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State-of-electrode (SOE) analytics of lithium-ion cells under overdischarge extremes

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ABSTRACT

Overdischarge is an electrical abuse that may arise in a Li-ion battery module when a voltage imbalance occurs between series-connected cells. Although a wide range of studies has investigated overdischarge-induced aging at the full cell scale, the role of each electrode in degradation mechanisms and impacts of C-rates still require fundamental understanding. While most previous studies focus on copper dissolution, the inter-electrode crosstalk which occurs under an overdischarge scenario remains an open question. To fill these gaps, we deconvolute anode and cathode characteristics from the full cell performance during overdischarge abuses by fabricating Li-ion cells with a reference electrode configuration. Electrode potentials vs. Li/Li⁺ are measured and interpreted for increasingly severe overdischarge cycles under various C-rates. Deterioration of state of health is tracked by monitoring cell surface temperature, internal resistance, volumetric expansion, capacity retention, and impedance evolution. Surface microscopic characterizations are implemented to explore morphological changes and chemical state variations of electrodeposition with particle deformation. This study reveals the dual effect of the C-rate on explicit anode-centric failure mechanisms and implicit cathode-centric degradation pathways, providing new insights on overdischarge abuse fundamentals and effective mitigation strategies.

1. Introduction

As one of the most promising energy storage devices to power portable electronics and electric vehicles (EVs), lithium-ion (Li-ion) batteries have become an essential candidate to drive the advancement of this rechargeable world and push the frontier of clean energy utilization [1–3]. However, Li-ion cells often suffer from catastrophes when subjected to off-normal conditions [4], which are frequently encountered in the pursuit of high energy density and stable fast charging performance. Unfortunately, the growing prosperity of EV markets in the past decade has been shadowed by overwhelming concerns about safety incidents [5,6]. For example, an EV caught fire while charging at a station in 2016 due to an overcharge-induced internal short circuit (ISC) [5]. In 2018, another similar model EV drove off the road and burned out after crashing, caused by separator collapse and cell deformation [7]. Although these accidents were initiated by either electric (overcharge) or mechanical (crash) abuse, ISC was believed to be the common feature that triggered the onset of thermal runaway (TR). Therefore, a fundamental understanding of the relationship between ISC and TR [8], ISC-induced TR characteristics [9], and effective ISC mitigation strategies [10] are significant to reinforce the safety performance of Li-ion batteries.

Among various ISC mechanisms in Li-ion batteries, piercing the separator by metallic dendrites is critical and challenging to detect. Under circumstances of overcharge or overdischarge, dynamic lithium or copper plating might break through the microporous polymer separator architecture and contact the counter electrode. Fundamentals of overcharge failure have been scrutinized by a wide range of study efforts [11–13], whereas overdischarge challenges are absent from meticulous investigations, given the marginal safety hazards [14]. In practice, overdischarge could be a common event in a battery pack if there is a mismatch of internal resistance in parallel-connected cells but the battery management system fails to balance the caused nonuniform current distributions in aged cells with inferior capacities [15,16]. Copper dissolution from the graphite anode current collector has been identified as the primary side reaction and thus attracted much infant research attention [17-20]. However, no consensus has been reached about the onset of copper oxidation and reduction due to diverse cell chemistries and abusive conditions in past investigations [21-24]. Although several studies have reported the formation of micro-ISC caused by copper

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Received 23 June 2022; Received in revised form 22 September 2022; Accepted 13 October 2022 Available online 15 October 2022 2405-8297/© 2022 Elsevier B.V. All rights reserved. dendrite growth after a single extreme overdischarge abuse [14,21,22, 25–27], in most cases, they are benign due to the ultra-low state of charge (SOC). Furthermore, a state-of-the-art discussion reveals that species of copper deposition are electrically non-conductive before the reverse of full cell voltage [28], which considerably mitigates the probability of disasters by circumventing the massive release of electric energy from inter-electrode copper bridge pathways.

However, the mild risks of ISC at the end of a single extreme overdischarge phase do not necessarily indicate similar safety characteristics when the cell is recharged. Driven by the reversed electric field, the copper-based electrodeposition at the positive electrode will be reoxidized to copper ions and dissolved in the electrolyte. These copper ions are forced to migrate through the separator and compete with Li-ion intercalation at the negative electrode to block their intercalation sites, deform graphite host structures, and induce lithium and copper plating [27–31]. These processes lead to accelerated capacity fade and internal resistance rise at the cell level [32]. Even worse, if the cell is subjected to long-term cycling, the growth of lithium deposition is more likely to present a dendritic morphology [29]. The resulting ISC will be periodically coupled with high SOC to cause aggravated temperature rise and threaten the cell thermal stability [33]. Therefore, the underlying safety hazards of aging-centric overdischarge degradations should never be underestimated.

State-of-the-art characterization techniques have greatly advanced the research frontier in this field, including 7Li nuclear magnetic resonance [34], X-ray computed tomography [16,29], X-ray photoelectron spectroscopy, and X-ray absorption fine structure analysis [28,31]. These analytical tools have investigated the chemical states of copper-based depositions, and further revealed their microstructures through radiographs and three-dimensional reconstructions to substantiate that a single overdischarge to the extent before or after voltage reversal is innocuous due to little safety concern from ISC events. Meanwhile, several early warning and mitigation strategies have been proposed to maximize the overdischarge abuse tolerance of cell chemistries. Irregular changes in ohmic, solid electrolyte interphase (SEI), and charge transfer resistances from impedance spectroscopy could indicate impending overdischarge failure [35]. The introduction of a pre-lithiated anode can benefit the long-term storage of cells at near-zero voltage [36,37], and effective electrolyte additives can significantly reinforce the cycling stability of cells [38]. Besides, modified cathode materials could be more stable under overlithiation status, strengthening their rechargeability and reducing cell swelling [30, 39-41].

Despite many detailed investigations of the various degradation mechanisms at play during overdischarge, a comprehensive study on the evolution of these mechanisms during cycling as a function of lower cutoff voltage has yet to be presented. To meet this challenge, we conducted a series of experiments to fully understand the overdischargeinduced degradation mechanisms on a three-electrode (3E) commercial Li-ion pouch cell under various C-rates. Electrode potentials vs. Li/ Li+ of graphite anode and NCA cathode are decoupled from the full cell voltage at discharge, relaxation, and charge phases to probe the transient state of electrodes (SOE) and their roles in dictating cell failure. Surface temperature, internal resistance (IR), and volumetric expansion of the cells are monitored at different full-cell cutoff limits and analyzed based on electrode potential behaviors to estimate the onset and evolution of adverse side reactions. Degraded electrodes after overdischarge failure are fabricated in coin format half cells and subjected to galvanostatic testing and electrochemical impedance spectroscopy (EIS) to determine the effects of C-rates on the capacity fade and impedance rise. Visual inspection, optical microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) are employed to characterize physicochemical variations of electrodes after overdischarge abuses, revealing evolutions of spatial distributions, microstructural morphologies, elemental quantifications and chemical states of electrodepositions at various C-rates.

2. Experimental methods

A series of well-designed experiments were carried out to fundamentally understand the overdischarge degradation mechanisms of Liion cells. Testing procedures are comprehensively illustrated in Fig. 1, while Table 1 summarizes the testing conditions of all different cells in this study. Experimental details are specifically discussed from Sections 2.1–2.7.

2.1. Reference electrode preparation

A copper wire coated with lithium titanate (LTO) was used as the reference electrode (RE), as demonstrated in our previous work [42,43]. The RE was prepared by including it in the fabrication of a Li-Li symmetric CR2032 coin cell and charged to 2.25 V vs. Li/Li⁺, discharged to 1.25 V vs. Li/Li⁺, and then charged to 50% SOC at a 0.05C rate [44] to monitor the RE electrochemical performance while ensuring that the final RE potential was stagnated at the characteristic plateau and stabilized at 1.564 V vs. Li/Li⁺. Lithiation and delithiation profiles of a typical RE are shown in Fig. S1.

