

Electrochemical initiation and chemical reaction cascades in dual-stage thermal runaway in sulfide-based all-solid-state batteries

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This study investigates the influence of electrochemically formed LPSC decomposition products on the thermal stability of sulfide all-solid-state batteries. The fully charged NCM exhibits thermal instability with solid electrolytes containing electrochemical decomposition products, whereas composites consisting of the charged NCM and pristine solid electrolytes show less exothermic reactions. These indicate that the decomposition of solid electrolytes during charge also contributes to thermal runaway mechanisms. Furthermore, the authors introduce Li₄GeS₄, which has improved chemical stability with NCM, and demonstrate its higher thermal stability compared to other sulfide solid electrolytes. These findings provide novel insights into the thermal instability induced by the electrochemically formed interfacial species. Therefore, I would recommend the publication of this paper after addressing minor comments.

1. Rui et al. reported that thermal runaway between NCM and LPSC follows a solid-solid reaction (Energy Environ. Sci., 2023, 16, 3552-3563). This implies that the degree of contact between NCM and solid electrolytes has influence on thermal behavior. In addition, hand grinding of fully charged NCM and LPSC leads to violent burning even under inert atmospheres. How did the authors prepare the De-NCM/SE composites? Were the samples pelletized or loosely contacted?
2. Adiabatic ramp tests showed a rapid temperature increase of the 100% SOC composite cathode near 200 °C without further temperature rises, while several exothermic peaks appeared in DSC. Why is there a discrepancy between the two methods? In addition, the amounts of sample used for ARC and DSC were significantly different: 200 mg for ARC and 10 mg for DSC. Does this difference have influence on the thermal behavior?
3. The authors claimed that thermal runaway mechanisms are divided into two stages. The initial heat generation is driven by reactions between delithiated NCM and electrochemically formed interfacial species. At elevated temperatures, sulfur-oxygen interdiffusion leads to bulk exothermic reactions. Although Li₄GeS₄ showed improved thermal stability, it is still unclear in which stage Li₄GeS₄ mitigated the detrimental reactions. Therefore, it would be helpful to clarify the role of Li₄GeS₄ by performing DSC and XPS on De-NCM/pristine LGS and De-NCM/4.5V-(LGS-VGCF) samples. In addition, NCM811-LGS ASSBs were cycled at 45 °C, which is higher than the operating temperature of NCM811-LPSC cells. This increased operating temperature could influence the electrochemical decomposition. Figure 5c shows a higher content of sulfate and sulfite products in the 100% SOC composite cathode compared to those in Figure 2d.
4. When the valence band edge of the solid electrolyte is above the Fermi level of the cathode, electron transfer from the solid electrolyte to the cathode leads to the oxidation of the solid electrolyte (ACS Appl. Energy Mater. 2022, 5, 2, 2045–2053).
5. The sentences from line 346 to 352 need references to support it.
6. Please add a scale bar in DSC Figures and specify the carrier gas used for MS measurements.

Reviewer #2

(Remarks to the Author)

This paper investigates thermal runaway mechanisms in sulfide-based all-solid-state batteries, focusing on NCM811/LPSC composite systems. It proposes a two-stage thermal degradation mechanism where early exothermic reactions arise from electrochemically formed interphase species, followed by bulk S-O interdiffusion at higher temperatures. Systematic thermal characterization reveals that charged cathodes (100% SOC) show greater thermal instability than discharged ones due to

reactive interphase decomposition products like -S-S-, -P-S-P-, and Li₃PS₄. The study extends this to other sulfide electrolytes (LGPS, LSPSC) and suggests Li₄GeS₄ (LGS) for interface engineering, enhancing thermal safety by reducing thermodynamic driving forces for S-O exchange. DFT calculations support improved interfacial compatibility and experimental results indicate elevated thermal runaway temperatures, rising from 228°C to 312°C. However, this paper has significant theoretical inconsistencies and methodological limitations that undermine its scientific rigor. The computational analysis focuses on pristine materials (0% SOC), while the critical experimental work centers on delithiated states (100% SOC), creating a mismatch between theory and experiment. The band theory explanation contains errors in the direction of electron transfer and inaccurately compares electronic properties without proper interface analysis. The electronic structure calculations overlook the actual reactive species crucial to the proposed mechanism, indicating a major gap in understanding. Experimental reproducibility is questionable, as thermal safety data are presented without statistical analysis, error bars, or multiple trials, which are vital for safety applications. The novelty of the Ge substitution approach is limited due to prior work by the same group, and practical validation is insufficient for real-world implementation. Furthermore, the paper exhibits numerical inconsistencies, inadequate figure descriptions, and unclear reaction energetics that further undermine its reliability. Due to these deficiencies and lack of completeness, I do not recommend this manuscript in its current form, published in Nature Communications.

