

Thermal runaway mechanisms and early-warning strategy determination of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ batteries through material and cell levels analysis

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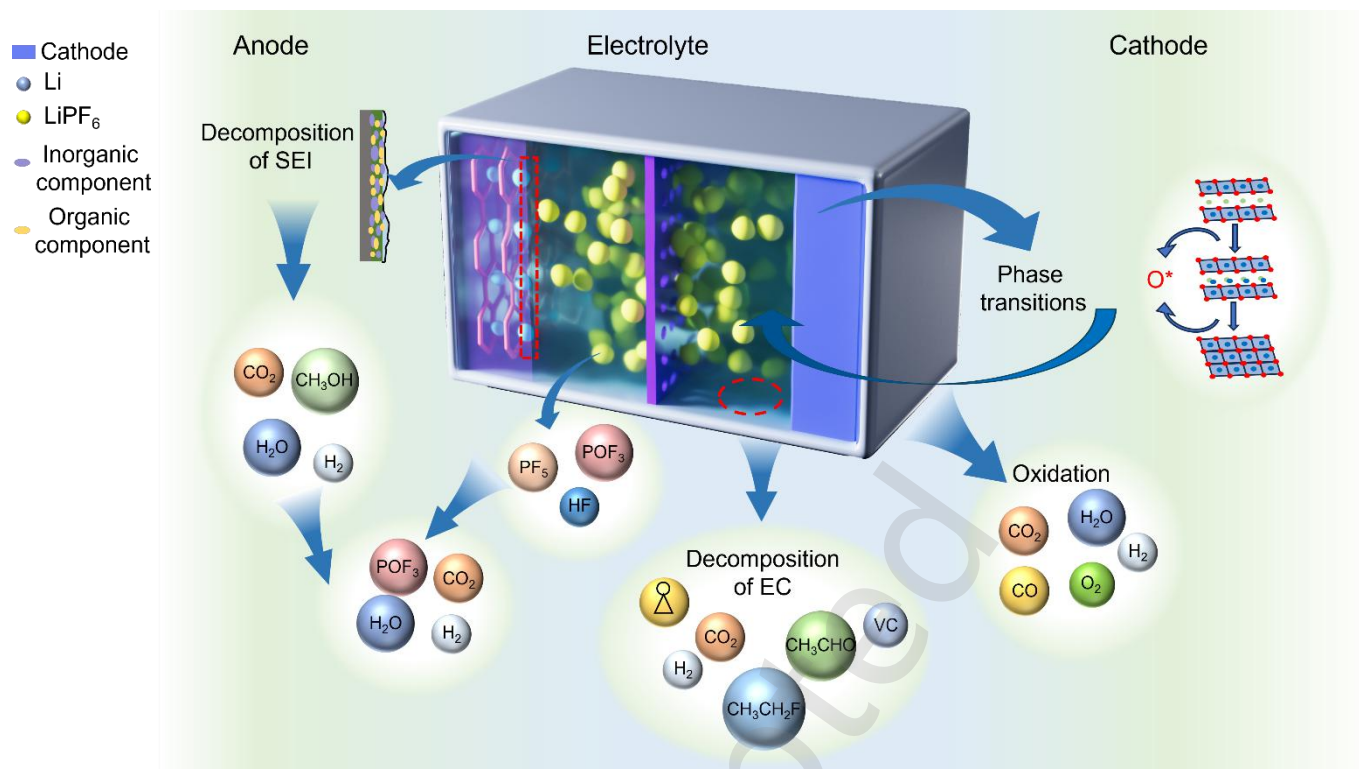
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Through integrated material and cell levels experiments, this work introduces a three-stage chain-reaction pathway termed initiation-acceleration-runaway in high-nickel NCM811 batteries for the first time and establishes a four-level early-warning strategy by correlating the revealed mechanisms with multidimensional signals.

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ABSTRACT: Thermal runaway (TR) remains the most critical safety challenge limiting the large-scale application of lithium-ion batteries. A comprehensive understanding of the internal chain reaction mechanisms and their correlation with external early-warning signals is urgently required. This study establishes a stepwise analytical framework from single component and binary/ternary mixtures to full cells to bridge the gap between material-level reaction mechanisms and cell-level signal features. TG-DSC-MS experiments on designed component combinations revealed the underlying reaction mechanisms. These mechanisms were correlated with the synchronous evolution of multidimensional signals, including temperature, expansion force, voltage, and the concentrations of five characteristic gases (H_2 , CO , CO_2 , HF , and VOCs), during cell-level overheating tests. Through this cross-scale correlation, a three-stage “initiation-acceleration-runaway” chain-reaction pathway is identified for the first time at material level and subsequently validated against cell-level signal evolution, clarifying the transition from internal chemistry to observable failure. Specifically, the initiation stage is driven by cathode/electrolyte interfacial reactions, while the acceleration stage is governed by EC ring-opening polymerization occurring in the presence of lithiated graphite, and the runaway stage is triggered by the uncontrolled oxidative reactions initiated by cathode oxygen release. The TR process is further divided into five consecutive stages with distinct critical signal thresholds. Based on this mechanism-signal correspondence, a four-level hierarchical early-warning strategy is established, enabling early detection up to 698 seconds before TR. This work offers a viable pathway for translating mechanistic insights into quantifiable warning indicators, thereby bridging the gap between mechanistic understanding and engineering application.

KEYWORDS: lithium-ion battery, thermal runaway, reaction mechanism, early-warning strategy, cross-scale correlation

1 Introduction

Lithium-ion batteries (LIBs) have emerged as the primary energy carriers in fields such as electric vehicles and energy storage systems[1, 2], owing to their high energy density, low self-discharge rate, and long cycle life[3–6]. However, safety remains a major bottleneck constraining their widespread application[7, 8]. Under thermal, electrical, or mechanical abuse conditions, a series of exothermic side reactions occur among the internal components, specifically the cathode, anode, electrolyte, and separator [9, 10]. The resulting heat and gases accumulate rapidly within the confined cell volume, leading to a sharp temperature rise that can escalate into fire or even explosion, a phenomenon known as thermal runaway (TR)[11, 12]. With the increasing demand for higher energy density, Ni-rich layered oxide cathodes, such as $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811), have been widely adopted[13]. While offering substantial energy-density advantages, these materials suffer from severe deterioration in thermal and structural stability as the Ni content increases, thereby exacerbating the risk of TR[14,

15]. Consequently, a comprehensive understanding of the TR mechanisms and the establishment of effective early-warning strategies have become urgent priorities in the pursuit of safe high-energy-density battery systems.

It is generally recognized that the evolution of TR involves a series of reactions, including the decomposition of the solid electrolyte interphase (SEI)[16], reactions between the lithiated anode and electrolyte[17], and redox between oxygen released from the cathode and electrolyte/anode[18]. However, for the NCM811 LIBs, the triggering sequence, heat release, and interplay among these reactions remain subjects of ongoing debate. In particular, the identity of the initial exothermic reaction and the dominant heat source have been central and persistently contentious issues. Specifically, these refer to what triggers the cascade and what drives the acceleration.

To address these scientific questions, current research has largely followed two distinct pathways. The first pathway adopts a material-level deconstruction approach[19, 20]. Extensive studies have systematically investigated the thermal decomposition behavior of single component and binary/ternary

mixtures using techniques such as differential scanning calorimetry (DSC), thermogravimetry-mass spectrometry (TG-MS), and in situ X-ray diffraction (XRD). These investigations have revealed the intrinsic thermal stability of individual materials and the exothermic characteristics of their interactive reactions. Li et al.[21] employed DSC to examine the thermal behavior of individual components (cathode, anode) and their combinations (cathode + electrolyte, cathode + electrolyte + anode) in NCM811 cells, observing a sharp exothermic peak at approximately 215 °C for the cathode + electrolyte combination. Using in situ XRD and Transmission Electron Microscope (TEM) characterization, they identified the exothermic reaction between the highly reactive oxygen species (O^- , O_2^- , O_2^{2-} , collectively denoted as O^*) released from the charged cathode and the electrolyte as the trigger factor for TR. Further work by Hou et al.[22] quantitatively revealed two pathways for the oxygen released from the NCM811 cathode. Approximately 41% of the released oxygen reacted with ethylene carbonate (EC) at the cathode/electrolyte interface, serving as the triggering reaction, while the remainder diffused to the lithiated anode and contributes approximately 65% of the total heat release, acting as the primary heat source during TR. In a more systematic study, Kim et al.[23] designed a comprehensive matrix of experiments involving Ca, An, Ele, Sep, and their combinations in NCM811 cells, through which they thoroughly characterized the thermal behavior and gas generation characteristics utilizing DSC and TG-MS. Their findings indicated that the SEI on the anode began to decompose at approximately 130 °C, serving as the initial inducement, while the structural transition of the cathode above 220 °C released oxygen and triggered cascading exothermic reactions that ultimately lead to TR. The second pathway operates at the cell level[24]. Researchers have employed commercial or fabricated full cells using accelerating rate calorimetry (ARC) or combustion chambers to characterize TR features, including trigger temperature, temperature rise rate, gas evolution products, and thermal propagation behavior. Based on ARC tests, a TR evaluation framework centered on three characteristic temperatures has been established[25, 26]: T_1 (the self-heating onset temperature), T_2 (the TR trigger temperature), and T_3 (the maximum temperature). Furthermore, preliminary correlations between these characteristic temperatures and internal reaction processes have been established. T_1 is generally associated with SEI decomposition[9], T_2 is typically triggered by internal short circuits (ISC), by reactions between cathode-released oxygen and electrolyte, or by reactions between the lithiated anode and electrolyte[27], while T_3 correlates with the total heat release throughout the TR process[10].

However, both pathways have inherent limitations. Material-level studies have elucidated the intrinsic reaction characteristics of internal components but fail to account for the synergistic and competitive mechanisms among components in real cells. Conversely, cell-level investigations, in which internal reactions overlap temporally and thermally, cannot directly resolve the chronological sequence or reaction priorities based solely on macroscopic features. Notably, a few studies have begun to bridge these two levels. Jiang et al.[28] conducted a comparative investigation of TR characteristics and phase transition behavior at both material and cell levels for NCM batteries with varying nickel contents (Ni = 60%, 80%, and 90%)

using DSC and ARC. Their results revealed that TR in Ni = 60% cells occurred after cathode phase transition, whereas in Ni = 80% or 90% cells, it occurred prior to phase transition. On this basis, they proposed that TR in high-nickel LIBs (Ni $\geq$ 80%) is dominated by exothermic cathode/electrolyte interfacial reactions, while in low-nickel systems (Ni $\leq$ 60%), it is governed by phase-transition-induced oxygen release and subsequent oxidation reactions. However, such studies remain confined to specific material combinations and comparative analyses, without establishing a complete stepwise analytical chain from single component to mixed systems and ultimately to full cells. In particular, the correlation between material-level reaction sequences and cell-level multidimensional signals remains elusive, making it difficult to systematically unravel the true contributions and interaction mechanisms of individual components throughout the TR process.

In the early-warning research, monitoring dimensions have expanded from traditional parameters[29, 30] such as voltage and temperature to multidimensional physical signals[31–34] including gas, expansion force and acoustic signals, with hierarchical warning strategies proposed based on signal evolution patterns. Zhang et al.[35] simultaneously monitored the temperature, expansion force, voltage, and mass loss of NCM811 pouch cells, revealing the evolution patterns of casing expansion force and temperature. They quantified the advance warning times provided by the change rates of expansion force ($dF/dt \geq 0.5$ N/s) and temperature ($dT/dt \geq 0.1$ °C/s) relative to TR onset, and accordingly constructed a four-level hierarchical early-warning framework capable of progressively identifying risks. Li et al.[36] conducted a comparative study on the temporal evolution characteristics of expansion force, temperature, voltage, and gas evolution signals in NCM (Ni = 50%, 60%, and 80%) and LiFePO₄ batteries under overheating and overcharging conditions. They found that expansion force anomaly ($dF/dt \geq 5$ N/s) preceded gas, voltage, and temperature signals, serving as an effective early-warning indicator. Based on expansion force anomaly, cell venting, and ISC, they proposed a hierarchical warning strategy through multidimensional signal fusion, achieving a maximum warning time of 677 seconds. However, existing early-warning strategies commonly exhibit a decoupling between the underlying mechanisms and the observed signals. The TR mechanisms of NCM batteries have yet to be translated into quantifiable early-warning indicators, leaving most parameter thresholds derived from statistical patterns rather than established correlations with specific internal reaction stages.

To address the aforementioned challenges in mechanistic understanding and early-warning prediction, this study focuses on NCM811/graphite batteries and establishes a progressive thermal analysis chain extending from single component and binary/ternary mixtures to full cells. At the material level, comparative Thermogravimetry analysis-differential scanning calorimetry-mass spectrometer (TG-DSC-MS) tests experiments are conducted to elucidate the reaction sequences and gas evolution products associated with each component combination. At the cell level, the temporal evolution of multidimensional signals during TR, including surface temperature, expansion force, voltage, and characteristic gas concentrations, is correlated with the internal reaction mechanisms identified at the material level. Finally, based on the established

mechanism-signal correspondence, a hierarchical early-warning strategy is developed. Through cross-scale temporal alignment, this progressive analytical framework enables mechanistic insights derived from material-level analyses to directly inform the quantification of early-warning indicators at the cell level. Accordingly, it offers a viable pathway to bridge the gap between intrinsic reaction mechanisms and observable signals.