2.2. 3E pouch cell fabrication

Commercial Li-ion pouch cells from a reputable vendor were used in this study. The active materials of cathode and anode are lithium nickel cobalt aluminum (NCA) oxide and graphite, respectively. The electrolyte is lithium hexafluorophosphate (LiPF₆) in a binary solvent of ethylene carbonate (EC) / ethyl methyl carbonate (EMC). The nominal capacity is 3.3 Ah, and the recommended voltage window is between 2.7 and 4.2 V. The lithiated RE with a stable potential of 1.56 V vs. Li/Li⁺ was extracted from dissembled coin cells and fabricated into the pouch cells. The RE was inserted approximately 0.5 cm from the top left corner of the aluminum pouch, away from two electrode tabs and not inbetween the separator layers. A few drops of 1 M LiPF₆ in EC/EMC (v/v 1:1) were added to moisten the RE before sealing the pouch with epoxy resin to prevent further electrolyte evaporation and air permeation. The schematic illustration and appearance of a pristine 3E pouch cell are shown in Fig. S2. The entire procedure was carried out in an argon-filled glovebox where oxygen and water levels were stably less than 0.01 ppm.

2.3. Conditioning test

The fabricated 3E pouch cell was fully discharged before cycling three times using an Arbin-BT2000 battery cycler. The cell was charged to 4.2 V at a constant current (CC) rate of 0.2C, followed by a constant voltage (CV) step at 4.2 V until the applied current decreased to 66 mA (0.02C). The cell was then discharged to 2.7 V at a 0.2C rate. Measurement of IR was executed using a 1.5C direct current pulse for 100 ms at 70% depth of discharge (DOD) during the discharge phase in each cycle. A 30 min rest was applied between the charge and discharge phase. A T-type Omega thermocouple was attached to the surface of the pouch near the anode and cathode terminals to monitor the sensitive cell temperature response. The behaviors of full cell voltage, anode potential, and cathode potential during conditioning tests are shown in Fig. S3. All the tests introduced in this section were run at the 20 $^{\circ}$ C ambient temperature in the laboratory.

2.4. Extreme overdischarge test

After the conditioning test, a fabricated 3E pouch cell (marked as EOT-1) was CC charged to 4.2 V at 0.1C rate, followed by a CV charge step at 4.2 V until the current decreased to 0.02C rate. The cell was rested for 30 min and then CC discharged at a 0.1C rate until 120% DOD.



Fig. 1. Testing matrix of the overdischarge study.

Table 1	
Testing conditions of all different cells in the overdischarge study.	

Testing Names	Objectives	Upper / Lower Cutoff Limit	Charge / Discharge C-rate
RE Preparation	Reference Electrodes	2.25 V / 1.25 V	0.05C / 0.05C
Conditioning Tests	EOT-1 Full Cell EOT-2 Full Cell MOT-1 Full Cell MOT-2 Full Cell	4.2 V / 2.7 V	0.2C / 0.2C
Extreme Overdischarge Tests	MOT-3 Full Cell EOT-1 Full Cell EOT-2 Full Cell	4.2 V / 120% DOD	0.1C / 0.1C
Multi-level Overdischarge- recharge Tests	MOT-1 Full Cell	4.2 V / 2.5 V, 2.0 V, , -3.0 V, End Point	0.1C / 0.1C
	MOT-2 Full Cell	4.2 V / 2.5 V, 2.0 V, , -3.0 V, End Point	0.5C / 0.5C
	MOT-3 Full Cell	4.2 V / 2.5 V, 2.0 V, , -3.0 V, End Point	1.0C / 1.0C
Half-cell Galvanostatic Tests	MOT-1 Graphite Anode MOT-2 Graphite Anode MOT-3 Graphite Anode	1.5 V / 0.005V	0.02C / 0.02C
	MOT-1 NCA Cathode MOT-2 NCA Cathode MOT-3 NCA Cathode	4.2 V / 2.5V	0.02C / 0.02C

Another pristine pouch cell (marked as EOT-2) without RE configuration was operated under the same protocols and circumstances after the conditioning test to evaluate the impacts of RE introduction on the extreme overdischarge behaviors of cells. T-type Omega thermocouples were attached to the surface of the EOT-1 and EOT-2 near anode and cathode terminals to monitor their sensitive cell temperature responses. All the tests introduced in this section were carried out at the 20 °C ambient temperature in the laboratory.

2.5. Multi-level overdischarge-recharge test

After conditioning tests, three fabricated 3E pouch cells (marked as MOT-1, MOT-2, and MOT-3) were CC charged to 4.2 V at a 0.1C rate, followed by a CV charge step at 4.2 V until the current decreased to 0.02C rate. After resting for 30 min, multi-level overdischarge tests were implemented on all three cells where the full-cell cutoff limits were sequentially defined as [2.5 V, 2.0 V, 1.5 V, 1.0 V, 0.5 V, 0.0 V, -0.5 V, -1.0 V, -1.5 V, -2.0 V, -2.5 V, -3.0 V, EP]. Here the abbreviation EP means End Point. It represents the minimum value of full cell voltage during overdischarge extremes in each case. In order to understand the effect of

C-rates, MOT-1, MOT-2, and MOT-3 were discharged at 0.1C, 0.5C, and 1.0C rates, respectively. For instance, the protocol for MOT-1 was programmed as CC overdischarged to 2.5 V at 0.1C rate, rested for 30 min, and then CCCV recharged to 4.2 V at 0.1C rate followed by a 30 min rest. In the next cycle, CC overdischarged to 2.0 V at 0.1C rate, rested for 30 min, then CCCV recharged to 4.2 V at 0.1C rate, followed by a 30 min rest, etc. Protocols of MOT-2 and MOT-3 were the same as that of MOT-1 except at different C-rates during both charge and discharge. Fig. 2 shows the representative full-cell performances of MOT-2 as an example to demonstrate the increasingly severe overdischarge cycles. Please note that the CV phase and the following rest phase of each cycle are not presented because they are beyond our concerns. T-type Omega thermocouples were attached to the surface of all three cells near anode and cathode terminals to monitor their sensitive temperature responses. Cell IR was measured at 70% DOD by applying the same 1.5C current pulse for 100 ms in the discharge phase for every cutoff limit. Volumetric expansions of cells are quantified by submerging the entire cell body into the pump oil [45] at every two cutoff limits and measuring fluid displacement. All the tests introduced in this section were carried out at 20 °C ambient temperature in the laboratory.

2.6. Half-cell galvanostatic and EIS studies

MOT-1, MOT-2, and MOT-3 after overdischarge failure and a pristine cell after the conditioning test were disassembled in an inert argon-filled glovebox. A graphite anode electrode and a NCA cathode electrode from each cell were extracted from jelly rolls. One side of the coating layer on the electrodes was rinsed with N-methyl-2-pyrrolidone (NMP) solvent, and the active material was removed by light scraping until exposure of the current collectors. 9/16" diameter one-sided electrodes were punched out and assembled into CR2032 coin cells using lithium metal as counter electrodes and 1 M LiPF₆ in EC/EMC (v/v 1:1) as electrolyte. Hence, eight types of half cells (marked as HC-1 to HC-8) were fabricated. HC-1 to HC-4 were assembled with the harvested graphite anodes from MOT-1, MOT-2, MOT-3, and the pristine cell and were cycled two times between 0.005 and 1.5 V vs. Li/Li $^+$ at a 0.02C rate, while HC-5 to HC-8 were assembled with harvested NCA cathode from MOT-1, MOT-2, MOT-3, and the pristine cell and were cycled for two times between 2.5 and 4.2 V vs. Li/Li⁺ at a 0.02C rate to understand the electrode-level capacity retention after overdischarge failure under various C-rates. After galvanostatic testing, all eight half cells were charged to 50% SOC, and EIS measurement was performed from 1 MHz to 1mHz to explore their impedance evolution. Equivalent circuit (EC) models were applied to fit the EIS curve and estimate the resistance of electrode-electrolyte interphase and charge transfer kinetics. All the tests introduced in this section were carried out at 20 °C ambient temperature in the laboratory.

