L/).

ACKNOWLEDGMENTS

Financial support from Texas Instruments (TI) University Research Partnership program, National Science Foundation (NSF award: 1806566), and the Office of Naval Research (ONR awards: N00014-19-1-2529, N00014-18-1-2397) is gratefully acknowledged.

REFERENCES

(1) Birkid, C. R.; Roberts, M. R.; McTurk, E.; Bruce, P. G.; Howey, D. A. Degradation Diagnostics for Lithium Ion Cells. J. Power Sources 2017, 341, 373–386.
(2) Waldmann, T.; Hogg, B. I.; Wohlfahrt-Mehrens, M. Li Plating as Unwanted Side Reaction in Commercial Li-Ion Cells - A Review. J. Power Sources 2018, 384, 107–124.
(3) Liu, Y.; Zhu, Y.; Cui, Y. Challenges and Opportunities towards Fast-Charging Battery Materials. Nat. Energy 2019, 4 (7), 540–550.
(4) Tomaszewska, A.; Chu, Z.; Feng, X.; O’Kane, S.; Liu, X.; Chen, J.; Ji, C.; Endler, E.; Li, R.; Liu, L.; Li, Y.; Zheng, S.; Vetterlein, S.; Gao, M.; Du, J.; Parkes, M.; Ouyang, M.; Marinscu, M.; Ofer, G.;
Wu, B. Lithium-Ion Battery Fast Charging: A Review. eTransportation 2019, 1, 100011.

(5) knehr, k. w.; hodson, t.; bommer, c.; davies, g.; kim, a.; steingart, d. a. understanding full-cell evolution and non-chemical electrode crosstalk of li-ion batteries. joule 2018, 2 (6), 1146–1159.

(6) zinth, v.; von lüders, c.; hofmann, m.; hattendorff, j.; buchberger, l.; erhard, s.; rebelo-kornmeier, j.; jossen, a.; gilles, r. lithium plating in lithium-ion batteries at sub-ambient temperatures investigated by in situ neutron diffraction. j. power sources 2014, 271, 152–159.

(7) Bauer, M.; Wachtler, M.; Stöwe, H.; Persson, J. V.; Danzer, M. A. understanding the dilation and dilation relaxation behavior of graphite-based lithium-ion cells. J. power sources 2016, 317, 93.

(8) Schindler, S.; Bauer, M.; Petzl, M.; Danzer, M. A. voltage relaxation and impedance spectroscopy as in-operando methods for the detection of lithium plating on graphite anodes in commercial lithium-ion cells. J. power sources 2016, 304, 170–180.

(9) Hou, J.; Girod, R.; nianias, n.; shen, T.-H.; fan, J.; tilelli, V. lithium-gold reference electrode for potential stability during in situ electron microscopy studies of lithium-ion batteries. J. electrochem. soc. 2020, 167 (11), 110515.

(10) Rajmakers, L. H. J.; Lammers, M. J. G.; Notten, P. H. L. A new method to compensate impedance artefacts for li-ion batteries with integrated micro-reference electrodes. Electrochim. acta 2018, 259, S17–S33.

(11) abraham, D. P.; poppen, s. d.; jansen, A. N.; liu, J.; dees, D. W. application of a lithium-tin reference electrode to determine electrode contributions to impedance rise in high-power lithium-ion cells. Electrochim. acta 2004, 49 (26), 4763–4775.

(12) hoshi, Y.; narita, Y.; honda, K.; ohtaki, T.; shitanda, l.; itagaki, M. optimization of reference electrode position in a three-electrode cell for impedance measurements in lithium-ion rechargeable battery by finite element method. J. power sources 2015, 288, 168–175.

(13) li, Y.; han, X.; feng, X.; chu, z.; gao, X.; li, R.; du, J.; lu, L.; ouyang, M. errors in the reference electrode measurements in real lithium-ion batteries. J. power sources 2021, 481, 228933.

(14) delacourt, C.; ridgway, P. L.; srinivasan, V.; battaglia, V. measurements and simulations of electrochemical impedance spectroscopy of a three-electrode coin cell design for li-ion cell testing. J. electrochem. soc. 2014, 161 (9), A1253.

(15) la mantia, F.; wessells, C. D.; deshazer, H. D.; cui, Y. reliable reference electrodes for lithium-ion batteries. electrochim. commun. 2013, 31, 141–144.

(16) chu, Z.; feng, X.; liaw, B.; li, Y.; lu, L.; li, J.; han, X.; ouyang, M. testing lithium-ion battery with the internal reference electrode: an insight into the blocking effect. J. electrochem. soc. 2018, 165 (14), A3240–A3248.

(17) belt, J. R.; bernardi, D. M.; utgikar, V. development and use of a lithium-metal reference electrode in aging studies of lithium-ion batteries. J. electrochem. soc. 2014, 161 (6), A1116–A1126.

(18) rangarajan, S. P.; barsukov, Y.; mukherjee, P. P. in operando signature and quantification of lithium plating. J. mater. chem. A 2019, 7, 20683–20695.

(19) rangarajan, S. P.; barsukov, Y.; mukherjee, P. P. in operando impedance based diagnostics of electrode kinetics in li-ion pouch cells. J. electrochem. soc. 2019, 166 (10), A2131.