2 Experimental

Table 1 The detailed information about cells

Parameters	Coin cells	Pouch cells
Size (mm)	20 (diameter) × 3.2 (thickness)	190 (length) × 84 (width) × 8.5 (thickness)
Cathode	Single-crystal NCM811, super P, polyvinylidene fluoride (PVDF)	
Anode	Graphite, super P, sodium carboxymethyl cellulose (CMC), styrene-butadiene rubber latex (SBR)	
Electrolyte	1.0 M LiPF ₆ ethylene carbonate (EC) / dimethyl carbonate (DMC) (1:1 vol)	
Separator	Polyethylene (PE)/ceramic	

2.2 Material level experiments

2.2.1 Sampling for reaction analysis

The fully charged coin cells were disassembled within an argon-filled glove box to obtain delithiated cathode and lithiated anode, which were then immersed in DMC and soaked overnight to remove residual lithium salts and solvents from the electrode surfaces[23]. Subsequently, the electrodes were dried in the glove box for 2 h to eliminate any remaining DMC.

2.2.2 TG-DSC-MS

Table 2 TG-DSC-MS tests samples (Electrolyte: Ele, Cathode: Ca, Anode: An)

Sample No.	Composition	Loading Ratio
1	Ele	27 μ L
2	Ca	9 mg
3	An	9 mg
4	Ca + Ele	9 mg + 27 μ L
5	An + Ele	9 mg + 27 μ L
6	Ca + An	9 mg + 9 mg
7	Ca + An + Ele	4.5 mg + 4.5 mg + 27 μ L

2.2.3 X-ray diffraction (XRD)

XRD measurements were carried out using a Bruker D8ADVANCE diffractometer with Cu K α radiation. The dried cathode electrodes, with pretreatment temperatures of 25 $^{\circ}$ C, 205 $^{\circ}$ C, and 355 $^{\circ}$ C for the Ca and 25 $^{\circ}$ C, 235 $^{\circ}$ C, and 330 $^{\circ}$ C for the Ca + Ele, were sealed with polyimide film to prevent air exposure. XRD scans were then performed over a 2θ range of 10 $^{\circ}$ to 90 $^{\circ}$ at a rate of 10 $^{\circ}$ /min.

2.2.4 X-ray photoelectron spectroscopy (XPS)

XPS analysis of the anode surface was performed on a PHI 5000 Versa Probe III system (ULVAC- PHI). The dried graphite anode electrode was mounted using conductive carbon tape. All spectra were calibrated against the C 1s peak at 284.8 eV, with charge compensation applied. Survey scans were recorded at a pass energy of 280 eV to identify the primary surface elements, followed by high-resolution narrow scans for Li, P, C, O, and F at a pass energy of 69 eV.

2.1 Cell preparation

Coin cells and 15 Ah pouch cells of NCM811 were selected for material-level and cell-level tests, respectively. Their detailed specifications are listed in Table 1. All cells were charged to 100% state of charge (SOC) under a constant current-constant voltage (CC-CV) mode. The CC phase was performed at a 1 C rate with a cutoff voltage of 4.2 V, after which the voltage was held constant until the current decayed to 0.05 C.

TG-DSC-MS tests were performed using a NETZSCH STA449C-DSC214-QMS403C system. The cell components (Table 2), including the cathode and anode materials scraped from electrodes, were loaded into 100 μ L gold-plated crucibles. To mimic the internal stacking of a real cell, the components were arranged in a layered structure and sealed with a disc featuring a 15 μ m vent hole. Measurements were conducted under argon flow (40 mL/min) from room temperature to 500 $^{\circ}$ C at a heating rate of 2 $^{\circ}$ C/min.

2.3 Cell level experiments

2.3.1 Experimental setup for cell-level overheating abuse tests

TR tests were conducted in a custom 1 m³ explosion-proof chamber (Fig. 1). A 100 W electric heater, dimensionally matched to the cell surface, was employed to trigger TR under side-heating conditions. The cell was clamped between two 20 mm-thick mica plates for thermal insulation, with a flat-plate force sensor integrated into the clamping fixture to record the expansion force during TR (Fig. 1(b)).

The gas released during TR was sampled via an inlet positioned 5 cm above the cell and directed to a detection chamber housing sensors for H₂, CO, CO₂, HF, and VOCs, before being recirculated. Three K-type thermocouples were attached to the cell surface at the tab (T_1), geometric center (T_2), and bottom (T_3), with an additional thermocouple (T_0) monitoring the heater temperature (Fig. 1(c)). Cell voltage was recorded by a NEWARE battery tester. The entire process was recorded by a high-resolution camera through the chamber's explosion-proof window.

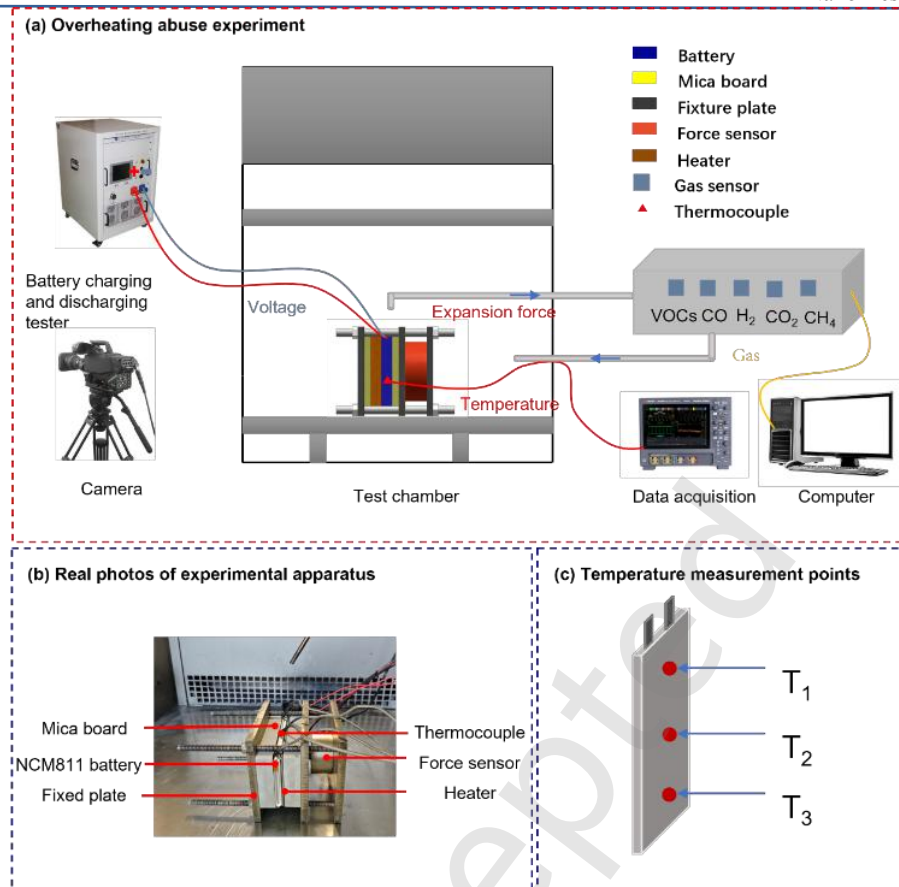


Figure 1 Experimental setup. (a) Schematic illustration of overheating abuse experiment. (b) Real photos of experimental apparatus. (c) Temperature measurement points.

2.3.2 Key devices and measurement parameters

Potential uncertainties in the test results primarily stem from manufacturing tolerances of the heater, the cell and the mica

plates, as well as manual assembly variations in sensor positioning. The key devices and their parameters are summarized in Table 3.

Table 3 Devices and parameters utilized in the experiment

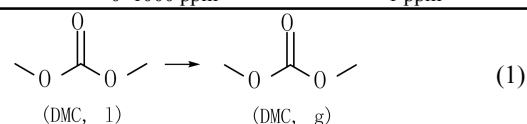
Device	Model	Range	Accuracy
Battery charging and discharging tester	NEWARE CT-4004-60V20A-NA		
Thermocouple	KPS-FB-BP-K	0–1300 °C	0.1 °C
Force sensor	DYLF-102	0–2000 N	0.01 N
VOCs sensor	StoxPlus-TVOC-1%-SEC-01	0–10000 ppm	1 ppm
CO ₂ sensor	StoxPlus-CO ₂ -5%-SEC-01	0–50000 ppm	10 ppm
CO sensor	StoxPlus-CO-1000-SEC-01	0–1000 ppm	1 ppm
H ₂ sensor	StoxPlus-H ₂ -2%-SEC-01	0–20000 ppm	10 ppm
HF sensor	StoxPlus-HF-1000-SEC-01	0–1000 ppm	1 ppm

3 Results and Discussion

3.1 Investigation of TR mechanisms based on material level

3.1.1 Electrolyte reaction mechanisms

As illustrated in Fig. 2(a), the heat flow and thermogravimetric changes of the electrolyte can be broadly divided into two stages. In the first stage, the DSC curve exhibits an endothermic peak at approximately 114.4 °C accompanied by a significant mass loss of 35.3%, which corresponds to the volatilization of the low-boiling-point solvent DMC (Eq. (1)). The mass spectrum of the released gas matches the standard reference spectrum of DMC, as shown in Fig. 2(b). This process is also one of the primary sources of gas released in the early stage of TR.



The second stage shows a strong endothermic peak accompanied by a substantial mass loss of 60.2% at 267.8 °C, characterized by multiple simultaneous reactions. First, Fig. 2(c) confirms the evaporation of the EC solvent at this stage (Eq. (2)). Meanwhile, LiPF₆ undergoes thermal decomposition (Eq. (3)), with the characteristic mass spectrum of the resulting PF₅ shown in Fig. 2(d). PF₅ rapidly reacts with trace H₂O present in the system (Eq. (4)), producing POF₃ and HF (Fig. 2(e)). As strong Lewis acids, both PF₅ and HF significantly catalyze the decomposition of the EC solvent (Eqs. (5)–(8)) [37–39], yielding products such as CO₂, CH₃CH₂F, CH₃CHO, ethylene oxide, H₂, and vinylene carbonate (VC), as evidenced by the characteristic MS signals in Figs. 2(f)–2(j). Although the catalyzed

ring-opening reactions are exothermic, the large-scale volatilization of EC absorbs significant heat, resulting in an overall endothermic state for this stage.

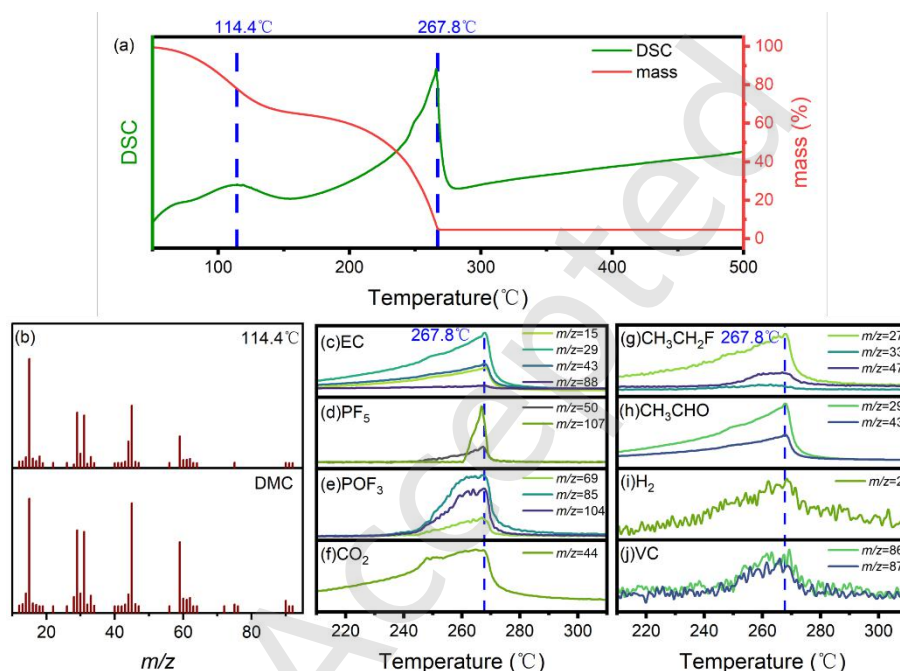
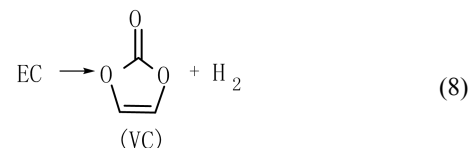
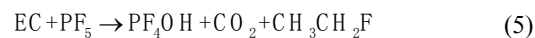
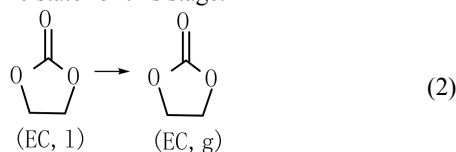


Figure 2 TG-DSC-MS results of the Ele with a scanning rate of 2 °C/min. (a) Heat flow and weight loss. (b) Comparison of the experimental and standard spectrum of DMC. (c)–(j) MS signals of EC, PF₅, POF₃, CO₂, CH₃CH₂F, CH₃CHO, H₂, and VC.

3.1.2 Cathode system reaction mechanisms

Thermal analysis of the Ca indicates that its decomposition process primarily involves two stages of phase transformation accompanied by gas release. The DSC curve shows two exothermic peaks (Fig. 3(a)). The first peak at 202.6 °C, located between 170.0 °C and 220.0 °C, corresponds to the transformation of the NCM cathode from layered structure (R $\bar{3}$ m) to spinel structure (Fd $\bar{3}$ m) (Eq. (9))[22, 40]. The second exothermic peak at 353.9 °C, observed between 320.0 °C and 376.0 °C, is associated with the further transition from the disordered Fd $\bar{3}$ m to rock-salt phase (Fm $\bar{3}$ m) (Eq. (10))[40]. The XRD results in Fig. S1 in the Electronic Supplementary Material (ESM), obtained at different temperatures, confirm that the layered-spinel-rock salt transformation occurs at specific temperatures identified in the TG-DSC-MS analysis.