Comment 1) Figures 1a–1c present the ARC HWS and DSC traces for only one specimen, leaving the reproducibility of your thermal-safety metrics unclear. Please repeat the ARC-HWS and DSC tests at least three times under identical conditions (sample mass, cell pressure, HWS step length, purge gas, etc.) and report the mean $\pm$ standard deviation for the key parameters (Tonset, T_{tr}, and ΔH).

Comment 2) There is a fundamental inconsistency between the computational and experimental approaches. The DFT calculations are performed on pristine materials representing 0% SOC conditions, while the critical thermal runaway analysis focuses on 100% SOC delithiated states. This mismatch severely undermines the theoretical justification for experimental observations, as the electronic properties of delithiated NCM811 differ significantly from the pristine state used in calculations.

Comment 3) Similar to Comment 2, there is ambiguity regarding the lithiation state of NCM811 used in the reaction energy calculations shown in Figure 5a. The authors do not specify whether the computational analysis employs delithiated NCM811 (relevant to 100% SOC conditions) or lithiated NCM811 (relevant to 0% SOC conditions). Given that the thermal runaway mechanism is critically dependent on the delithiation state, this specification is essential for the proper interpretation of the calculated energetics and their relevance to experimental conditions.

Comment 4) The electronic structure analysis is incomplete and fails to address the actual reactive species driving the thermal runaway mechanism. While the authors calculate band alignments between bulk NCM811 and LPSC, they ignore the Fermi levels and electronic properties of the key reactive intermediates (Li₃PS₄, Li₂S, Li₂S_x, -S-S-, -P-S-P-) that they identify as primary thermal runaway initiators. For a mechanism centered on electrochemical interphase decomposition, the electronic structure of these species is crucial for understanding electron transfer processes.

Comment 5) The band theory analysis contains fundamental conceptual errors in explaining electron transfer mechanisms. The authors state that "electron transfer from NCM811 to LPSC was energetically favorable" based on LPSC's VBM being 1.47 eV higher than NCM811's Fermi level. However, this interpretation is incorrect: electrons naturally flow from higher to lower energy levels, so if LPSC's VBM is higher than NCM811's Fermi level, electron transfer should occur from LPSC to NCM811, not the reverse. Furthermore, the authors inappropriately compare VBM (a material property of LPSC) with the Fermi level (a material property of NCM811) without a proper band alignment analysis that accounts for interface formation, band bending, and equilibrium conditions.

Comment 6) The novelty of the proposed Ge substitution strategy is questionable given that the role of Ge in improving sulfide electrolyte stability has been previously established by the same research group's earlier publications, Kim et al. [13]. The authors should clearly articulate what new insights or improvements their Li₄GeS₄ approach provides beyond existing Ge-based solutions and provide adequate differentiation from prior work.

Comment 7) There is a numerical inconsistency in the reported Tonset. The authors state "Post-cycling 0% SOC LGS composites maintained stability to 450°C, contrasting with LPSC's 303°C exothermic initiation (Figure 5d vs 2a)" and "For the 0% SOC sample, two exothermic events were recorded at 303°C ($\Delta H=75.1$ J/g) and 379°C ($\Delta H=268.8$ J/g) (Figure 2a)." However, Figure 2a shows the onset temperature as 302°C, not 303°C as reported in the text. This discrepancy requires correction for accuracy.

Comment 8) The manuscript contains inconsistent abbreviation usage. The authors define "valence band maximum (VBM)" on page 4, but subsequently use the full term again in "the calculated valence band maximum (VBM) of LPSC was 1.47 eV higher than the Fermi level of NCM811" (Figure S14). According to standard scientific writing conventions, once an abbreviation is defined, it should be used consistently throughout the manuscript rather than alternating between full terms and abbreviations.

Comment 9) Figure 4b lacks any description or discussion in the manuscript text. The authors present this figure without adequate explanation of its content, methodology, or relevance to the overall mechanism. This omission leaves readers unable to interpret the significance of the data presented, representing an incomplete presentation of the results.