2.7. Post-mortem analysis

Graphite anodes, NCA cathodes, and polymer separators from MOT-1, MOT-2, MOT-3, and the pristine cell were subject to visual inspections and optical microscopy observations with a magnification of 30X. SEM imaging with magnifications of 1kX and 5kX was taken on all graphite anodes and NCA cathodes after rinsing with EMC solvent to remove the electrolyte residue. Elemental distributions on the surface of electrodes



Fig. 2. Time-dependent full-cell voltage and temperature profiles of MOT-2 during the multi-level overdischarge-recharge tests. Cell IR was measured at 70% DOD of each cycle, and post-mortem analysis was implemented at the end of all cycles.

were mapped and quantified through EDS characterizations, while chemical states of the electrodeposition were investigated through XPS techniques. Binding energy scales for all XPS results are calibrated based on the hydrocarbon C 1s peak at 284.8 eV. The raw spectra are deconvoluted using a weighted Gauss-Lorentz function (7:3) with Shirley background correction and symmetric curvature profile. SEM and EDS were employed using a Hitachi S-4800 field emission scanning electron microscope with a maximum resolution of 2.0 nm and a variable accelerating voltage from 0.5 to 30 kV. XPS was operated through a Kratos AXIS Ultra DLD Imaging X-ray Photoelectron Spectrometer with a lateral resolution of 5 μ m.

3. Results and discussion

3.1. Extreme overdischarge interpretations

Full cell voltages of EOT-1 and EOT-2 during extreme overdischarge tests are delineated in Fig. 3(a) to better understand the impact of RE instrumentation on cell performance. Although the full cell voltage of EOT-1 is slightly shifted compared to that of EOT-2, both present synchronized characteristics. Their behaviors start to diverge after around 115% DOD due to massive Cu deposition and micro ISC that make the full cell voltage unstable. Therefore, the RE introduction is a reliable technique to decipher the complex overdischarge mechanisms without significantly changing the electrochemical signatures of the cell.

Electrode potentials and full cell voltage of EOT-1 are illustrated in Fig. 3(b) to present electrochemical signatures of the graphite anode and NCA cathode. Four phases could be defined according to the revealed degradation mechanisms. Phase 1 occurs before 100.5% DOD, where deintercalation of lithium from the graphite anode and intercalation into the NCA cathode occur in a highly reversible manner, as intended during regular cell operation. Phase 2 is defined between 100.5 and 107.6% DOD, where full cell voltage rapidly drops from 2.56 to -1.18 V, primarily attributed to a rapid increase of graphite anode potential from 0.57 to 4.38 V vs. Li/Li⁺. Simultaneously, NCA cathode potential

experiences two concaves and subtly changes from 3.12 to 3.21 V vs. Li/ Li⁺, showing the negligible contribution to the decline of full cell voltage. Hence, Phase 2 is dictated by anode-centric degradation with SEI layer decomposition and copper dissolution from the current collector resulting from an excessively high anode potential. Between 107.6% DOD and 114.7% DOD, graphite anode potential remains around 4.5 V vs. Li/Li⁺, indicating that the copper oxidation reaction keeps dominant at the anode. The decline of full cell voltage from -1.18 V to the minimum point of -2.78 V is attributed to the drop of cathode potential from 3.21 V to the minimum value of 1.64 V vs. Li/Li⁺. Therefore, cell degradation in Phase 3 is dictated by copper dissolution from the anode current collector and copper deposition on the surface of the cathode. Beyond 114.7% DOD, an increase of cathode potential and a decrease of anode potential result in a rebound of full cell voltage against the minimum plateau. The full cell voltage and electrode potentials start to behave capriciously with frequent data noise, suggesting the formation of inter-electrode micro ISC. As a result, Phase 4 is governed by redox-centric failure due to the overwhelming propagation of Cu-based depositions on both electrodes and separators, which is substantiated by the visual inspections of the opening EOT-1 shown in Fig. S6.

3.2. Multi-level overdischarge-recharge interpretations

Overdischarge performances of MOT-1, MOT-2, and MOT-3 are presented in Fig. 4 to understand cell degradation behaviors at different full-cell cutoff limits and various operating C-rates. Fig. 4(a)–(c) show the profile of full cell voltage, anode potential, and cathode potential of MOT-1 operated at a 0.1C rate, respectively. In Fig. 4(a), the cell suffers negligible capacity degradation from 3.43 Ah to 3.42 Ah before the cutoff limit of -1.0 V. However, the cell capacity rapidly drops to a lower value between 2.77 Ah and 2.52 Ah when the cutoff limit is between -1.5 and -3.0 V, indicating a moderate capacity loss and a significant deterioration of the state of health (SOH). The cell demonstrates a substantial fade of discharge capacity to 1.94 Ah when overdischarge to the



Fig. 3. Cell performances during extreme overdischarge tests: (a) Full cell voltage profiles with RE and without RE. (b) Full cell voltage, anode potential, and cathode potential profiles of the cell with RE.



Fig. 4. Discharge phase profiles: full cell voltage and electrode potentials of 3E cells during multi-level overdischarge-recharge tests. (a) Full cell voltage at 0.1C. (b) Anode potential at 0.1C. (c) Cathode potential at 0.1C. (d) Full cell voltage at 0.5C. (e) Anode potential at 0.5C. (f) Cathode potential at 0.5C. (g) Full cell voltage at 1.0C. (h) Anode potential at 1.0C. (i) Cathode potential at 1.0C.

cutoff limit of EP and could not be recharged afterward. Meanwhile, profiles of electrode potentials provide insights into how the electrochemical behaviors of graphite anode and NCA cathode significantly change with the decay of the cell characteristics. Following differential voltage analysis (DVA) on the anode potential shown in Fig. S4, the onset points of SEI breakdown and copper oxidation from the graphite anode are assumed to be 1.28 V vs. Li/Li⁺ and 3.21 V vs. Li/Li⁺, respectively. The rationale for these peak assignments is supported by similar values reported in peer studies [18,20,22,23] and by the fact that MOT-1 suffers substantial capacity fade as soon as the anode potential exceeds 3.21 V vs. Li/Li⁺. Therefore, in Fig. 4(b), we could infer that the SEI breakdown happens at the full cell cutoff limit of 1.0 V and the copper oxidation occurs at the full cell cutoff limit of -0.5 V. The anode potential reaches the plateau of 4.44 V vs. Li/Li⁺ at the cutoff limit of -1.5 V. introducing a large amount of unfavorable copper dissolution into the system. Behaviors of cathode potentials in Fig. 4(c) show consistent behavior before the cutoff limit of -1.0 V. The sharp voltage drop at the end of discharge indicates the complete lithiation of the NCA. Beyond this cutoff limit, fluctuations in the cathode potential are observed, which may be caused by loss of electrochemically active surface area (ECSA) and porosity in the cathode microstructure resulting from copper deposition.

Fig. 4(d)–(f) show the profiles of full cell voltage, anode potential, and cathode potential of MOT-2 operated at a 0.5C rate. In Fig. 4(d), the cell shows a mild capacity fade from 3.34 to 3.24 Ah when overdischarged to various lower cutoff limits before -1.5 V. A moderate capacity degradation is observed from 2.94 to 2.77 Ah when the cutoff limit is lowered from -1.5 to -3.0 V, and deep overdischarge to the cutoff limit of EP results in a substantial capacity loss down to 2.09 Ah. Following our previous discussion about the onset of SEI breakdown and copper oxidation, in Fig. 4(e), we can infer that the former happens at the full cell cutoff limit of -1.0 V and the latter occurs at the full cell cutoff limit of -2.0 V. The maximum plateau of the anode potential at 4.45 V vs. Li/

 Li^+ is obtained with the cutoff limit of -3.0 V and EP, indicating a dominant reaction of copper dissolution from the anode side to accelerate the cell failure. Overall, the cathode potential at various cutoff limits in Fig. 4(f) drops to lower values than MOT-1 due to greater overpotential and ohmic polarization under a higher C-rate. The cathode potential shows genuine profiles before the cutoff limit of -1.5 V. However, a minimum point and rebound are observed after the cutoff limit of -2.0 V. Similar mechanisms such as loss of ECSA and porosity due to copper blocking in the cathode microstructure are likely causes of such deformation of cathode profiles, while the possibility of additional phase transformations between copper deposition and lithium intercalation cannot be excluded. Besides, low values of cathode potential may go beyond the electrochemical stability window of electrolyte carbonates to result in electrolyte decomposition and passive layer formation, which is assumed to take place below 0.50 V vs. Li/Li⁺ [1].