TG and MS analyses reveal that the phase transition process is accompanied by continuous mass loss of 19.2% and steady release of O₂ (Fig. 3(b)), consistent with previous reports [41]. In addition, the release of CO₂ (Fig. 3(c)) begins at approximately 200.0 °C and reaches its maximum at 353.9 °C. This may be attributed to oxidation reactions between conductive carbon and the active oxygen species released from the cathode (Eq. (11)), providing further evidence for the

generation of O* during the phase transition process[42].

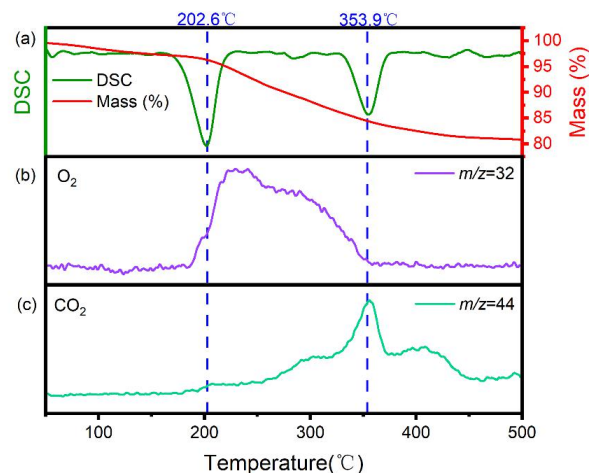
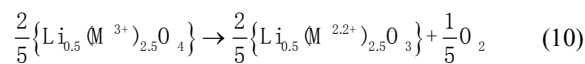
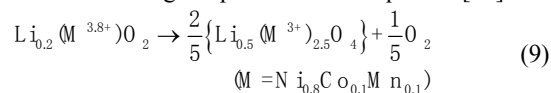


Figure 3 TG-DSC-MS results of the Ca with a scanning rate of 2 °C/min. (a) Heat flow and weight loss. (b)–(c) MS signals of O₂ and CO₂.

The phase transitions and gas release behaviors revealed by thermal analysis are fundamentally rooted in the structural destabilization and ionic migration within the cathode material upon heating, as illustrated in Fig. 4. At ambient temperature, NCM exhibits a layered structure of hexagonal crystal, which belongs to the R $\bar{3}$ m space group. Li⁺ occupies the octahedral 3a site, transition metal ions (TM = Ni, Co, Mn) occupy the octahedral 3b site. Upon heating, a portion of the TM ions, primarily the highly active Ni⁴⁺, migrate into the Li layers via octahedral interstices. During this migration process, Ni⁴⁺ is rapidly reduced to Ni²⁺ by accepting electrons. To maintain charge balance, adjacent lattice oxygen (O²⁻) is forced to lose electrons, forming O*. This charge compensation mechanism triggers structural rearrangements, leading to the transformation into Fd $\bar{3}$ m. As the temperature increases further, additional TM ions, such as Co³⁺, continue to migrate, resulting in the sustained generation of O*. This leads to complete collapse of the structure, resulting in the formation of the Fm $\bar{3}$ m. A portion of the O* reacts with conductive carbon to produce CO₂ (Eq. (11)), while the remainder combines to form O₂, which is released from the material.

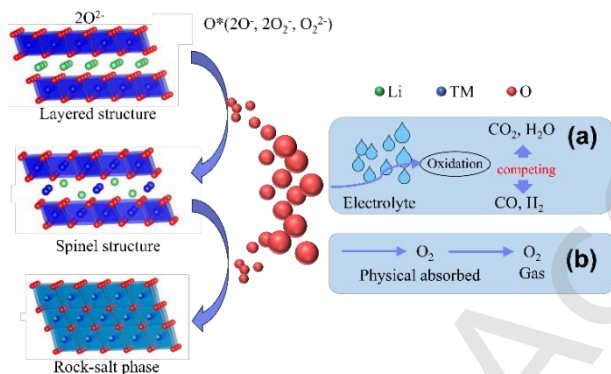
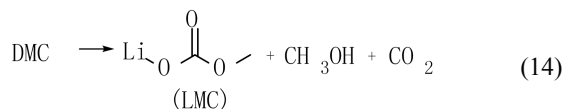
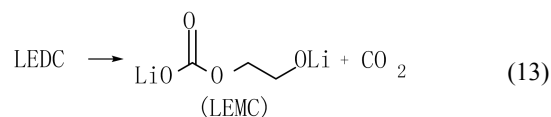
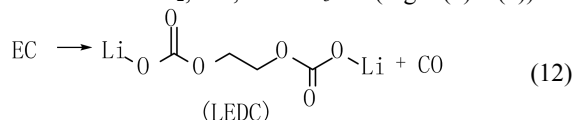


Figure 4 The phase transition process and O* migration processes.

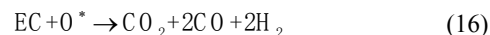
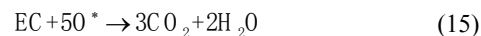
The TG-DSC-MS results of the Ca + Ele are presented in Fig. 5(a). Compared with the Ca, the introduction of the electrolyte significantly alters the thermal behavior of the system and triggers a series of complex reactions.

Near 92.0 °C, a distinct exothermic peak appears in the DSC curve, accompanied by a mass loss of approximately 3.8% (Fig. 5(a)). Mass spectrometry analysis indicates that the primary process during this stage is the volatilization of DMC (Fig. S2(a) in the ESM). In the presence of highly reactive TM⁴⁺ species (e.g., Ni⁴⁺, Co⁴⁺), carbonate-based electrolytes (e.g., EC, DMC) decomposing on the cathode surface constitutes an essential part of the exothermic chain reactions occurring at elevated temperatures (Eqs. (12)–(14)). The cathode/electrolyte interfacial reactions lead to the formation of lithium ethylene dicarbonate (LEDC), lithium ethylene monocarbonate (LEMC), and lithium methyl carbonate (LMC), as well as gaseous

byproducts such as CO₂, CO, and CH₃OH (Fig. 5(b)–5(d)).



Near 234.7 °C, a sharp endothermic peak appears in the DSC curve, corresponding to a mass loss of 31.5%. During this stage, multiple reactions are coupled together. First, the EC solvent experiences substantial volatilization (Eq. (2), Fig. S2(b) in the ESM), and this pronounced endothermic process governs the thermal effects observed during this phase. Meanwhile, in accordance with the Ele, EC undergoes ring-opening decomposition at elevated temperature (Eqs. (5)–(8), Figs. S2(c)–S2(g) in the ESM). Second, the cathode material begins to transform from R $\bar{3}$ m to Fd $\bar{3}$ m (Eq. (9)), releasing a large quantity of O*. As O* carries less negative charge than O²⁻, it exhibits higher reactivity than conventional lattice oxygen[43]. The subsequent reaction pathways of O* mainly consist of two competing pathways: (i) O* can undergo intense redox reactions with the electrolyte components (Eqs. (15)–(16), Fig. 5(e)–5(h)). The reactions are competitive, and the competitive intensity between the two pathways depends on the local concentration of O*[18], corresponding to the path in Fig. 4(a). (ii) O* can combine with each other to form O₂ (Fig. 5(i)), and this process corresponds to the path in Fig. 4(b). It is noteworthy that in the experiments, the release signal of O₂ is observed later than that of CO₂ (Fig. S3 in the ESM), since O₂ is retained on the material surface through physical adsorption, its release requires a higher temperature[43]. Third, decomposition of LiPF₆ occurs around 234.7 °C (Eqs. (3) and (4)), and the mass spectrum signals of its decomposition products (PF₅ and PO₂F₃) are detected (Figs. S2(h) and S2(i) in the ESM). As the temperature further increased to approximately 331.0 °C, a weak O₂ signal is again detected (Fig. S2(k) in the ESM). This corresponds to the further phase transition of the cathode material from Fd $\bar{3}$ m to Fm $\bar{3}$ m (Eq. (10)), as confirmed by XRD patterns which demonstrate the completion of the structural transformation at this stage (Fig. S4 in the ESM).



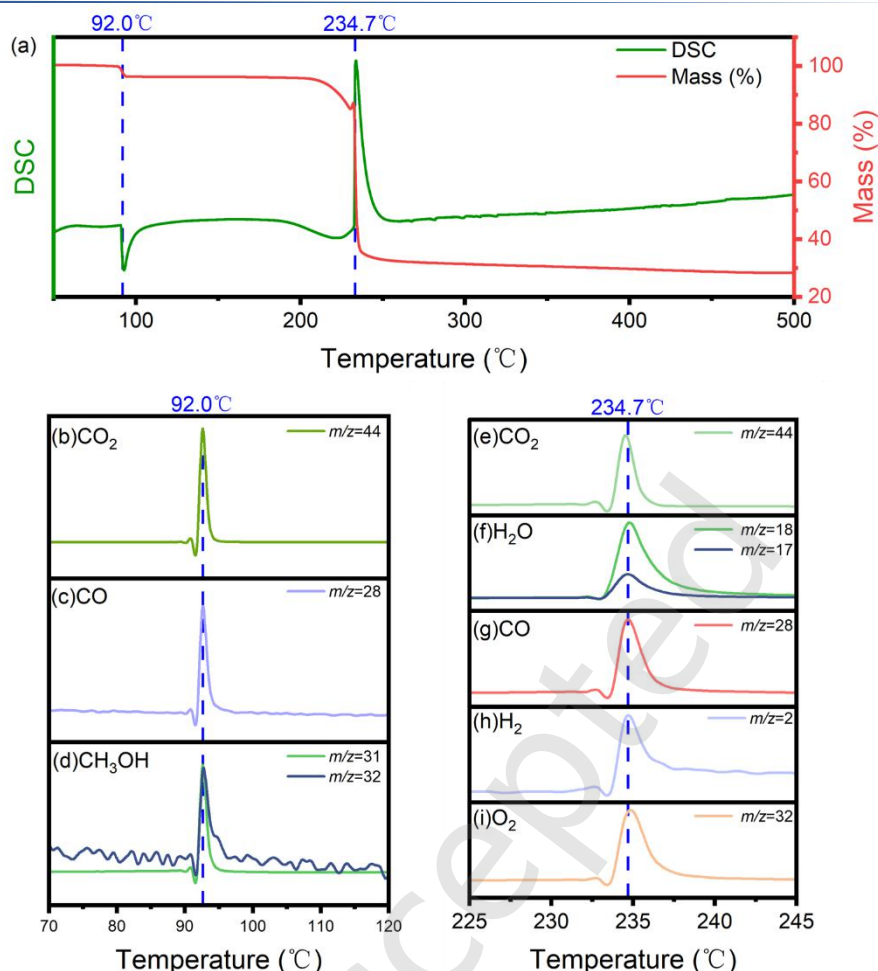


Figure 5 TG-DSC-MS results of the Ca + Ele with a scanning rate of 2 °C/min. (a) Heat flow and weight loss. (b)–(d) MS signals of CO₂, CO, and CH₃OH at 92.0 °C. (e)–(i) MS signals of CO₂, H₂O, CO, H₂, and O₂ at 234.7 °C.

3.1.3 Anode system reaction mechanisms

XPS was employed to probe the chemical composition of the SEI on the surface of the graphite anode. The full spectrum (0–1200 eV) confirms the presence of C, O, F, and Li (Fig. 6(a)), while high-resolution spectra reveal the typical organic-inorganic bilayer structure of the SEI (Figs. 6(b)–6(e)) [44, 45]. The inorganic layer is identified to comprise Li₂CO₃ [46], LiF [16], and Li₂O [47]. Specifically, Li₂CO₃ is evidenced by the C 1s peak at 290.2 eV, the O 1s peak at 532.1 eV, and the Li 1s peak at 53.8 eV. LiF is confirmed by the F 1s peak at 685.1 eV and the corresponding Li⁺ signal at 54.6 eV in the Li 1s spectrum. The presence of Li₂O is supported by the O 1s peak at 528.7 eV (O²⁻) and the associated Li⁺ peak at 52.7 eV. The organic layer consists of organo-oxygenated lithium salts (e.g., ROLi, ROCO₂Li) [48]. The characteristic peaks of

C-C and C-H bonds originate from the graphite substrate and alkyl-based constituents. Species containing C-O bonds are indicated by the peak at 286.0 eV in the C 1s spectrum, along with the organic oxygen signal at 530.9 eV in the O 1s spectrum. This composition aligns well with the expected decomposition products of the LiPF₆ DMC/EC electrolyte system, including LEDC, LMC, and lithium methoxide (CH₃OLi) [49]. It should be noted that lithium hydride (LiH), a SEI component reported in previous studies [50, 51], could not be definitively identified by XPS in the present work. This is primarily attributed to two limitations of XPS: (i) the characteristic Li 1s signal of LiH substantially overlaps with those of LiF and other lithium-containing species, and (ii) XPS is intrinsically insensitive to hydrogen, precluding direct detection of the H 1s signal.