Reviewer #3

(Remarks to the Author)

This manuscript investigates the thermal stability of sulfide-based all-solid-state batteries and elucidates the origin of thermal runaway, which is triggered by the interaction between the delithiated cathode and electrochemically decomposed LPSC. Furthermore, the authors provide insightful analysis on the role of VGCF in enhancing thermal safety, which is particularly meaningful for understanding how each component contributes to the overall thermal stability of ASSBs.

The study offers valuable insight into the safety aspects of sulfide-based solid-state batteries and makes a significant contribution by demonstrating that electrochemical decomposition products of the solid electrolyte at the cathode interface play a critical role in determining thermal stability. I believe this work is highly meaningful and recommend it for publication in Nature Communications, pending satisfactory responses to the following comments and questions.

Q1. If the thermal stability is mainly dependent on the cathode interfacial reaction as authors suggested, then, what is the origin of the difference of T_{tr} of SOC 100 between full cell and composite cathode as shown in Figure 1a and 1b. Additionally, even the HWS curve of SOC0 between full cell and composite cathode is seems to be different. Is there any interaction between cathode or anode (like cross-talk)?

Q2. According to the author's insists, the first exothermic reaction is due to the decomposition of interphase. Given the chemical composition of interphase is nearly same regardless of SOC (0 or 100) as shown in XPS (Fig 2b, d), can you explain the reason of decomposition temperature composite with SOC 100 is lower than composite with SOC 0? If the delithiated cathode participate in decomposition of interphase, what is the exact reaction mechanism? According to the references, SOC 100 cathode can also evolve the O_2 gas from the cathode when it converts to the spinel phase from layered structure. Then, is the reaction between O_2 gas and interphase? In addition, the reason should be explained that gaseous product is evolved only at the first step of exothermic reaction not the second step of rock salt phase transition where the much more amount of O_2 gas can be evolved.

Q3. The evaluation of the interaction between Li_2S , S, Li_3PS_4 and delithiated NCM is quite reasonable to investigate the effect of electrochemically degraded LPSC1 on thermal stability as interphase. Can you explain why the S or Li_3PS_4 can evolve the SO_2 gas evolution through the interaction with delithiated NCM? (in contrast to pristine LPSC).

Q4. To emphasize the effect of interphase on thermal stability depending on the interaction with cathode, it is recommended to note the interfacial decomposition mechanism of SOC 0 also for comparison with SOC 100 (like as shown in Figure 4a).

Reviewer #4

(Remarks to the Author)

The manuscript presents a comprehensive investigation into the thermal runaway behavior of sulfide-based all-solid-state batteries (ASSBs), emphasizing the role of electrochemically formed interphases and chemical cascade reactions at the cathode-electrolyte interface. The use of multiscale calorimetry, gas analysis, and advanced structural characterization to support a two-stage decomposition mechanism is novel. The authors correlate material-level interfacial reactions with cell-level thermal behavior and propose a paradigm shift from bulk stability to interfacial thermodynamics as the primary safety determinant. The following comments should be addressed.

1. While the authors attribute the first exothermic peak at 0% SOC to electrochemical interphase breakdown, it is unclear how such interphases persist or form under discharged conditions. Can the authors clarify whether residual sulfur species or kinetically trapped decomposition products contribute, and how this behavior is decoupled from active redox at 100% SOC?
2. The author states that there is a sequential progression from interphase breakdown to bulk NCM-LPSC reactions but does not define the temperature boundaries or timing clearly. Could the authors specify more definitively when LPSC becomes actively involved?
3. While the authors report multiple exothermic peaks, there are no normalized quantitative comparisons of reaction enthalpies (ΔH) across pristine, uncycled, and cycled cathodes. This makes it difficult to rank or compare thermal risk attributed to specific interfacial chemistries across states of charge. Can the authors elaborate on this to allow a clearer comparison?
4. The authors present in-situ heating XRD and identify NiO formation, but it is unclear whether NiO arises from lattice oxygen evolution, sulfur-induced destabilization, or both. Can the authors clarify this? NiO is typically associated with the oxidative decomposition of NCM cathodes, whereas sulfur-rich environments tend to reduce transition metals.
5. In section 2.3, the authors use NCM811 cathodes with a 4 nm coating, but do not explore whether this thickness is optimal. Given prior literature showing non-linear effects of coating thickness on both ionic conductivity and interfacial stability, can the authors comment on why 4 nm was chosen and whether thicker or thinner coatings were evaluated?
6. While LGS shows good interfacial stability with NCM811 on the cathode side, the authors employ a Li-Si anode in full-cell validation without evaluating its interfacial compatibility with LGS or LPSC. Given known issues of volume expansion and potential interfacial reactivity in Si-based alloys, the absence of any post-mortem analysis or thermal characterization at the anode-SE interface limits the comprehensiveness of the system-level safety claims. Can the authors provide a discussion on whether the LGS impacts long-term anode stability or interacts chemically?