Full cell voltage, anode potential, and cathode potential of MOT-3 operated at a 1.0C rate are displayed in Fig. 4(g), Fig. 4(h), and Fig. 4 (i), respectively. In Fig. 4(g), the cell experiences an insignificant capacity drop from 3.29 Ah to 3.27 Ah as the overdischarge voltage limit is lowered before -1.5 V, while the shift of full cell voltage at the same discharge capacity indicates an increase of ohmic polarization and overpotential. An abrupt capacity loss from 2.72 to 2.29 Ah occurs when the cutoff limit is lowered from -2.0 to -3.0 V, and the cell fails to recharge after overdischarge to the cutoff limit of EP. Following our previous discussion about the onset of SEI breakdown and copper oxidation, in Fig. 4(h), we could infer that the former happens at the full cell cutoff limit of -1.5 V and the latter occurs at the full cell cutoff limit of -2.0 V. No stable plateau is observed in the anode potential profiles for all cases of overdischarge cutoff limits. The maximum anode potential is 3.77 V vs. Li/Li⁺ at the cutoff limit of -2.5 V, significantly lower than the maximum values of 4.45 V vs. Li/Li⁺ in MOT-2 and 4.52 V vs. Li/Li⁺ in MOT-1. It suggests less copper dissolution in MOT-3 given the reduced anode potential and less time spent in the copper oxidation regime. The cathode potential in Fig. 4(i) shows natural profiles before the cutoff limit of -1.5 V with greater ohmic polarization and overpotential than MOT-2. Their shapes are remarkably stretched and deformed between the cutoff limit of -2.0 and -3.0 V, probably due to similar degradation mechanisms such as loss of ECSA and porosity in the cathode microstructure resulting from copper deposition. The decomposition and reduction of electrolyte carbonates may occur when the cathode potential goes below 0.50 V vs. Li/Li⁺ [1].

Charge phases of MOT-1, MOT-2, and MOT-3 are illustrated in Fig. 5 to reveal the recharge capabilities of cells after being subjected to different overdischarge cutoff limits and various operating C-rates. Fig. 5(a)–(c) present the full cell voltage, anode potential, and cathode potential of MOT-1 charged at a 0.1C rate. In Fig. 5(a), the cell could be charged to the capacity between 3.28 and 3.35 Ah before the overdischarge cutoff limit of -1.0 V, then a faster degradation is noticed. A moderate capacity fade is observed between the cutoff limit of -2.5 and -1.5 V, where the cell could be recharged with capacity recordings between 2.36 and 2.48 Ah. A substantial capacity loss appears at the cutoff limit of -3.0 V, at which only 1.86 Ah recharge capacity could be obtained. In Fig. 5(b), behaviors of the anode potential are consistent until the cutoff limit of -1.0 V. The minimum value decreases to 0.09 V vs. Li/ Li⁺ when the cutoff limit declines from -1.5 to -2.5 V and further drops to 0.08 V vs. Li/Li⁺ when the cutoff limit is -3.0 V. This change corresponds to the moderate and substantial capacity fade of the cell. It suggests an increased anode resistance probably due to the reduced contact area between the active material and current collector resulting from the dissolution of the copper current collector and a loss of ECSA because of copper deposition. It is worth noting that the anode potential remains above 0.0 V vs. Li/Li⁺ despite the degeneration of Li-ion intercalation kinetics, indicating no occurrence of unfavorable lithium plating. Profiles of cathode potentials in Fig. 5(c) do not significantly change until the cutoff limit of -3.0 V. The growing cathode resistance, overpotential, and ohmic polarization probably contribute to the overshoot of cathode potential at an initial stage and the loss of characteristic plateaus between 1.0 and 1.5 Ah charge capacity.

Fig. 5(d)-(f) present the full cell voltage, anode potential, and cathode potential of MOT-2 charged at a 0.5C rate. In Fig. 5(d), charge capacity fades mildly from 2.91 to 2.68 Ah before the overdischarge cutoff limit of -1.0 V. A moderate capacity degradation from 2.22 to 1.70 Ah is observed when the cutoff limit is lowered from -1.5 to -2.5 V. The cell suffers from a substantial capacity loss at the cutoff limit of -3.0 V, where only 0.71 Ah charge capacity could be obtained. The profile of anode potential in Fig. 5(e) is very similar for all cycles before the cutoff limit of -2.0 V. The minimum anode potential decreases to 0.07 V vs. Li/ $\rm Li^+$ at the cutoff limit of -2.5 and 0.10 V vs. $\rm Li/\rm Li^+$ at the cutoff level of -3.0 V, suggesting an increase in anode resistance and a degeneration of Li-ion intercalation and diffusion kinetics. Still, anode potentials remain above 0.0 V vs. Li/Li⁺ for all full cell cutoff limits, indicating that the adverse lithium plating reaction does not occur. The profile of cathode potential in Fig. 5(f) presents a characteristic plateau between charge capacity of 1.0 and 1.5 Ah and does not show significant variations before the cutoff limit of -2.5 V, except for an increasing voltage overshoot at the beginning of charge. However, at the cutoff limit of -3.0 V, the cathode potential instantly spikes to above 4.2 V vs. Li/Li⁺, indicating a severe resistance increase on the cathode side. Copper deposition and excessive interphase formation on the NCA particles likely contribute to the dramatic performance loss.

Full cell voltage, anode potential, and cathode potential of MOT-3 charged at a 1.0C rate are delineated in Fig. 5(g), Fig. 5(h), and Fig. 5 (i), respectively. In Fig. 5(g), the cell suffers a mild capacity fade from 2.67 to 2.13 Ah as the overdischarge limit is lowered before -1.0 V. A moderate capacity degradation from 1.26 Ah to 0.92 Ah is observed when the cutoff limit is lowered from -1.5 to -2.0 V. A substantial capacity loss appears when the cutoff limit is lowered from -2.5 to -3.0 V, during which the charge capacity declines from 0.37 to 0.04 Ah and indicates the non-functionality of the cell. The anode potential in Fig. 5



Fig. 5. Charge phase profiles: full cell voltage and electrode potentials of 3E cells during multi-level overdischarge-recharge tests. (a) Full cell voltage at 0.1C. (b) Anode potential at 0.1C. (c) Cathode potential at 0.1C. (d) Full cell voltage at 0.5C. (e) Anode potential at 0.5C. (f) Cathode potential at 0.5C. (g) Full cell voltage at 1.0C. (h) Anode potential of at 1.0C. (i) Cathode potential at 1.0C.

(h) behaves coherently before the cutoff limit of -1.5 V. However, the minimum anode potential falls to 0.05 V, -0.07 V, and -0.34 V vs. Li/Li+ at the cutoff limits of -2.0 V, -2.5 V, and -3.0 V, respectively. The anode potential below 0.0 V vs. Li/Li⁺ demonstrates the onset of adverse lithium plating, suggesting that the reaction rate of lithium ions on the graphite surface has exceeded the intercalation or diffusion limits of graphite particles as a result of severe anode degradation. This observation reveals that if the cell is repeatedly overdischarged and recharged at a high C-rate, it is more likely to introduce thermally and electrochemically unstable lithium plating to undermine the safety performance of Li-ion batteries. The profile of cathode potential in Fig. 5(i) remains consistent before the cutoff limit of -1.0 V, except for a growing overshoot at the initial stage due to higher cathode resistance, overpotential, and ohmic polarization. Profiles of the cathode potential lose their characteristic plateau between 1.0 Ah and 1.5 Ah charge capacity when the cutoff limit is below -1.5 V.