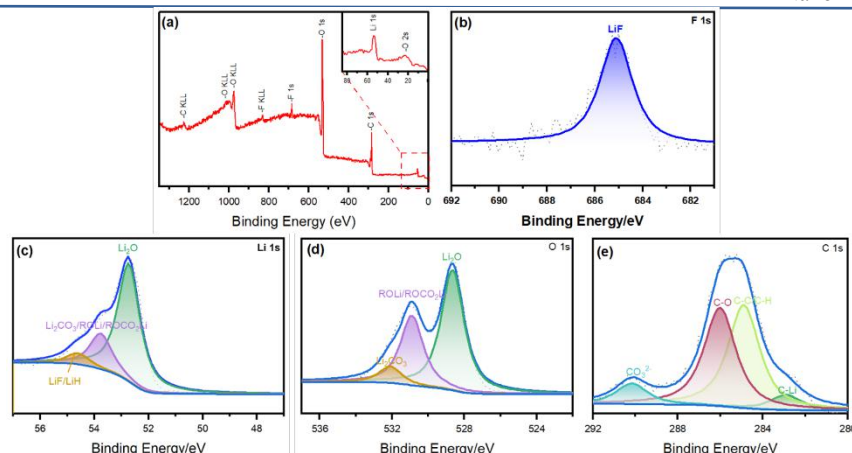
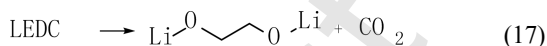


Figure 6 XPS spectra of the SEI on the surface of the anode. (a) Full spectrum. (b)–(e) Spectrum of F 1s, Li 1s, O 1s, and C 1s.

Even in the absence of corrosive byproducts from the electrolyte, the SEI, particularly its organic components, is susceptible to thermal decomposition. As shown in Fig. 7(b), an initial signal peak for CO_2 emerges around 138.9 °C, indicating the decomposition of the organic components such as LEDC and LMC. Since no C_2H_4 signals ($m/z = 26, 27$, and 28) are detected, the commonly reported decomposition pathway[52, 53] yielding C_2H_4 and CO_2 is not dominant in this system. Instead, the primary reaction route involves the generation of CO_2 , as described by Eqs. (17) and (18). Concurrently, the aqueous binders CMC and SBR undergo physical water desorption (Fig. 7(d)). Given the high moisture sensitivity of alkyl lithium carbonates, hydrolysis reactions of LEDC and LMC take place (Eqs. (19) and (20)), further contributing to gas evolution. Additionally, the thermal degradation of LiH (Eq. (21)) is proposed to account for the partial release of H_2 (Fig. 7(c)), indirectly corroborating the presence of LiH inferred from the XPS analysis. Despite these gas generation reactions, the DSC curve in Fig. 7(a) exhibits no discernible exothermic peak. This observation, consistent with previous studies[54, 55], is likely attributed to the low absolute mass of the SEI, which generates heat flow below the detection limit of the instrument.



The signal peak at $m/z = 2$ exhibits significant enhancement at temperatures exceeding 231.7 °C (Fig. 7(c)), which may indicate the reaction between CMC binder and lithium intercalated in the anode, accompanied by the generation of H_2 (Eq. (22))[56–58]. As the temperature further increases beyond 340.0 °C, CMC undergoes continuous decomposition (Eq. (23)), releasing CO_2 (Fig. 7(b)) and H_2O (Fig. 7(d))[59, 60].

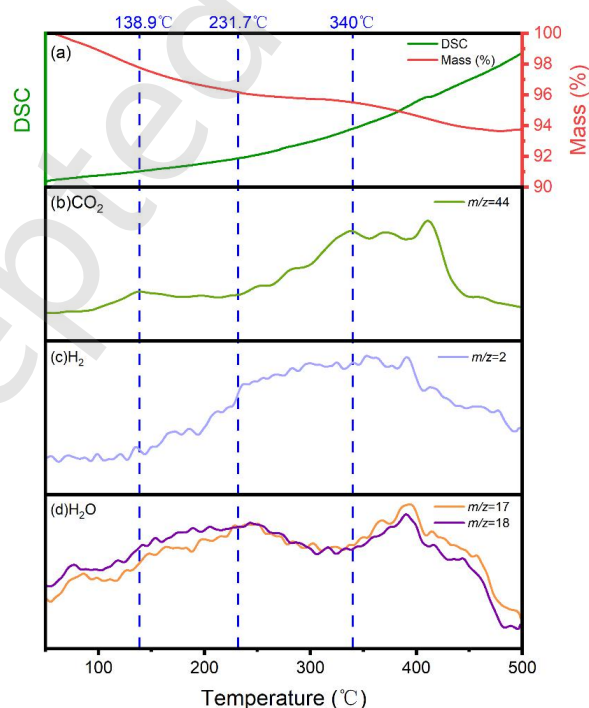
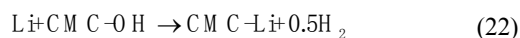
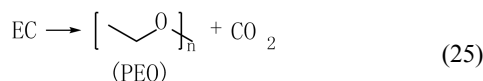


Figure 7 TG-DSC-MS results of the An with a scanning rate of 2 °C/min. (a) Heat flow and weight loss; (b)–(d) MS signals of CO_2 , H_2 , and H_2O .

Compared with the Ele and the An, the heat flow and mass change of the An + Ele are more complex, as shown in Fig. 8(a), and can be approximately divided into three stages. In the first stage, a broad endothermic peak appears at approximately 127.3 °C, accompanied by a significant mass loss of 26.7%. Consistent with the changes observed in the Ele and the An within this temperature range, this stage primarily involves the volatilization of DMC (Eq. (1), Fig. S5(a) in the ESM), the decomposition and hydrolysis reactions of the SEI (Eqs. (17)–(21), Figs. S6(a) and S6(b) in the ESM), and the physical desorption of water from CMC and SBR (Fig. S6(c) in the ESM).

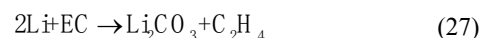
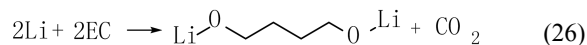
In the second stage, the DSC curve reveals an exothermic peak at 202.7 °C, accompanied by a relatively small mass loss of approximately 4.6%. Compared with the Ele, LiPF_6 decomposition (Eqs. (3) and (4)) occurs at a significantly reduced temperature, about 65 °C lower, as evidenced by the earlier evolution of POF_3 signals in Fig. 8(c). This catalytic effect may be attributed to the electron-donating effect of lithiated graphite and interfacial adsorption, which collectively

lower the activation energy for the decomposition of LiPF_6 . As a strong Lewis acid, PF_5 subsequently reacts with inorganic SEI components such as Li_2CO_3 (Eq. (24), Figs. 8(b) and 8(c))[9], while simultaneously catalyzing the ring-opening polymerization of EC to form PEO (Eq. (25), Fig. 8(b)) and other polymeric species, accompanied by the release of CO_2 . Notably, neither the Ele nor the Ca + Ele exhibits significant exothermic reactions in this temperature range. The absence of substantial mass loss or detectable gas evolution suggests that the observed strong exothermic peak is attributed to the polymerization of the solvent EC occurring in the presence of the lithiated graphite. However, due to limitations in characterization techniques employed in this study, the specific reaction equation remains to be elucidated, warranting further investigation.



The third stage is marked by an endothermic peak at approximately 271.9°C , together with a notable mass loss of 36.7%. Consistent with the changes observed in the Ele and the An within this temperature range, this stage primarily involves

volatilization of the solvent EC (Eq. (2), Fig. S5(b) in the ESM), thermal decomposition of EC (Eqs. (5)–(8), Figs. S5(c)–S5(g) in the ESM), and decomposition of CMC (Eqs. (22) and (23), Figs. S6(d)–S6(e) in the ESM). The decomposition of the SEI creates vacancies on the anode surface. In the presence of the electrolyte, the exposed lithiated graphite further reduces EC, leading to the formation of Li_2CO_3 and other compounds (Eqs. (26) and (27)). This process is accompanied by the release of gases such as CO_2 and C_2H_4 , as confirmed by MS signals in Figs. 8(d) and 8(e).



The primary reactions of the An and the An + Ele encompass three categories: the SEI decomposition, reactions between the lithiated anode and the electrolyte, and the binder decomposition. Compared with the barely detectable heat flow observed in the An, the introduction of the electrolyte significantly intensifies the exothermic heat flow of the An + Ele. This observation strongly supports the well-established consensus that the reactions between the lithiated graphite anode and the electrolyte constitute a critical internal trigger for TR in LIBs[9, 54].

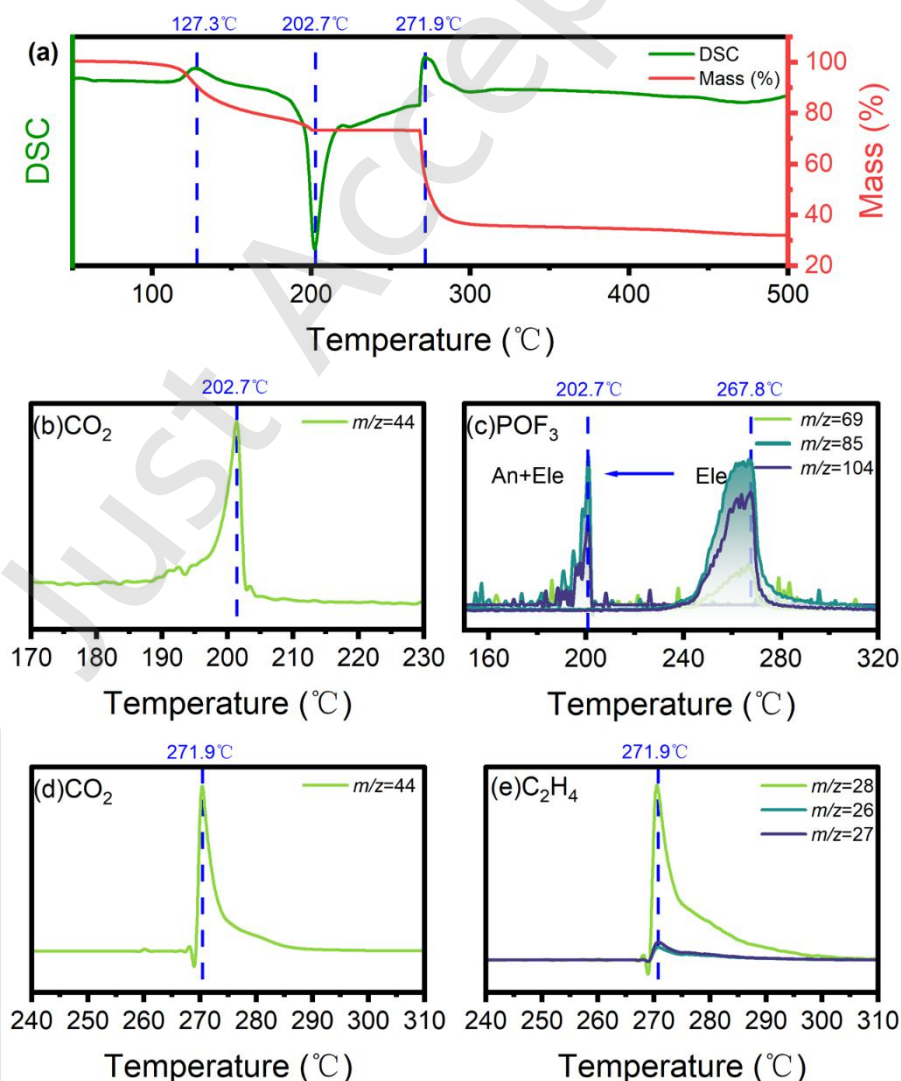


Figure 8 TG-DSC-MS results of the An + Ele with a scanning rate of $2^\circ\text{C}/\text{min}$. (a) Heat flow and weight loss. (b) MS signals of CO_2 at 202.7°C . (c)

Comparison of LiPF₆ decomposition temperature in the Ele and the An + Ele. (d)–(e) MS signals of CO₂ and C₂H₄ at 271.9 °C.

3.1.4 Cathode and Anode mixed system reaction mechanisms

The heat generation profiles of the Ca, the An, and the Ca + An are compared in Fig. 9(a), with the corresponding peak temperatures and heat release summarized in Table 4. The data indicate that the Ca and the An exhibit limited heat release. In contrast, a pronounced exothermic peak emerges at 242.3 °C for their mixture, accompanied by a significant increase in overall heat release. This finding suggests a vigorous interaction between the cathode and anode materials, which is a critical step in triggering and promoting TR in LIBs.

To elucidate the mechanism of this exothermic reaction, we further analyze the MS signals. As shown in the MS plots for the Ca, the An, and the Ca + An in Fig. 9(b), the Ca begins to undergo a phase transition accompanied by the release of O₂ around 184.0°C. However, in the components combination of the Ca + An, the corresponding oxygen signal peak is significantly weakened or even disappears. This directly indicates that the O* released from the cathode does not accumulate in the gas phase, but is rapidly consumed by the highly reductive lithiated anode, thereby triggering vigorous oxidative reactions. The mass spectrometry signal for CO₂

presented in Fig. 9(c) provides critical evidence. Neither the Ca nor the An exhibits a distinct CO₂ signal, whereas a pronounced CO₂ peak emerges synchronously with the exothermic peak at 242.3 °C in the Ca + An. This confirms that O*, which diffuses from the cathode to the anode, undergoes vigorous oxidation reactions with SEI, graphite and intercalated lithium, resulting in the generation of substantial amounts of CO₂ and the release of heat. In summary, the experimental results indicate that under thermal abuse conditions O* released from cathode decomposition migrates to the anode surface and is rapidly consumed. This rapid oxidative reaction, with CO₂ as one of the primary products, constitutes the direct origin of the strong exothermic peak observed at 242.3 °C. This reaction serves as the critical link connecting cathode decomposition to the subsequent intensification of TR.