(20) juarez-robles, D.; chen, C.-f.; barsukov, Y.; P. mukherjee, P. impedance evolution characteristics in lithium-ion batteries. J. electrochem. soc. 2017, 164 (4), A837–A847.

(21) osaka, T.; mukoyama, D.; nara, H. review—development of diagnostic process for commercially available batteries, especially lithium ion battery, by electrochemical impedance spectroscopy. J. electrochem. soc. 2015, 162 (14), A2529–A2537.

(22) raccichini, R.; amores, M.; hind, G. critical review of the use of reference electrodes in li-ion batteries: a diagnostic perspective. Batteries 2019, 5 (1), 12.
(43) Vetter, J.; Novák, P.; Wagner, M. R.; Veit, C.; Möller, K. C.; Besenhard, J. O.; Winter, M.; Wohlfahrt-Mehrens, M.; Vogler, C.; Hammouche, A. Ageing Mechanisms in Lithium-Ion Batteries. J. Power Sources 2005, 147 (1-2), 269-281.

(44) Berecibar, M.; Dubarry, M.; Omar, N.; Villarreal, I.; Van Mierlo, J. Degradation Mechanism Detection for NMC Batteries Based on Incremental Capacity Curves. World Electr. Veh. J. 2016, 8 (2), 350-61.

(45) Dubarry, M.; Baure, G.; Devie, A. Durability and Reliability of EV Batteries under Electric Utility Grid Operations: Path Dependence of Battery Degradation. J. Electrochem. Soc. 2018, 165 (5), A773.

(46) Li, Y.; Abdel-Monem, M.; Gopalakrishnan, R.; Berecibar, M.; Nanini-Maury, E.; Omar, N.; van den Bossche, P.; Van Mierlo, J. A Quick On-Line State of Health Estimation Method for Li-Ion Battery with Incremental Capacity Curves Processed by Gaussian Filter. J. Power Sources 2018, 373, 40-53.

(47) Petz, M.; Danzer, M. A. Nondestructive Detection, Characterization, and Quantification of Lithium Plating in Commercial Lithium-Ion Batteries. J. Power Sources 2014, 254, 80-87.

(48) Bloom, I.; Jansen, A. N.; Abraham, D. P.; Knuth, J.; Jones, S. A.; Battaglia, V. S.; Henriksen, G. L. Differential Voltage Analyses of High-Power Lithium-Ion Cells: I. Technique and Application. J. Power Sources 2005, 139 (1-2), 295-303.

(49) Sarkar, S.; Mukherjee, P. P. Synergistic Voltage and Electrolyte Mediation Improves Sodiation Kinetics in M-Sn Alloy-Anodes. Energy Storage Mater. 2021, 43, 305-316.

(50) Simon, F. J.; Blume, L.; Hanauer, M.; Sauter, U.; Janek, J. Development of a Wire Reference Electrode for Lithium All-Solid-State Batteries with Polymer Electrolyte: FEM Simulation and Experiment. J. Electrochem. Soc. 2018, 165 (1), A1363-A1371.

(51) Nam, Y. J.; Park, K. H.; Oh, D. Y.; An, W. H.; Jung, Y. S. Diagnosis of Failure Modes for All-Solid-State Li-Ion Batteries Enabled by Three-Electrode Cells. J. Mater. Chem. A 2018, 6, 14867-14875.

(52) Barsukov, Y. P.; Vega, M. A.; Alongi, B. P. Methods and Apparatus for Optimal Fast Battery Charging. Texas Instruments Inc. Pat. US Pat. 10,566,819, 2020; pp 25.

(53) Ji, Y.; Zhang, Y.; Wang, C.-Y. Li-Ion Cell Operation at Low Temperatures. J. Electrochem. Soc. 2013, 160 (4), No. A636.

(54) Baker, D. R.; Verbrugge, M. W.; Hou, X. X. A Simple Formula Describing Impedance Artifacts Due to the Size and Surface Resistance of a Reference-Electrode Wire in a Thin-Film Cell. J. Electrochem. Soc. 2017, 164 (2), A407-A417.

(55) Simon, F. J.; Blume, L.; Hanauer, M.; Sauter, U.; Janek, J. Development of a Wire Reference Electrode for Lithium All-Solid-State Batteries with Polymer Electrolyte: FEM Simulation and Experiment. J. Electrochem. Soc. 2018, 165 (1), A1363-A1371.

(56) Fang, J.; Shen, W.; Cheng, S. H. S.; Ghoshghe, S.; Shahzad, H. K.; Chung, C. Y. Four-Electrode Symmetric Setup for Electrochemical Impedance Spectroscopy Study of Lithium-Sulfur Batteries. J. Power Sources 2019, 441, 227202.

(57) Schwan, H. P.; Ferris, C. D. Four-Electrode Null Techniques for Impedance Measurement with High Resolution. Rev. Sci. Instrum. 1968, 39 (4), 481.

(58) Simon, F. J.; Hanauer, M.; Henss, A.; Richter, F. H.; Janek, J. Properties of the Interphase Formed between Argyrodite-Type Li6PS5Cl and Polymer-Based PEO10:LiTFSI. ACS Appl. Mater. Interfaces 2019, 11 (45), 42186-42196.