3.3. State of cell at cutoff limits

Key electrochemical and physical parameters of MOT-1, MOT-2, and MOT-3 during the multi-level overdischarge-recharge studies are statistically interpreted. Cell surface temperature, anode potential, cathode potential, and normalized IR are recorded at the end of each discharge phase, while cell volumetric expansion is measured at the end of every two discharge phases. Fig. 6(a) shows how the exterior temperatures of MOT-1, MOT-2, and MOT-3 increase when they are deeply overdischarged with different C-rates. MOT-3, operated at a 1.0C rate, shows

the most significant temperature rise to 63.0 °C at the cutoff limit of -3.0 V. It exceeds the safety limit of 60 °C after the cutoff limit of -2.0 V, which threatens the thermal stability of the cell. MOT-2, operated at a 0.5C rate, reaches a maximum temperature of 50.5 °C at the cutoff limit of EP, while MOT-1 shows the mildest temperature rise to 27.8 °C at the cutoff limit of EP. The additional heat generation during overdischarge abuses could be caused by extreme ionic concentration polarization [22], strong internal exothermic reactions such as SEI layer breakdown at a high anode potential [35], and micro internal short circuits due to the inter-electrode copper bridge formation [21]. A state-of-the-art research investment also discussed the possibility that it is caused by the formation of aluminum reduced from the alumina coating layers on the separator [26]. Our investigations in Fig. 6(a) demonstrate that the heat generation of the overdischarged cell is highly dependent on lower cutoff limits of full-cell voltages and operating C-rates. Joule's law states that a high current will lead to more heat generation. The internal resistance of the overdischarged cell will also significantly increase due to internal gas generation caused by SEI layer collapse, electrode impedance rise driven by SEI layer breakdown or CEI layer growth with lithium or copper depositions, and interfacial electrolyte consumptions accelerated by extreme electrode potentials. The temperatures observed under various overdischarge conditions are generally not exorbitant, with the lowest discharge rate showing an almost negligible increase.

In Fig. 6(b), statistics of anode potential at the end of each cutoff limit reveal new insights into how the onset of SEI breakdown and copper dissolution change with different C-rates. Following our previous discussion, the onset points of SEI breakdown and copper oxidation from



Fig. 6. States of 3E cells at the end of each overdischarge cutoff limits: (a) Surface temperature at 0.1C, 0.5C and 1.0C. (b) Anode potentials at 0.1C, 0.5C and 1.0C. (c) Cathode potentials at 0.1C, 0.5C and 1.0C. (d) Normalized IR at 0.1C, 0.5C and 1.0C. (e) Volumetric expansion at 0.1C, 0.5C and 1.0C.

the graphite anode are assumed to be 1.28 V vs. Li/Li⁺ and 3.21 V vs. Li/Li⁺, respectively. Therefore, both processes first occur in MOT-1 operated at a 0.1C rate, where the SEI degradation starts at the full cell cutoff limit of 1.0 V and copper dissolution appears at the full cell cutoff limit of -0.5 V. In contrast, the onset of SEI breakdown and copper dissolution in MOT-2 operated at a 0.5C rate is delayed to the cutoff limits of -1.0 V and -2.0 V, respectively, and the onset of SEI breakdown and copper dissolution in MOT-3 operated at a 1.0C rate is further postponed to the cutoff limit of -1.5 V and -2.0 V, respectively. These observations suggest that the onset of overdischarge-induced degradation resulting from SEI collapse and copper oxidation could be delayed by high-rate operation.

Meanwhile, Fig. 6(c) reveals behaviors of cathode potentials at the end of each cutoff limit. The cathode potential of MOT-1 operated at a 0.1C rate stays above 2.0 V vs. Li/Li⁺ until the cutoff limit of -2.5 V. Nevertheless, the cathode potential of MOT-2 operated at a 0.5C rate drops early and reaches a minimum value of 0.34 V vs. Li/Li⁺ at the cutoff limit of -0.5 V, while the cathode potential of MOT-3 operated at a 1.0C rate starts to decline at the beginning of overdischarge abuse and reaches a minimum value of -0.17 V vs. Li/Li⁺ at the same cutoff limit of -0.5 V. These observations suggest that the cathode potential will be driven to low values under high-rate overdischarge, which is likely to cause an extra CEI evolution to increase the cathode resistance and make transport kinetics of the cell cathode-limited.

The normalized IR of MOT-1, MOT-2, and MOT-3 at each cutoff limit is presented in Fig. 6(d) based on the average values of IR during each conditioning test. The normalized IR of MOT-1, operated at a 0.1C rate, starts to increase at the cutoff limit of -1.0 V and reaches a maximum

value of 10.43 at the cutoff limit of -3.0 V. Similarly, the normalized IR of MOT-3, operated at a 1.0C rate, begins to increase at the cutoff limit of -1.5 V and reaches the maximum value of 10.24 at the cutoff limit of -3.0 V. The IR rise of MOT-2, operated at a 0.5C rate, is much milder, reaching a maximum value of 3.71 at the cutoff limit of -3.0 V. These observations indicate that operating at a moderate C-rate might decelerate the overdischarge-induced resistance evolution at the full cell scale. Volumetric expansions of MOT-1, MOT-2, and MOT-3 at every two cutoff limits are illustrated in Fig. 6(e). The cell swelling first appears in MOT-1 when the cutoff limit is 0.0 V and keeps increasing to the maximum value of 20 mL at the cutoff limit of EP. The next cell to swell is MOT-2 when the cutoff limit is -1.0 V and keeps rising to a peak value of 16 mL at the cutoff limit of EP. In contrast, the volumetric expansion of MOT-3 starts when the cutoff limit is -2.0 V and reaches a maximum value of 10 mL at the cutoff limit of -3.0 V. Based on these statistics, we notice that the cell volumetric expansion matches the onset of SEI breakdown and the resulting internal gas generation. Therefore, highrate overdischarge could delay the onset of cell swelling due to hysteresis SEI breakdown and gas generation side reactions. However, it does not necessarily mean that a high-rate operation is the best strategy to minimize overdischarge-induced hazards due to a significant temperature evolution. A trade-off balance between cell swelling and selfheating needs to be deliberated before determining the optimal charge and discharge rates.



Fig. 7. Capacity and impedance characteristics of 0.1C Graphite Anode, 0.5C Graphite Anode, 1.0C Graphite Anode, and Pristine Graphite Anode: (a) Discharge phase. (b) Charge phase. (c) EIS profiles at 50% SOC. Capacity and impedance characteristics of 0.1C NCA Cathode, 0.5C NCA Cathode, 1.0C NCA Cathode, and Pristine NCA Cathode: (d) Discharge phase. (e) Charge phase. (f) EIS profiles at 50% SOC.

3.4. Electrode capacity retention and impedance evolution

Electrode samples from the three multi-level overdischarge test cells were harvested and assembled into coin cells with a lithium counter electrode. The capacity degradation and impedance evolution of the graphite anodes and NCA cathodes after overdischarge failure at different C-rates are illustrated in Fig. 7 compared to their performance at pristine status. Discharge phases of half cells constructed from 0.1C graphite anode (HC-1), 0.5C graphite anode (HC-2), 1.0C graphite anode (HC-3), and pristine graphite anode (HC-4) are presented in Fig. 7 (a). The embedded subplot shows the local zoom-in view below 0.3 V vs. Li/Li⁺ to better visualize the details of intercalation plateaus. HC-1, containing the 0.1C graphite anode, shows the lowest areal capacity of 2.49 mAh/cm². HC-3, containing the 1.0C graphite anode, demonstrates a moderate areal capacity of 3.25 mAh/cm², while HC-2, containing the 0.5C graphite anode, has the highest areal capacity of 3.87 mAh/cm^2 . However, they are less than the maximum areal capacity of 3.98 mAh/ cm² obtained from the pristine graphite anode. Therefore, we could infer that a moderate C-rate is likely to minimize the capacity degradation of graphite anode during overdischarge abuses. The capacity loss of the 0.1C graphite anode might be attributed to the delamination of the graphite coating layer from the current collector due to severe copper dissolution and the resulting loss of active material (LAM). In contrast, the capacity fade of the 1.0C graphite anode might be attributed to the loss of Li-ion intercalation sites due to widespread lithium plating on the copper deposition. Charge phases of 0.1C graphite anode (HC-1), 0.5C graphite anode (HC-2), 1.0C graphite anode (HC-3), and pristine graphite anode (HC-4) are presented in Fig. 7(b) with areal capacity retentions of 2.00 mAh/cm², 3.65 mAh/cm², 3.17 mAh/cm² and 3.74 mAh/cm², respectively. It is worthwhile to notice that there is an evident deviation between discharge and charge capacities of 0.1C graphite anode, suggesting a reduced Coulombic efficiency and a LAMdictated inconsistent electrode performance caused by severe detachment between the graphite coating layer and copper current collector.