Table 4 The Ca, the An, and the Ca + An peak temperature and heat release

	Ca			Ca + An
	An	Peak 1	Peak 2	
peak temperature (°C)	—	202.6	353.9	242.3
Heat release (J/g)	—	1.864	1.346	6.836

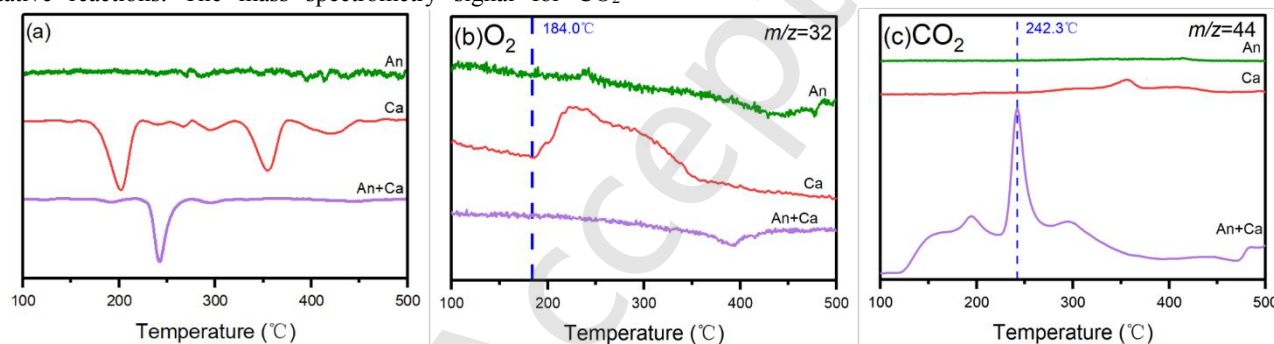


Figure 9 Comparative TG-DSC-MS analysis of the Ca, the An, and the Ca + An with a scanning rate of 2 °C/min. (a) Heat flow. (b) MS signals of O₂. (c) MS signals of CO₂.

The DSC curves of the Ca + Ele, the An + Ele, and the Ca + An + Ele are compared in Fig. 10, with their peak temperatures summarized in Table 5. Comparative analysis between the single and mixed systems elucidates the specific roles and synergistic effects of each component within the TR chain reactions.

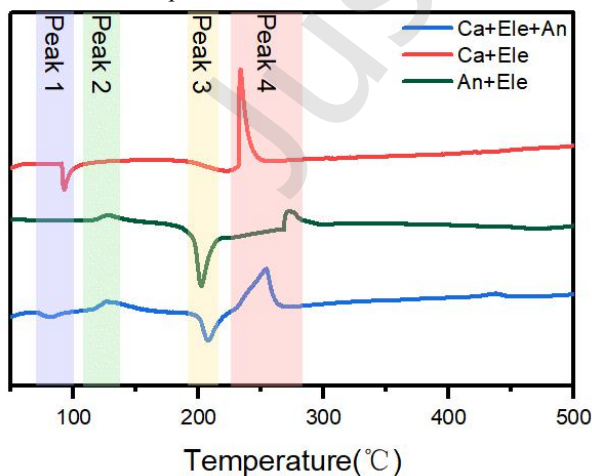


Figure 10 Comparative DSC analysis of the Ca + Ele, the An + Ele, and the Ca + An + Ele with a scanning rate of 2 °C/min.

Table 5 The Ca + Ele, the An + Ele, and the Ca + An + Ele peak temperatures

Composition	Peak 1	Peak 2	Peak 3	Peak 4
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Ca + Ele	92.0 °C	—	—	234.7 °C
An + Ele	—	127.3 °C	202.7 °C	271.9 °C
Ca + An + Ele	81.9 °C	125.6 °C	207.3 °C	254.0 °C

Peak 1 appears only in systems containing the cathode (the Ca + Ele, the Ca + An + Ele), corresponding to the cathode/electrolyte interfacial reactions catalyzed by highly reactive TM⁴⁺ species. These reactions provide the initial heat at a relatively low temperature, challenging the conventional view that SEI decomposition dominates early heat generation[50]. Peak 2 is observed in systems that include the anode (the An + Ele, the Ca + An + Ele), which is attributed to DMC volatilization and decomposition of the SEI. Due to the relatively thin thickness of the SEI, the overall process is characterized by endothermic behavior. However, its breakdown exposes the highly reactive lithiated anode, preparing the active interface for subsequent violent exothermic reactions. Peak 3 represents the most intense exothermic peak, which strictly depends on the presence of the electrolyte and lithiated anode, as observed in both the An + Ele and the Ca + An + Ele. It is attributed to the ring-opening polymerization of EC associated with the lithiated graphite. The substantial heat released from these reactions induces the rapid temperature increase, thereby accelerating the progression of subsequent side reactions. Peak 4 presents in all systems, but its intensity and onset temperature vary with composition. Compared to the An + Ele, systems

containing the cathode release O^* , facilitating the reactions at lower temperatures, with onset temperatures 37.2°C and 20.7°C lower for the $\text{Ca} + \text{Ele}$ and the $\text{Ca} + \text{An} + \text{Ele}$, respectively. Under semi-open testing conditions, DMC volatilization contributes to endothermic effects. However, O^* initiates vigorous oxidative reactions in the electrolyte, resulting in a significant exothermic effect. This leads to a self-accelerating process characterized by heat release, oxidative reactions and further heat release, indicating the transition into an uncontrollable phase[61].

In summary, the TR of NCM811 LIBs follows a three-stage

chain-reaction process: initiation-acceleration-runaway, as shown in Fig. 11. The initiation stage is driven by the exothermic cathode/electrolyte interface reactions, where the released initial heat causes an increase in system temperature, subsequently triggering further reactions. The acceleration stage is dominated by the EC ring-opening polymerization, which releases majority of heat and leads to a swift increase in temperature within the system. The runaway stage culminates in oxidative reactions triggered by the released O^* from cathode, leading to complete loss of heat release control via the autocatalytic cycle.

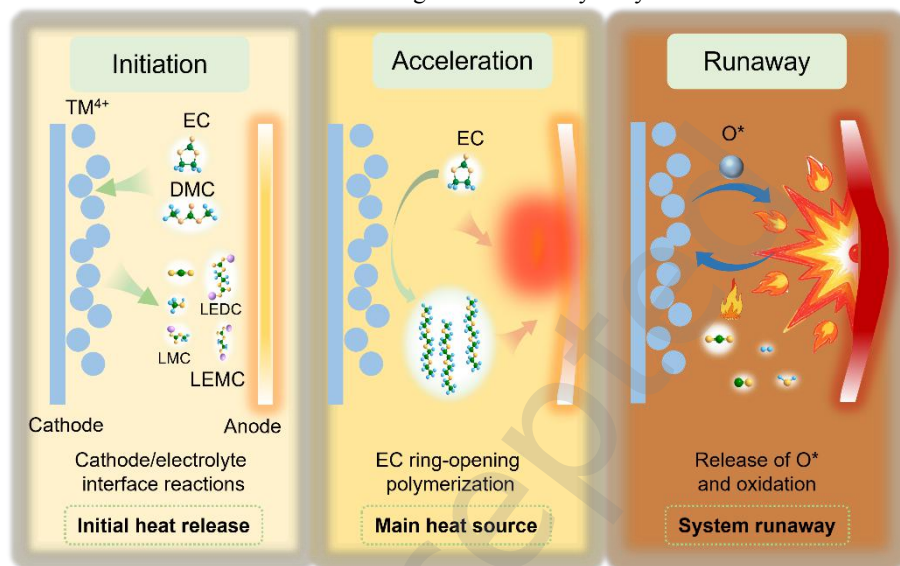


Figure 11 Schematic diagram of the three-stage TR chain-reaction process: initiation-acceleration-runaway.

3.2 Analysis of TR mechanisms based on cell level

Although previous studies have identified several key stages and their warning potential during the TR process[62, 63], the intrinsic correspondence between these observed signals and the internal chain reaction mechanisms has not been systematically elucidated. This section correlates the TR reaction mechanisms with the evolution sequences of multidimensional signals synchronously monitored during the overheating process of a 100% SOC pouch cell, including expansion force (F), gas concentrations (G), voltage (U), and temperature (T), as shown in Fig. 12. Based on this correlation, the overheating-induced TR process is precisely divided into five consecutive stages. The transition into each stage is defined by distinct and measurable thresholds of key signals, which directly correspond to changes in internal failure modes. The stage definitions, key signal thresholds, and associated mechanisms are summarized in Fig. 14.

Normal Operation Stage. During the initial heating stage, the expansion force increased linearly at a slow rate, with dF/dt being less than 0.49 N/s , which is primarily attributed to the gradual vaporization of the low-boiling electrolyte solvent DMC (Eq. (1)). Additionally, due to thermal conduction, the cell surface temperature increased gradually, with the change rate (dT/dt) below 0.1°C/s . Although subjected to thermal abuse, no irreversible internal reactions had yet occurred, indicating that the cell remained in a safe state.

Initial Exothermic and Pressure Buildup Stage. This stage commenced at 732 s (t_{Abn}), marked by the first significant jump in the expansion force change rate (dF/dt), which reached 1.47

N/s . This signal anomaly, detectable well before any notable surface temperature rise ($dT/dt < 0.1^\circ\text{C/s}$), corresponds to the initiation of the cathode/electrolyte interfacial reactions (Eqs. (12)–(14)) and decomposition of SEI on the anode (Eqs. (17)–(21)), marking the occurrence of irreversible internal exothermic reactions[64]. As the heating plate continued to supply heat, the internal temperature of the cell rose steadily, accelerating gas generation. This led to a significant increase in the expansion force growth rate, which peaked at 7.84 N/s . The expansion force exhibited a more sensitive response to the early evolution of internal reactions than other monitored parameters[65, 66]. Accordingly, a dF/dt threshold exceeding 1 N/s can be established as a sensitive and early indicator for this initial mechanistic stage.

Venting and Gas Detection Stage. At 1030 s (t_v), the expansion force reached its peak value (F_{max}) of 1592.5 N , indicating that the internal pressure exceeded the mechanical limits of the cell case, leading to rupture and venting (Fig. 13(b)). The ejection of high-temperature gas-liquid mixture caused the first observable abnormal surge in surface temperature approximately 5 seconds later ($t = 1035 \text{ s}$), with rates of 2.4 , 1.3 and 0.9°C/s at T_1 , T_2 and T_3 , respectively. Thereafter, the temperature returned to a relatively steady rising trend with dT/dt below 1°C/s . Following venting, the internal gases were released. At 1051 s (t_g), the H_2 signal was first detected ($dG/dt > 0 \text{ ppm/s}$), with CO , CO_2 , and VOCs appearing almost simultaneously. The detected gases originate from the following processes: (i) Oxidation reactions. This primarily involves reactions between the O^* released from the cathode decomposition and the electrolyte components, as described by

Eqs. (9), (10), (15) and (16). (ii) Reactions at the anode. Gases are generated from the interaction between the exposed lithiated anode and the electrolyte solvents, corresponding to Eqs. (26) and (27). (iii) Electrolyte decomposition and volatilization. This category includes the thermal decomposition of LiPF_6 (Eqs. (3) and (4)) as well as the volatilization and decomposition of the EC solvent (Eqs. (2), (5)–(8) and (25)). With continued heating by the electric heating plate, internal side reactions intensified, leading to a continuous rise in the concentration of each gas. Therefore, the condition $F = F_{\max}$, the first occurrence of $dT/dt \geq 1^\circ\text{C/s}$ at least two measurement points simultaneously and $dG/dt > 0$ ppm/s defines the onset of active gas release and intensified chain reactions.

Internal Short Circuit and Voltage Collapse Stage. As the battery approached the critical point of TR, internal exothermic reactions intensified drastically and gas generation increased sharply, which resulted in a second abnormal rise in expansion force at 1421 s, with dF/dt exceeding 1 N/s once again. Immediately after that, the voltage began to drop sharply at 1424 s (t_{ISC}) with a change rate (dU/dt) of -0.30 V/s, while the cell surface temperatures were 102.1°C , 113.7°C , and 115.7°C at T_1 , T_2 , and T_3 , respectively. At this stage, the separator had completely collapsed, resulting in a large-area internal short circuit (ISC)[10]. This result aligns with the conclusion reported in the previous literature that ISC typically occurs prior to

TR[67]. Therefore, a second significant jump in the expansion force change rate with $dF/dt > 1$ N/s and a rapid voltage drop with $dU/dt \leq -0.1$ V/s can serve as an indicator of ISC within the cell.

Thermal Runaway and Explosion Stage. The Joule heat released from ISC drove the internal reactions into a self-accelerating stage[68]. As the temperature climbs further, decomposition of the binder (Eqs. (22) and (23)) occurred. At 1430 s (t_{TR}), TR was triggered, defined as the moment when the temperature rise rate again exceeded 1°C/s at multiple measurement points ($dT_1/dt = 0.6^\circ\text{C/s}$, $dT_2/dt = 6.45^\circ\text{C/s}$, and $dT_3/dt = 2.7^\circ\text{C/s}$). The flammable gas mixture inside the chamber was then ignited, resulting in explosive combustion with an instantaneous temperature spike to 628.3°C at T_3 within 11 seconds after TR (Fig. 13(e)), as well as drastic surge in gas generation and heat release. Gas monitoring indicated that H_2 , CO , VOCs, and HF reached their peak concentrations approximately 60 s after TR, while the CO_2 peak lagged, occurring at 885 s. This discrepancy likely arises from the fact that H_2 , CO , VOCs, and HF generation peak rapidly at the onset of TR, whereas the sustained oxidation of graphite anodes at elevated temperatures occurs at a comparatively slower rate. Consequently, a sustained temperature rise with $dT/dt \geq 1^\circ\text{C/s}$, which requires no fewer than two measurement points, is the definitive confirmation threshold for TR.