The impedance spectroscopy and EC model fitting of the 0.1C graphite anode (HC-1), 0.5C graphite anode (HC-2), 1.0C graphite anode (HC-3), and pristine graphite anode (HC-4) are presented in Fig. 7 (c). Two primary semicircles characterizing interfacial and charge transfer resistances and a straight tail reflecting diffusion kinetics of graphite can be observed in all three cases [46-48]. The interfacial and charge transfer resistance values are estimated through EC model fitting and summarized in Table 2. An SEI resistance of 20.10 Ω and charge transfer resistance of 22.45 Ω are obtained from the pristine graphite anode as a baseline impedance. The 0.5C graphite anode shows the lowest impedance evolution among all three cases, with an SEI resistance of 32.03 Ω and low charge transfer resistance of 5.81 Ω , to which some conductive surface depositions may contribute. This result is consistent with the fact that the 0.5C graphite anode has the maximum capacity retention. The 0.1C graphite anode and the 1.0C graphite anode share similar SEI resistances of 76.90 Ω and 71.89 Ω , but the former shows a higher charge transfer resistance of 47.36 Ω than the latter one of 11.97 Ω . Given the severe and moderate capacity fade on 0.1C and 1.0C graphite anodes, these observations further suggest that SEI

Table 2

Estimated SEI and charge transfer resistance of 0.1C Graphite Anode, 0.5C Graphite Anode, 1.0C Graphite Anode, and Pristine Graphite Anode, followed by estimated CEI and charge transfer resistance of 0.1C NCA Cathode, 0.5C NCA Cathode, 1.0C NCA Cathode, and Pristine NCA Cathode calculated from EC model fitting.

C-rate	Graphite Ano R _{SEI} [Ω]	de R _{CT} [Ω]	NCA Cathode R _{CEI} [Ω]	R _{CT} [Ω]
0.1C	76.90	47.36	15.66	70.14
0.5C	32.03	5.805	16.39	246.7
1.0C	71.89	11.97	17.38	12.09
Pristine	20.10	22.45	2.818	5.625

resistance evolution on graphite anodes correlates to electrode capacity degradation.

Discharge phases of 0.1C NCA cathode (HC-5), 0.5C NCA cathode (HC-6), 1.0C NCA cathode (HC-7), and pristine NCA cathode (HC-8) are presented in Fig. 7(d). The 0.5C NCA cathode has a minimum areal capacity of 1.58 mAh/cm². The 0.1C NCA cathode retains a moderate areal capacity of 2.25 mAh/cm², and the 1.0C NCA cathode holds the highest areal capacity retention of 2.81 mAh/cm². However, they are less than the maximum areal capacity of 3.14 mAh/cm² obtained from the pristine NCA cathode. Therefore, we can infer that a high-rate overdischarge mitigates the capacity degradation of the NCA cathode. Charge phases of 0.1C NCA cathode (HC-5), 0.5C NCA cathode (HC-6), 1.0C NCA cathode (HC-7), and pristine NCA cathode (HC-8) are presented in Fig. 7(e) with the areal capacities being 2.27 mAh/cm^2 , 1.59 mAh/cm², 2.83 mAh/cm², and 3.17 mAh/cm², respectively. The areal charge capacity matches the areal discharge capacity for all four cases, contrasting with the significant mismatch observed in the 0.1C graphite anode. This high Coulombic efficiency indicates the maintenance of integrity and robustness of the positive electrode under these overdischarge conditions.

The impedance spectroscopy and EC model fitting of 0.1C NCA cathode (HC-5), 0.5C NCA cathode (HC-6), 1.0C NCA cathode (HC-7), and pristine NCA cathode (HC-8) are presented in Fig. 7(f). Two primary semicircles characterizing CEI and charge transfer resistance and one straight tail reflecting diffusion kinetics of NCA particles could be identified [49,50]. Their values are estimated through EC model fitting and summarized in Table 2. CEI resistance of 2.82Ω and charge transfer resistance of 5.63Ω are obtained from pristine NCA cathode as a baseline impedance. The CEI resistances of the 0.1C NCA cathode, 0.5C NCA cathode, and 1.0C NCA cathode are 15.66 Ω , 16.39 Ω , and 17.38 Ω , respectively, showing a continuous growth with an increase of C-rates. These results match the observation in Fig. 6(c), suggesting that a high-rate overdischarge will lead to a low cathode potential to result in CEI evolution and impedance rise. The charge transfer resistances of the 0.1C NCA cathode, 0.5C NCA cathode, and 1.0C NCA cathode are 70.14 Ω , 246.7 Ω , and 12.09 Ω , respectively. Given their capacity retention in Fig. 7(d) and (e), these observations indicate that the evolution of charge transfer resistance on NCA cathodes can also correlate to electrode capacity degradation.

3.5. Surface microscopic characterizations

Following disassembly of the cells, electrode samples from MOT-1, MOT-2, and MOT-3 after overdischarge failure at various C-rates are subjected to visual inspections at different scales to reveal the physicochemical evolution of electrodes and separators while understanding the morphology and distribution of electrodepositions. Fig. 8 shows the appearance of the graphite anode, NCA cathode, and polymer separator of MOT-1, MOT-2, and MOT-3, with embedded subplots showing depositions under optical microscopy at a magnification of 30X. For MOT-1, operated at a 0.1C rate, Fig. 8(a) and (b) display a small amount of copper plating at the corners of the graphite anode and NCA cathode. Broad areas of the separator, shown in Fig. 8(c), change from white to brownish yellow due to copper dissolution. This observation matches the behavior of anode potential in Fig. 6(b), where it remains at a high value under the 0.1C rate to accelerate massive copper oxidation. Fig. 8 (d) and (e) show the graphite anode and NCA cathode from MOT-2, operated at a 0.5C rate. The residue of separator material and clusters of copper deposition could be noticed on the graphite anode, with a sporadic distribution of copper deposition remaining on the NCA cathode. The amount of copper deposition on the NCA cathode of MOT-2 is visibly more than that of MOT-1, explaining why the 0.5C NCA cathode suffers the most severe capacity degradation and impedance rise in the prior half-cell experiments. The separator of MOT-2 is shown in Fig. 8(f) with a reduced brownish yellow area, indicating a less amount of copper dissolution than that of MOT-1. Fig. 8(g) and (h) show photographs of

MOT-1 (0.1C) MOT-2 (0.5C) MOT-3 (1.0C) (a) Graphite Anode **Graphite** Anode (g) Graphite Anode. (d) 30X 30X 30X NCA Cathode NCA Cathode (b) (e) (h) **NCA** Cathode 30X 30X 30X Cu deposition (c) Polymer Separator (f) Polymer (i) Polymer

Fig. 8. Post-mortem analysis: visual inspection and optical microscopy of 3E cells after multi-level overdischarge-recharge tests. (a) Graphite anode at 0.1C. (b) NCA cathode at 0.1C. (c) Polymer separator at 0.1C. (d) Graphite anode at 0.5C. (e) NCA cathode at 0.5C. (f) Polymer separator at 0.5C. (g) Graphite anode at 1.0C. (h) NCA cathode at 1.0C. (i) Polymer separator at 1.0C. All embedded subplots show the optical microscopic imaging of depositions with a magnification of 30X.

the graphite anode and NCA cathode of MOT-3, operated at a 1.0C rate. The proof of lithium plating existence is illustrated in Fig. S9 based on chemical interactions with isopropanol, and further discussed in the following SEM, EDS, and XPS analysis. Widespread lithium depositions densely cover the entire surface of the graphite anode with separator residues being observed underneath the lithium plating regime through optical microscopy imaging, while the distribution of lithium depositions on the NCA cathode is sporadic and nonuniform. The brownish yellow area on the MOT-3 separator is further reduced in Fig. 8(i), showing the minimum amount of copper dissolution among all three cases.