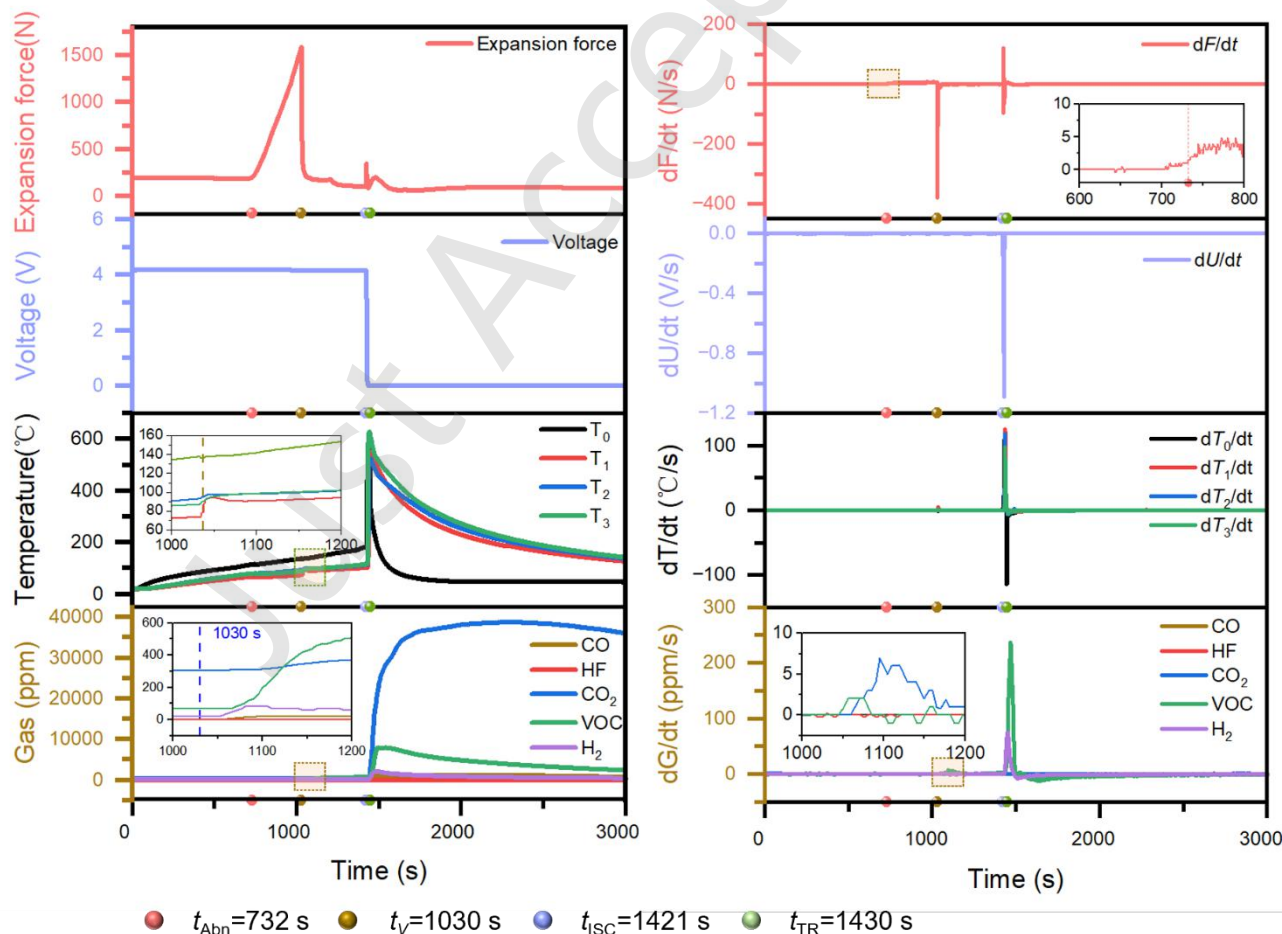


Figure 12 Multidimensional signal curves of cell during overheating process. (a)–(d) The temporal changes of expansion force, gas, temperature, and voltage over time; (e)–(h) The rate of change of each parameter over time.

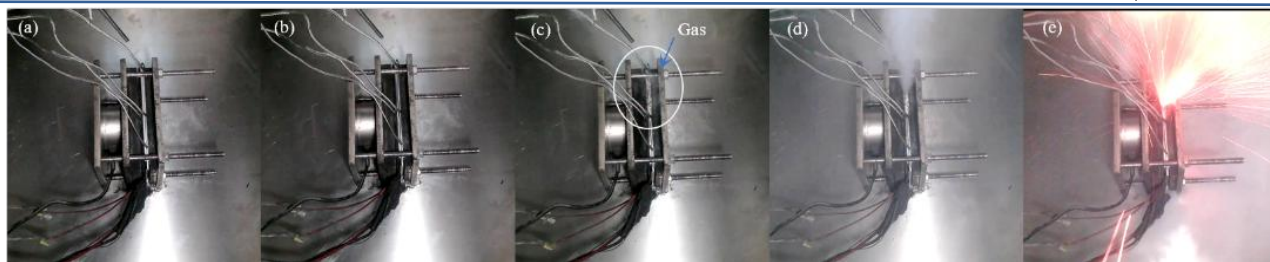


Figure 13 Cell failure characteristics during overheating process. (a) Normal state; (b)–(e) Cell failure characteristics at t_{Abn} , t_V , t_{ISC} , and t_{TR} .

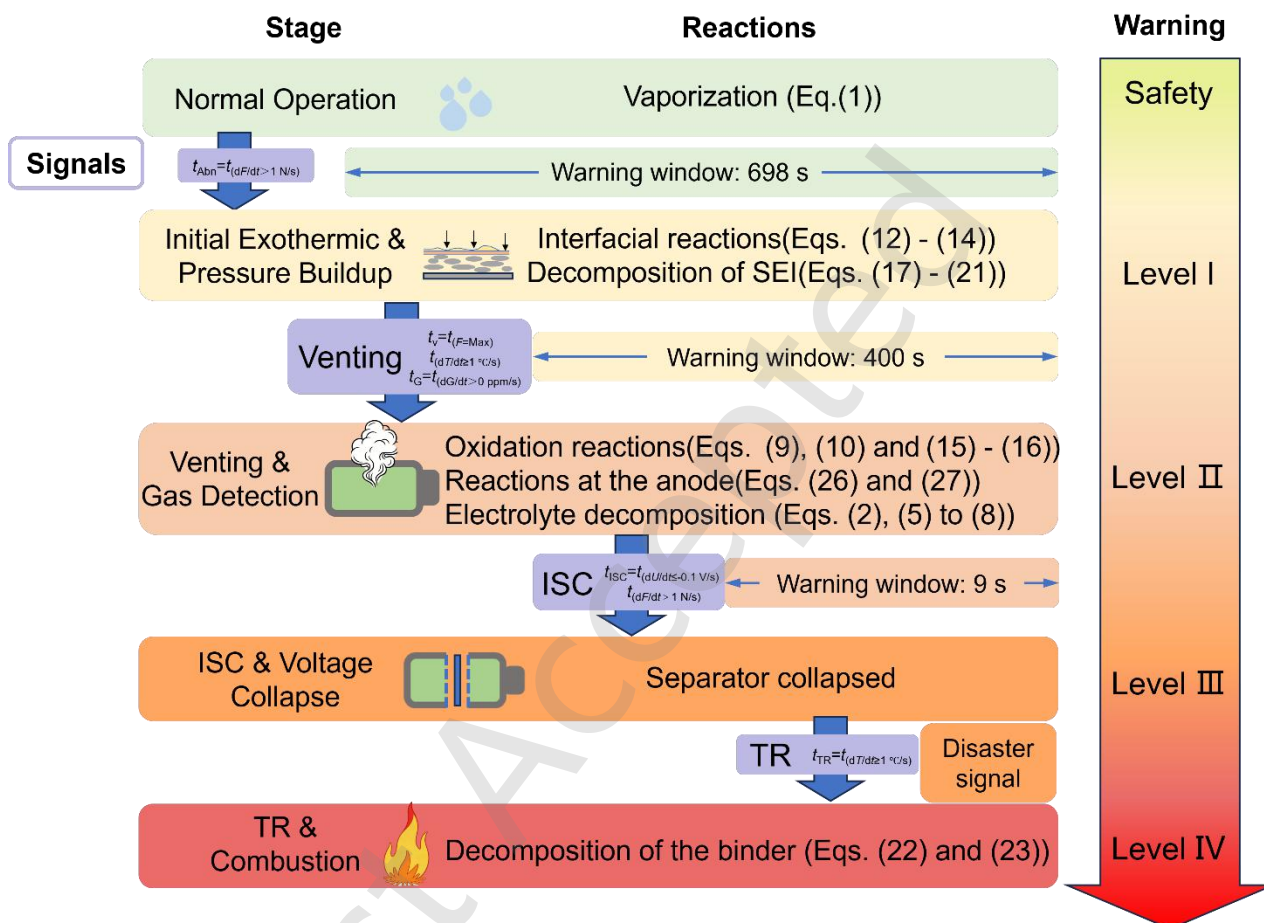


Figure 14 Schematic diagram of stage definitions, key signal thresholds, associated mechanisms, and hierarchical early warning strategy during the TR process.

3.3 Hierarchical early warning strategy based on multi-dimensional signals

Based on the established correlation between TR stages and characteristic signal thresholds, a refined hierarchical early- warning strategy comprising four levels is proposed, as illustrated in Fig. 14. This strategy enables progressive escalation of safety responses from early intervention to final emergency handling.

The first occurrence of the expansion force change rate exceeding 1 N/s ($dF/dt > 1 \text{ N/s}$) is classified as **level I**. This signal signifies the cathode/electrolyte interfacial reactions and the SEI decomposition on the anode, indicating the initiation of irreversible internal exothermic reactions. The cell surface temperature typically shows no significant anomaly at this point, highlighting the superior early sensitivity of the expansion force. This level provides the longest warning window of approximately 698 s, during which immediate response measures should include disconnecting the load and initiating enhanced cooling, alongside intensified monitoring of the battery system.

Level II is issued upon cell venting, which is marked by the expansion force reaching its peak magnitude ($F = \text{Max}$), combined with the first occurrence of the temperature rise rate exceeding 1 °C/s ($dT/dt \geq 1 \text{ °C/s}$), and the initial rise in the concentration of any characteristic gas ($dG/dt > 0 \text{ ppm/s}$). This integrated criterion indicates that the cell has ruptured and internal chain reactions have intensified, leading to the release of characteristic gases such as H_2 , CO , CO_2 , HF , and VOCs. The warning window at this stage is approximately 400 s before TR. Mandatory responses include immediate electrical isolation, activation of high-capacity emergency ventilation to disperse flammable and toxic gases, continuous isolation of the hazardous area, and preparation for escalation of emergency protocols.

Level III warning is triggered by a second abnormal rise in expansion force ($dF/dt > 1 \text{ N/s}$) and a sharp voltage drop ($dU/dt \leq -0.1 \text{ V/s}$), which serve as definitive indicators of a large-area ISC resulting from separator failure. This signal marks the point of catastrophic, uncontrollable self-heating and the imminent onset of TR, leaving only a few seconds for

response. Immediate actions must include the automatic activation of targeted fire-suppression systems and verification of complete personnel evacuation from the hazard zone.

Level IV warning is confirmed when a sustained sharp increase in the temperature-rise rate ($dT/dt \geq 1\text{ }^{\circ}\text{C/s}$) is observed at multiple measurement points. This criterion confirms that the cell is undergoing full TR, characterized by self-sustaining exothermic chain reactions, typically accompanied by ignition and violent combustion. As the final disaster confirmation signal, this level triggers the execution of the highest-level emergency, firefighting, and post-incident procedures.

4 Conclusion

This study systematically investigates the TR mechanisms of NCM811/graphite LIBs by establishing a stepwise analytical framework that spans from material components to full cells. A cross-scale correlation between the thermal reactions at material level and the characteristic signal evolution at cell level has been established, based on which a hierarchical early-warning strategy grounded in mechanism-signal correlation has also been developed.

(1) A three-stage chain-reaction pathway, termed initiation-acceleration-runaway, is proposed and experimentally validated for the first time, elucidating that the underlying cause of TR lies in the synergistic interaction of three core processes. The initiation stage is driven by exothermic anode/electrolyte interfacial reactions catalyzed by highly reactive TM^{4+} species around $90\text{ }^{\circ}\text{C}$, challenging the conventional view that SEI decomposition dominates early heat generation. The acceleration stage is governed by the ring-opening polymerization of EC occurring in the presence of lithiated graphite around $200\text{ }^{\circ}\text{C}$, which releases substantial heat that rapidly elevates the internal temperature. The runaway stage is triggered by the migration and rapid consumption of active oxygen species released from the cathode, leading to an autocatalytic oxidative cycle that culminates in complete loss of thermal control.

(2) By synchronously monitoring multidimensional signals including expansion force, temperature, voltage, and five characteristic gases (H_2 , CO , CO_2 , HF , and VOCs) during cell-level overheating tests, the TR process is divided into five consecutive stages based on the temporal evolution of these signals. Crucially, each stage is then correlated with its governing material-level reaction mechanism, endowing every signal threshold with a clear physicochemical meaning.

(3) A four-level hierarchical early-warning strategy is constructed based on the above mechanism-signal correlation. The Level I warning, triggered by the expansion force change rate exceeding 1 N/s , corresponds to the onset of cathode/electrolyte interfacial reactions and SEI decomposition, providing a warning window of up to 698 seconds prior to TR. Each subsequent level is directly linked to a specific internal failure mode, offering both theoretical rigor and practical operability for battery safety management.