SEM imaging and EDS characterizations on graphite anode samples extracted from MOT-1, MOT-2, and MOT-3 are illustrated in Fig. 9. A similar chemical analysis on a pristine graphite anode is also presented in Fig. S10 for comparison. Fig. 9(a) and (b) show the SEM images of MOT-1, operated at a 0.1C rate, with magnifications of 1kX and 5kX, respectively. EDS mapping proves that a large amount of copper nucleation covers the surface of graphite particles with spherical morphology. No evident cracking and crumbling appear on the graphite particles. Hence, the loss of active surface area and delamination between the current collector and the active material is the main reason for the low capacity retention observed in the 0.1C graphite anode. Fig. 9(c) and (d) show the SEM images of the MOT-2 anode, operated at a 0.5C rate, with magnifications of 1kX and 5kX, respectively. The copperbased deposition identified by EDS mapping shows mossy-like cluster morphology instead of a spherical one. The deposition layer is more uniform but less solid than that of MOT-1. Fig. 9(e) and (f) show the micrographs of the MOT-3 anode, operated at a 1.0C rate, with magnifications of 1 kX and 5 kX, respectively. The prominent interface between the deposition layer and graphite particles is differentiated by EDS mapping. It is worthwhile to notice that the lithium plating presents a filament morphology with a dendrite-like structure, which is more likely to penetrate porous separators and even cause the ISC and cell TR when coupled with high SOC. Therefore, the safety challenges of Li-ion batteries under high-rate overdischarge-recharge abuses should never be underestimated due to the potentially hazardous morphologies of electrodepositions, which are also substantiated by SEM and EDS characterizations on other regions of MOT-3 anode shown in Figs. S11 and S12.

Weight percentages of various chemical elements detected on graphite anode from the 5kX SEM imaging of MOT-1, MOT-2, MOT-3, and a pristine cell are demonstrated in Table 3. A 34.94 and 35.59 wt % copper element at 0.1C and 0.5C rates prove that the dominant deposition species is copper. 13.32 wt% oxygen element and 23.83 wt% fluorine element at a 0.5C rate probably indicate that the deposition comprises copper oxide and copper fluoride compounds [28]. A 0.44 and 0.73 wt% aluminum element at 0.1C and 0.5C rates reveal some chemical crosstalk from the NCA cathode to the graphite anode. This aluminum could originate from several possible sources, including corrosion of the cathode current collector or dissolution of the NCA active material. Meanwhile, 15.82 wt% oxygen and 18.06 wt% fluorine elements dictate the deposition chemistry at the 1.0C rate, whereas only 0.62 wt% copper element is detected. It demonstrates that the primary deposition component should be lithium rather than copper, probably in

MOT-1 (0.1C)MOT-2 (0.5C)MOT-3 (1.0C)Image: constraint of the dependence of the depende

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Fig. 9. SEM-EDS characterizations: graphite anodes of 3E cells after multi-level overdischarge-recharge tests. (a) 1kX SEM of graphite anode at 0.1C. (b) 5kX SEM of graphite anode at 0.1C. (c) 1kX SEM of graphite anode at 0.5C. (d) 5kX SEM of graphite anode at 0.5C. (e) 1kX SEM of graphite anode at 1.0C. (f) 5kX SEM of graphite anode at 1.0C. EDS mapping of each case is presented underneath, respectively.

Table 3

Chemical elements quantifications: graphite anodes from 3E cells after multilevel overdischarge-recharge tests at 0.1C, 0.5C, 1.0C, and a pristine cell.

C-rate	Graphite Anode (wt.%)						
	С	0	F	Р	S	Al	Cu
0.1C	57.01	-	6.21	1.20	0.19	0.44	34.94
0.5C	18.43	13.32	23.83	6.84	1.27	0.73	35.59
1.0C	64.26	15.82	18.06	0.88	0.30	0.06	0.62
Pristine	87.84	-	11.54	0.33	0.29	-	-

the form of lithium hydroxide, lithium carbonate, and lithium fluoride compounds [33]. This inference also matches the prior multi-level overdischarge-recharge interpretations of MOT-3 in Fig. 5(h), where anode potential drops below 0.0 V vs. Li/Li⁺ during the charge phase to introduce the unfavorable lithium plating.

SEM imaging and EDS characterizations on the NCA cathodes harvested from MOT-1, MOT-2, and MOT-3 are illustrated in Fig. 10. A similar chemical analysis on a pristine NCA cathode is also presented in

Fig. S10 for reference. Fig. 10(a) and (b) show the SEM images of MOT-1, operated at a 0.1C rate, with magnifications of 1 kX and 5 kX, respectively. A thick copper deposition layer substantiated by EDS mapping covers portions of the electrode. No noticeable cracking or crumbling is observed in the NCA particles. Fig. 10(c) and (d) show the SEM observation of MOT-2, operated at a 0.5C rate, with magnifications of 1kX and 5kX, respectively. A cracked copper deposition layer covering the NCA particles is visualized with a clear boundary. No great crumbling is observed on NCA particles, indicating high morphological stability. The loss of ECSA and porosity on the cathode microstructure due to observed copper blocking compose the degradation mechanism of the NCA cathode at low and moderate C-rates. Fig. 10(e) and (f) show the SEM observation of MOT-3, operated at a 1.0C rate, with magnifications of 1 kX and 5 kX, respectively. A regime of separator stripping is found to cover the surface of the NCA cathode instead of the layered copper deposition. Two ruptured cobalt-based particles are captured and identified by EDS mapping, characterizing LAM as the primary degradation pathway of NCA cathode under high-rate overdischarge.

The weight percentage of various elements on NCA cathodes

MOT-3 (1.0C) MOT-1 (0.1C) MOT-2 (0.5C) (e)strippin 1kX (\mathbf{d}) (\mathbf{b}) Ni particle 5k) 5kX 4800 20 0kV 17 0r n v5 00k SE(1 n x5 00k S \sim Ξo Al Ni AÌ Ni C C Ka1 2 C Ka1 2 F Kα1 2 Ö 0 ____

Fig. 10. SEM-EDS characterizations: NCA cathodes of 3E cells after multi-level overdischarge-recharge tests. (a) 1kX SEM of NCA cathode at 0.1C. (b) 5kX SEM of NCA cathode at 0.1C. (c) 1kX SEM of NCA cathode at 0.5C. (d) 5kX SEM of NCA cathode at 0.5C. (e) 1kX SEM of NCA cathode at 1.0C. (f) 5kX SEM of NCA cathode at 1.0C. EDS mapping of each case is presented underneath, respectively.

harvested from MOT-1, MOT-2, MOT-3, and a pristine cell are summarized in Table 4. 20.55 and 39.42 wt% copper elements are quantified at 0.1C and 0.5C rates to prove a leading role of copper deposition in cathode performance decay. In contrast, no copper element is detected at a 1.0C rate, indicating no copper-based deposition is accumulated within the focused area of interest.

XPS characterizations on graphite anodes and NCA cathodes of MOT-1, MOT-2, and MOT-3 are delineated in Fig. 11 to help identify the chemical states evolutions of electrodepositions after overdischarge abuses at different C-rates. Fig. 11(a) shows the Cu $2p_{3/2}$ orbital

spectrum of the deposition on graphite anode harvested from MOT-1, operated at 0.1C. Two peaks centered at 932.8 and 933.1 eV could be decoupled, indicating a chemical state of metallic copper [51,52]. This interpretation matches the results in the left column of Fig. 9, where the EDS mapping reveals that the primary element of deposition is merely copper. Fig. 11(c) shows the Cu $2p_{3/2}$ orbital spectrum of the deposition on graphite anode harvested from MOT-2, operated at a 0.5C rate. Three peaks with centers of 932.7, 933.2, and 936.8 eV can be deconvoluted from the raw spectrum, suggesting mixed chemical states including metallic copper, copper (II) oxide, and copper (II) fluoride [53–55]. The

 Table 4

 Chemical elements quantifications: NCA cathodes from 3E cells after multi-level overdischarge-recharge tests at 0.1C, 0.5C, 1.0C, and a pristine cell.

C-rate	NCA Cathode (wt%)								
	Ni	Со	Al	С	0	F	Р	S	Cu
0.1C	11.02	25.57	0.84	21.82	14.08	5.27	0.50	0.34	20.55
0.5C	5.93	23.19	0.04	10.75	9.79	8.80	1.67	0.41	39.42
1.0C	7.68	28.91	0.36	32.96	23.92	5.75	0.32	0.10	-
Pristine	17.47	18.76	0.43	32.39	26.22	4.63	0.06	0.03	-



Fig. 11. XPS characterizations: graphite anodes and NCA cathodes of 3E cells after multi-level overdischarge-recharge tests. (a) Cu $2p_{3/2}$ orbital spectrum of graphite anode at 0.1C. (b) Cu $2p_{3/2}$ orbital spectrum of NCA cathode at 0.1C. (c) Cu $2p_{3/2}$ orbital spectrum of graphite anode at 0.5C. (d) Cu $2p_{3/2}$ orbital spectrum of NCA cathode at 0.1C. (c) Cu $2p_{3/2}$ orbital spectrum of graphite anode at 0.5C. (d) Cu $2p_{3/2}$ orbital spectrum of NCA cathode at 0.1C. (f) O 1s orbital spectrum of graphite anode at 1.0C. The red and blue outlines in each figure delineate raw data and enveloped data after peak fitting, respectively. Rel. CPS means relative counts per second to indicate the signal magnitude.

determination of these chemical compounds is strongly supported by results in the middle column of Fig. 9, where the EDS mapping shows that fluorine and oxygen are also dominant elements to form the deposition layer besides copper. Figs. 11(e),(f), S15(a) and (b) describe the Li 1s, O 1s, C 1s, and F 1s orbital spectra of the deposition on graphite anode harvested from MOT-3, operated at a 1.0C rate, to significantly highlight the states transition of depositions with an increase of C-rate. Specifically, three peaks centered at 284.8 eV (calibrated), 286.5 eV, and 289.2 eV are observed in the C 1 s spectrum to represent chemical bonds of C—C, C—O, and C=O [56], respectively. Three peaks centered at 52.71, 55.32, and 58.19 eV can be observed in the Li 1s spectrum, and the one at 55.32 eV is believed to be metallic lithium [57]. Three peaks centered at 685.0, 687.0, and 689.1 eV can be observed in the F 1s spectrum, proving the existence of lithium fluoride and an organic fluoride with a similar molecular structure to polyvinylidene fluoride [58,59] on the surface of deposition. Three peaks centered at 531.5, 532.9, and 535.5 eV can be deciphered from the O 1s spectrum, representing lithium carbonate, organic O—C, and O—F chemical bonds [60], respectively. These analyzes consolidate our previous discussion that the formation of lithium deposition is a leading side reaction on the graphite anode after overdischarge cycling at a high C-rate, and the chemical states of lithium deposition comprise metallic lithium, lithium fluoride, and lithium carbonate. The determination of these chemical species also matches the right column of Fig. 9, where the EDS mapping illustrates that fluorine, carbon, and oxygen are prominent elements on the lithium deposition layer.

Fig. 11(b) illustrates the Cu $2p_{3/2}$ orbital spectrum of the deposition on NCA cathode harvested from MOT-1, operated at 0.1C. Two peaks centered at 933.1 and 935.6 eV can be identified. The one at 933.1 eV suggests metallic copper [52], indicating the same chemical state as that on graphite anode from MOT-1. Figs. 11(d) and S15(c) present Cu $2p_{3/2}$ and O 1s orbital spectra of the deposition on NCA cathode harvested from MOT-2, operated at 0.5C. In particular, two peaks centered at 933.1 eV and 936.8 eV can be factored in the Cu $2p_{3/2}$ spectrum to stand for the metallic copper and copper (II) fluoride [55]. Two peaks centered at 529.8 and 532.3 eV can be factored in the O 1s spectrum to stand for the copper (II) oxide and O=C chemical bonds [61]. The determination of metallic copper, copper (II) oxide, and copper (II) fluoride indicates that deposition layers on the NCA cathode and graphite anode harvested from MOT-2 share the same chemical species.

4. Conclusion

Li-ion pouch cell in a 3E format is a trusted approach to assess transient SOE and provide deep insights on cell degradation modes by deconvoluting the contribution and performance of each electrode. Two characteristic phases that accelerate cell failure are identified under extreme overdischarge abuse, including anode-centric degradation and cathode-anode degradation. The former indicates an exacerbated copper dissolution event, while the latter suggests a synergetic contribution of copper dissolution, CEI evolution, and electrolyte decomposition to the cell end-of-life.

The operating C-rate significantly impacts the degradation and safety performances of Li-ion batteries. Suppose the cell is under increasingly severe overdischarge cycles at a low C-rate. In that case, the anode potential will increase to the peak level with plenty of SEI breakdown, copper dissolution, and internal gas generation, indicating a series of anode-centric side reactions that causes rapid degeneration of cell SOH. Severe capacity loss is observed on the anode side with high impedance, and spherical copper nucleation dominates the microscopic deposition morphology on the graphite particle. The NCA cathode exhibited a moderate capacity loss and impedance rise in half-cell studies, mainly attributable to the blocking of active porous architecture caused by densely layered copper deposition formation.

Suppose the cell is under increasingly severe overdischarge cycles at a moderate C-rate. In that case, the cathode potential will decrease to a low level beyond the electrochemical stability window of carbonate electrolytes, suggesting a cathode-centric kinetic limitation that results in SOH decay due to CEI evolution and electrolyte decomposition. Severe capacity loss and impedance rise are observed on the NCA cathode with a growing copper deposition. Although copper dissolution played a significant role in the cell failure, the graphite anode keeps robust by showing high capacity retention and low impedance during half-cell analysis.

Suppose the cell is under increasingly severe overdischarge cycles at a high C-rate. In that case, the anode potential will drop below 0.0 V vs.

Li/Li⁺ during the charge phase, revealing the occurrence of unfavorable lithium plating due to the degeneration of graphite intercalation and diffusion limits. The maximum cell surface temperature is beyond the threshold of 60 °C, which approaches the critical temperature of self-exotherm and is sufficient to trigger the decomposition of the SEI layer and subsequent lithium dendrite reactions in contact with the electrolytes. Filament lithium plating with an offensive needle-like structure governs the microscopic deposition morphology on the graphite anode, which is likely to interact with the porous separator and pierce it to cause ISC and cell TR under high SOC. These hidden threats indicate that the electrochemical and thermal safety challenges of Li-ion batteries under overdischarge cycling abuses should never be underestimated and deserve more mechanistic study efforts to understand the fundamental degradation-safety interactions.

In summary, our study reveals that degradation mechanisms of Li-ion cells under increasingly severe overdischarge cycles are highly dependent on charge and discharge C-rates. Explicit anode-centric side reactions, including the early onset of SEI layer breakdown, copper dissolution, and the resulting internal gas generation, dictate the cell aging process at a low C-rate; However, implicit cathode-centric side reactions, such as CEI layer evolution, electrolyte decomposition, and the resulting capacity fade and impedance rise of the positive electrode, dominate the cell SOH decay when the C-rate increases to a moderate level; Furthermore, growing ISC risks and thermal safety hazards, featured by the invasive microstructures of lithium depositions on the graphite anode and the excessive temperature rise, become significant characteristics to accelerate the cell failure under a high C-rate. Therefore, a trade-off balance among each rate-dependent degradation mechanism is worth scrutinizing based on different situations of cell applications before adopting the optimal C-rate to minimize potential overdischarge-induced detriments.

CRediT authorship contribution statement

Hanwei Zhou: Conceptualization, Data curation, Methodology, Formal analysis, Writing – original draft. Conner Fear: Methodology, Formal analysis. Judith A. Jeevarajan: Conceptualization, Supervision, Writing – review & editing. Partha P. Mukherjee: Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ensm.2022.10.024.

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