This work not only deepens the fundamental understanding of TR mechanisms in high-energy-density LIBs but also closes the loop from mechanistic insight to engineering application through a mechanism-signal-strategy framework, pointing toward the development of intrinsically safer battery systems. Future work will validate the transferability of this hierarchical early-warning paradigm across diverse cell configurations and extend it to module-level thermal propagation scenarios.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

J. C. and F. Z.: Data curation, validation, writing manuscript, experimental design. J. S.: Funding acquisition, methodology, supervision, and writing. T. Z. and J. G. L.: Project administration, experiment, data curation. S. P. W.: Project administration, validation. Y. H. X. and B. W. W.: Investigation, and formal analysis. H. L.: Experimental support. All the authors have approved the final manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Thermal runaway mechanisms and early-warning strategy determination of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ batteries through material and cell level analysis

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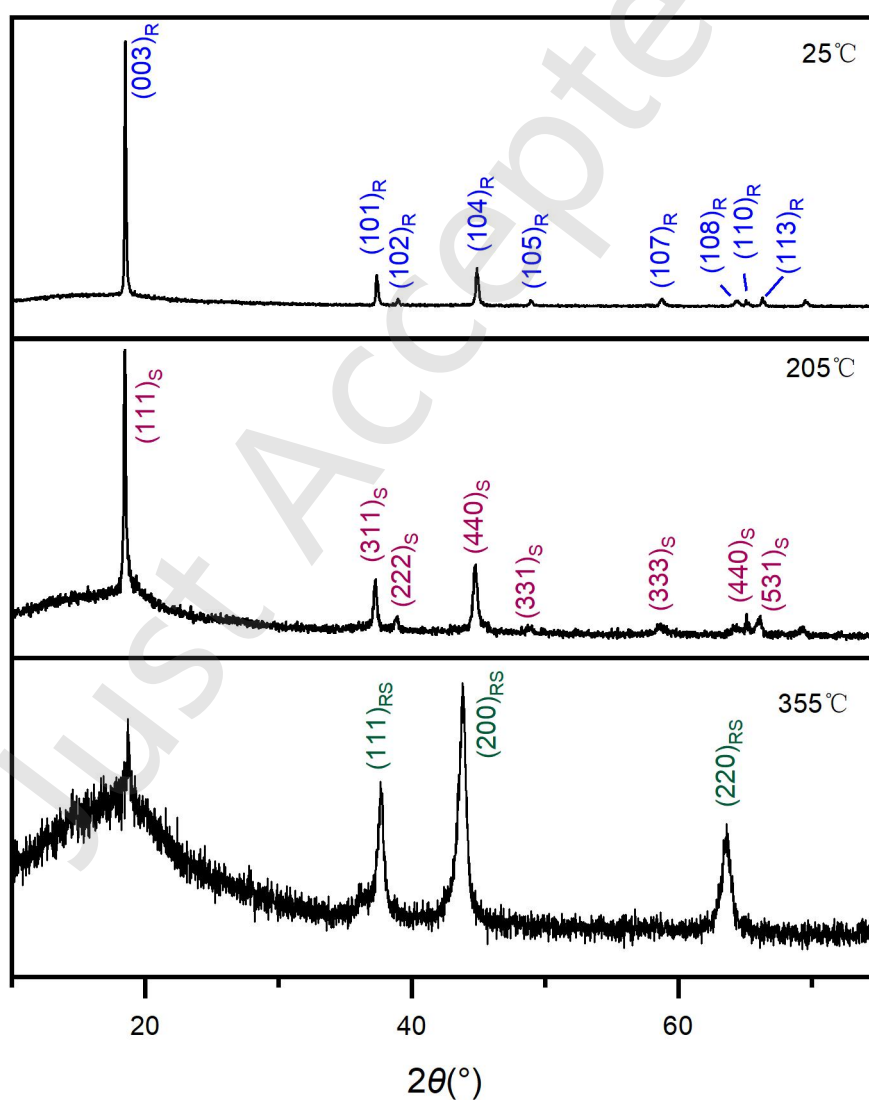
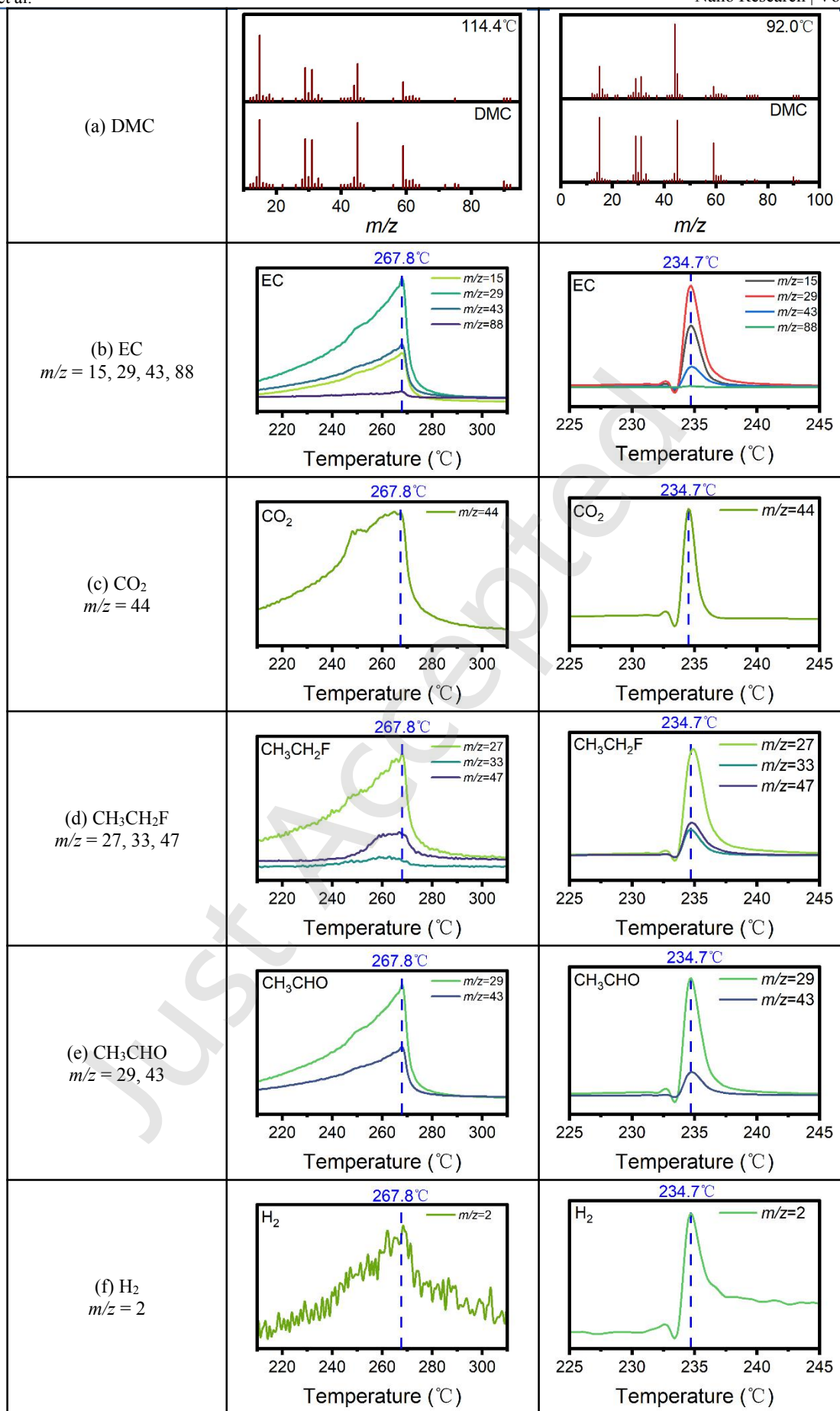


Figure S1. XRD results of the delithiated NCM811 electrode pretreated at 25 °C, 205 °C, and 355 °C (R: layered structure ($R\bar{3}m$), S: spinel structure ($Fd\bar{3}m$), RS: rock-salt structure ($Fm\bar{3}m$)).

	the Ele	the Ca + Ele
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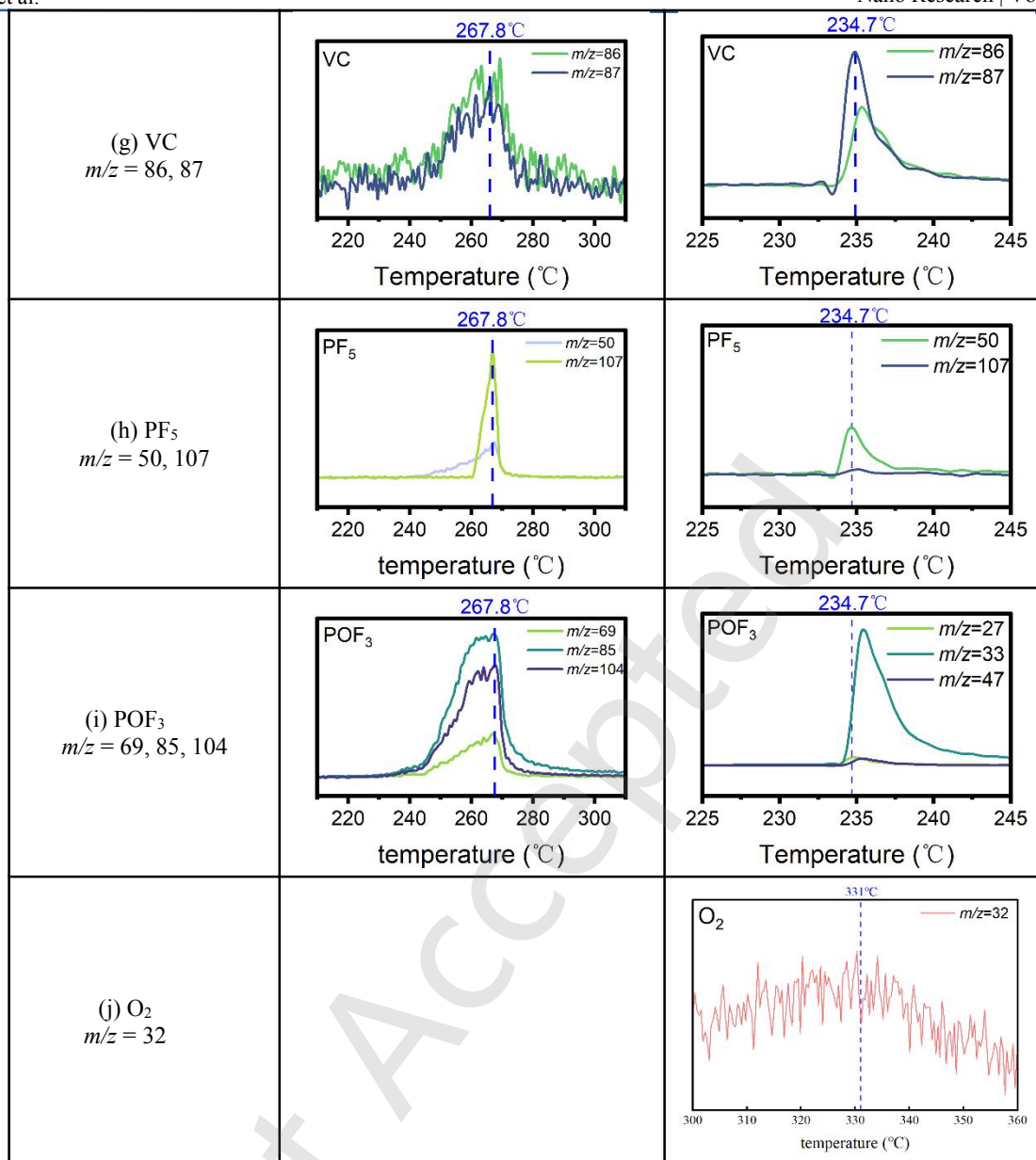


Figure S2. MS results of the Ele and the Ca + Ele with a scanning rate of 2 °C/min. (a) MS signals of DMC for the Ele at 114.4 °C and for the Ca + Ele at 92 °C. (b)-(i) MS signals of DMC, EC, CO₂, CH₃CH₂F, CH₃CHO, H₂, VC, PF₅, and POF₃ for the Ele at 267.8 °C and the Ca + Ele at 234.7 °C. (j) MS signals of O₂ for the Ca + Ele at 331.0 °C.

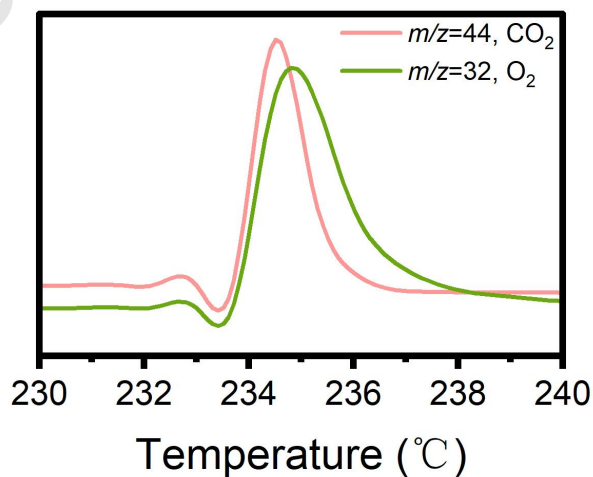


Figure S3 Comparison of the release time of O₂ and CO₂ for the Ca + Ele.

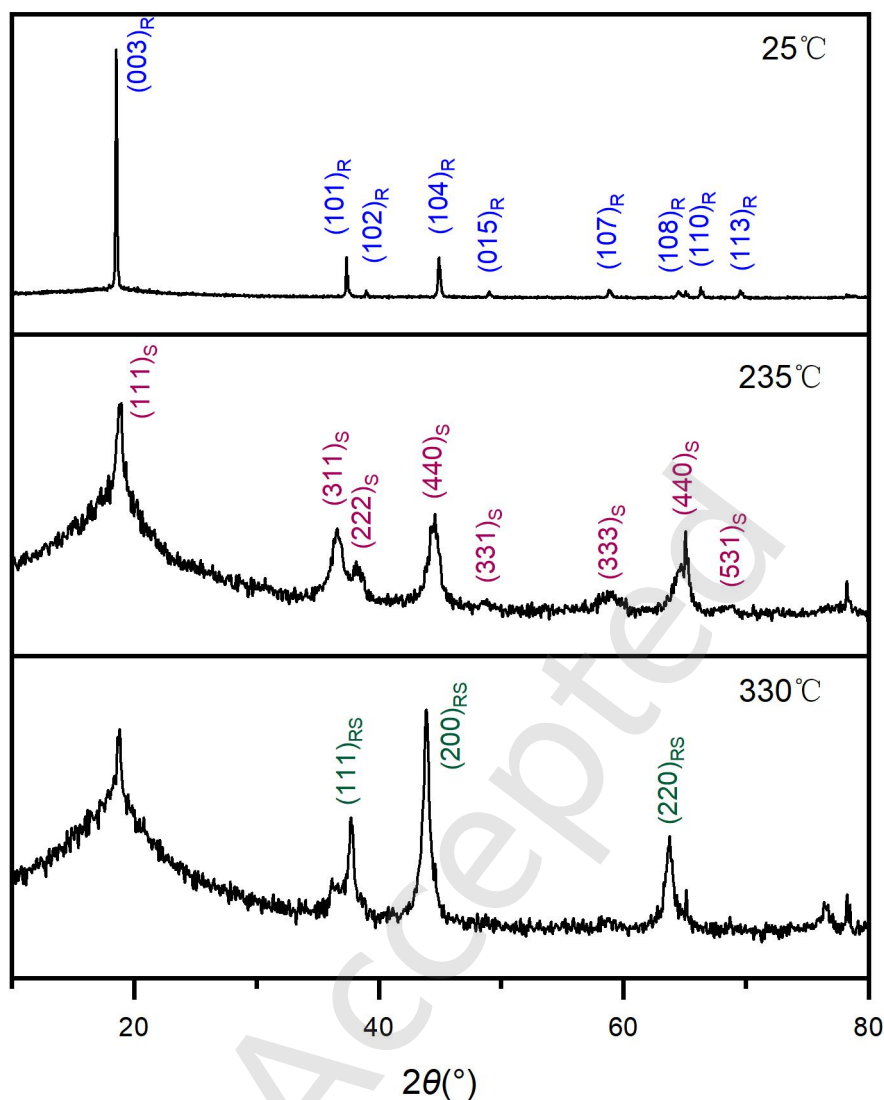
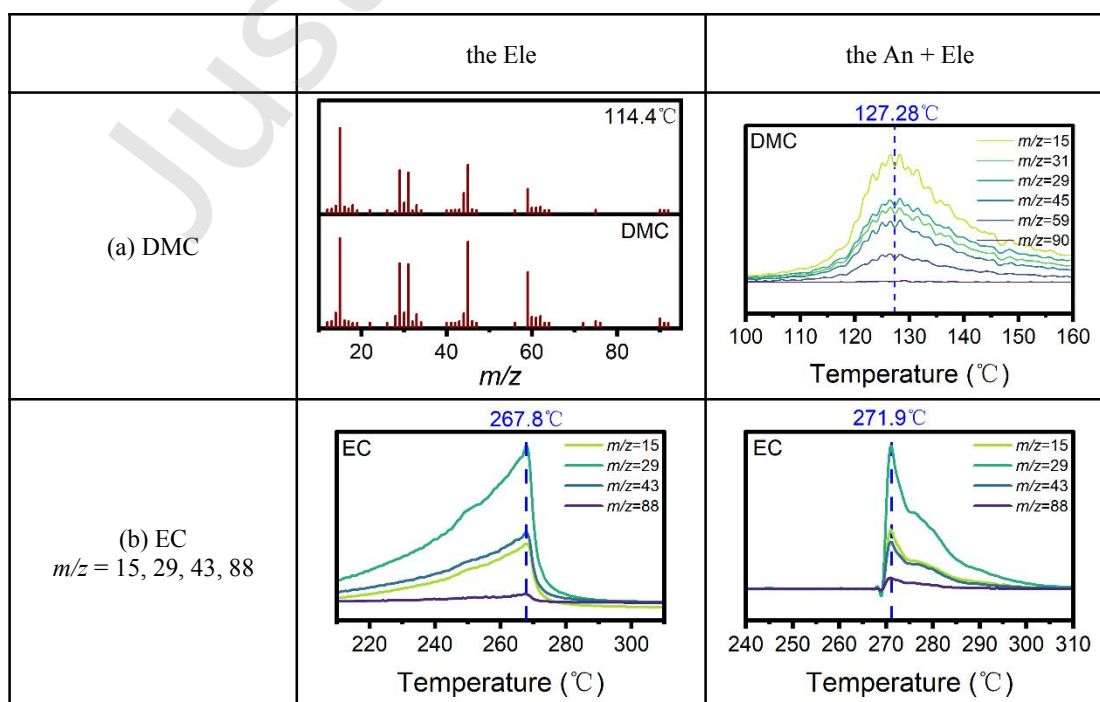


Figure S4 XRD results of the delithiated NCM811 electrode pretreated with electrolyte at 25 °C, 235 °C, and 330 °C (R: layered structure ($R\bar{3}m$), S: spinel structure ($Fd\bar{3}m$), RS: rock-salt structure ($Fm\bar{3}m$)).



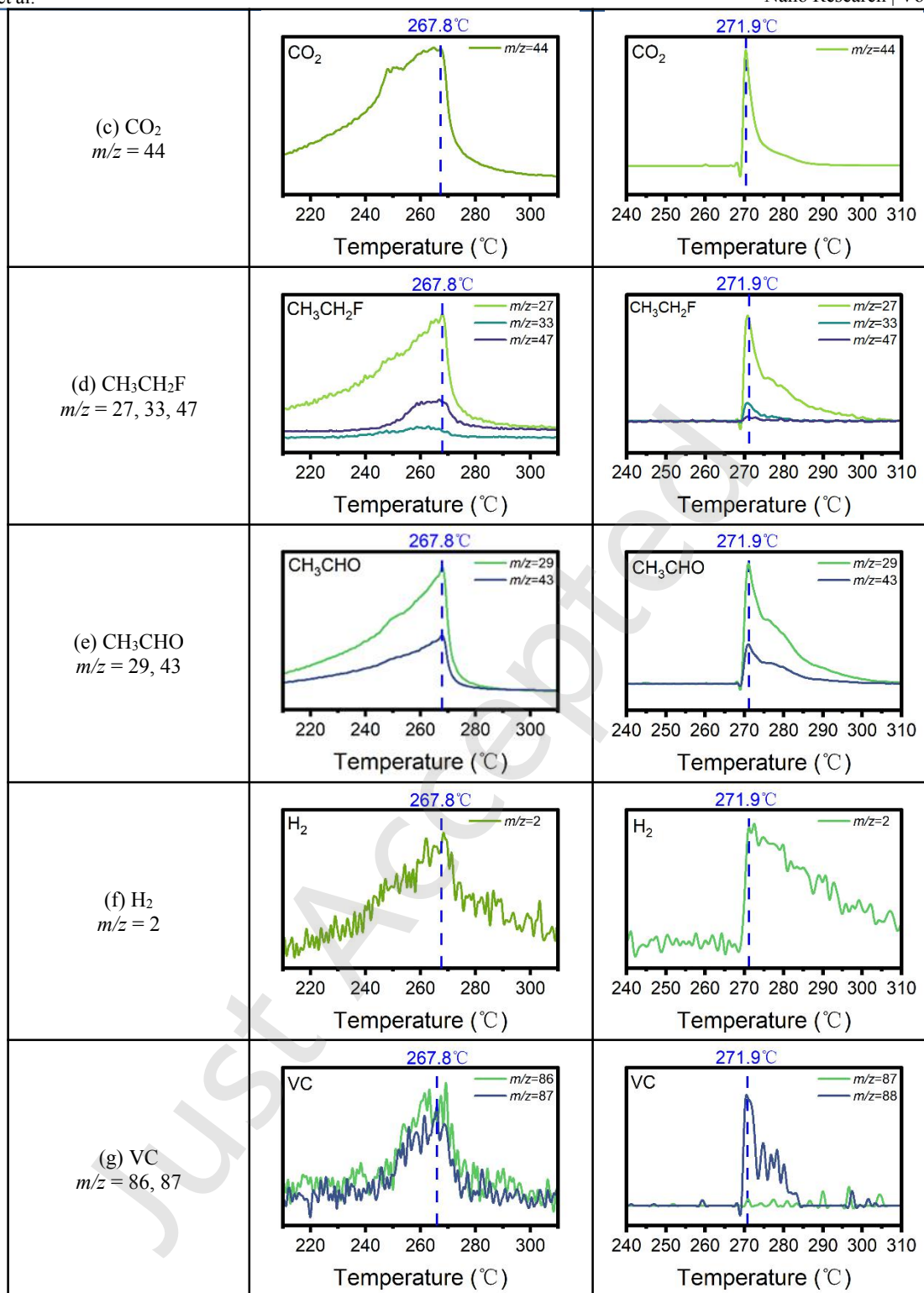


Figure S5 MS results of the Ele and the An + Ele with a scanning rate of 2 °C/min. (a) MS signals of DMC for the Ele + An at 127.8 °C and for the Ele at 114.4 °C. (b)-(g) MS signals of EC, CO_2 , $\text{CH}_3\text{CH}_2\text{F}$, CH_3CHO , H_2 , VC, and H_2O for the Ele at 267.8 °C and the An + Ele at 271.9 °C.

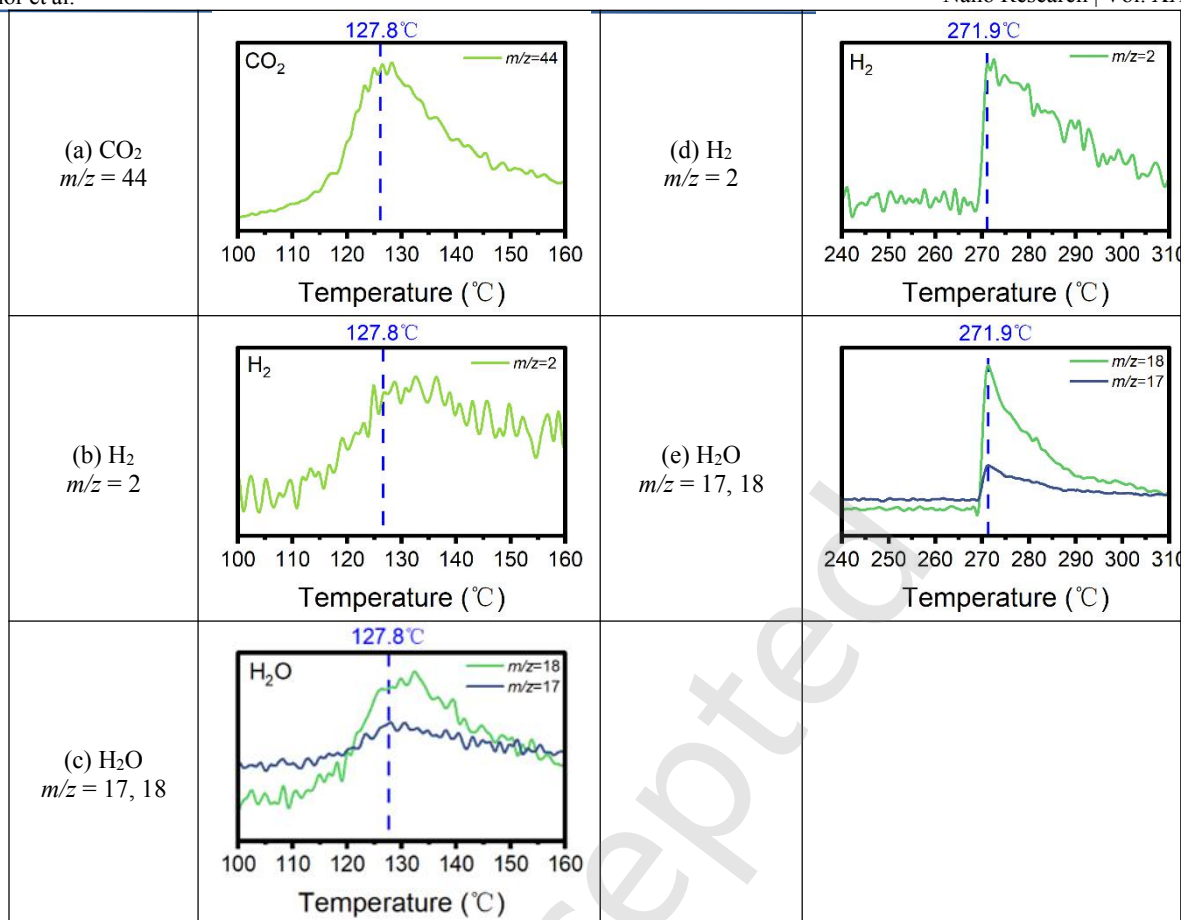


Figure S6 MS results of the Ele +An with a scanning rate of 2 °C/min.(a)-(c) MS signals of CO₂, H₂, and H₂O for the Ele +An at 127.8 °C. (e)-(f) MS signals of CO₂, H₂, and H₂O for the Ele +An at 271.9 °C.