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript has been revised based on the reviewers' previous comments. However, the interpretation of the computational and experimental results still remains questionable. The authors argue that the strong overlap of S and O in their DOS calculations indicates the feasibility of a bond exchange. Nevertheless, the XRD results after heat treatment suggest that it is not simply the delithiated NCM reacting with LPSCl to form NiS_2 while maintaining the oxidation state of Ni. Instead, the results imply that Ni^{4+} is reduced and NiS is formed. This suggests that the reaction is not a simple S–O exchange, but rather that S^{2-} transfers electrons to Ni and becomes oxidized, which could also result in the formation of gaseous species such as SO_2 .

In addition, the crystallographic data used for the DOS calculations need to be clearly provided. To perform DOS calculations, the initial crystal structures are required, but it is not specified whether these were obtained from databases such as Materials Project or derived from experimental XRD results. If refined XRD structures were used, then the corresponding refined XRD patterns together with the crystallographic information tables should be included to ensure reproducibility and reliability of the computational results.

Reviewer #2

(Remarks to the Author)

The author addressed the reviewers' comments to improve the completeness of the research. First, they clarified ambiguities in the experimental conditions by thoroughly analyzing the reactivity of NCM811 under 100% SOC conditions, which means fully delithiated NCM811, and is directly linked to thermal runaway phenomena. Additionally, by examining the Fermi levels of key reaction intermediates, the author strengthened the explanation of the electron transfer mechanism at the interface. They also corrected a conceptual error in the description comparing the VBM of LPSC and the Fermi level of NCM811 and provided the accurate direction of electron transfer based on energy levels, increasing the analysis's reliability. Through these revisions, the author has carefully addressed the reviewers' questions and further bolstered the paper's main arguments.

Despite revisions to several sections, this is an additional comment that a critical issue remains unresolved. The author's DFT calculations were based on pristine materials in their initial state (0% SOC), but the thermal runaway phenomenon, the main focus of analysis, occurs in a fully delithiated state corresponding to 100% SOC. This fundamental mismatch between the material state used in the calculations and the actual conditions of analysis makes the theoretical basis supporting the experimental results insufficient. The electronic properties of delithiated NCM811 differ significantly from those in the initial state, so the current calculation results alone have limitations in explaining the actual phenomenon.

Comment 1) The fundamental discrepancy between calculations and experimental conditions remains unresolved. While DFT calculations seem to assume the material is in its initial state (0% SOC), the critical thermal runaway analysis focuses on a fully delithiated state at 100% SOC. This inconsistency risks undermining the theoretical basis needed to support the experimental findings. Specifically, the cathode shown in Figure 3g appears to contain a considerable amount of lithium, raising doubt on the claim that it is fully delithiated. If the structure used by the authors is not a fully delithiated but instead represents a state where lithium is removed to the maximum extent possible while maintaining structural stability, then the exact chemical formula for this state must be clearly stated in the Computational Method section to ensure the model's accuracy and reproducibility.

Reviewer #3

(Remarks to the Author)

Authors successfully addressed the questions and comments that I have raised. Regarding the reply for the question 1 (difference of Ttr of SOC100 for full cell and composite cathode), it is recommended to add the discussion. After that, I would recommend the publication of this manuscript in Nature Communications.

Reviewer #4

(Remarks to the Author)

The authors have addressed the comments satisfactorily. The revised version is in excellent scientific standing.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed all the comments appropriately. The revised manuscript provides a thorough and insightful

discussion on the thermal stability in sulfide-based all-solid-state batteries.

Reviewer #2

(Remarks to the Author)

The authors addressed the final comments that I raised. I recommend the publication of this manuscript in Nature Communications when all other reviewers agree.

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Reviewer #1 (Remarks to the Author):

This study investigates the influence of electrochemically formed LPSC decomposition products on the thermal stability of sulfide all-solid-state batteries. The fully charged NCM exhibits thermal instability with solid electrolytes containing electrochemical decomposition products, whereas composites consisting of the charged NCM and pristine solid electrolytes show less exothermic reactions. These indicate that the decomposition of solid electrolytes during charge also contributes to thermal runaway mechanisms. Furthermore, the authors introduce Li_4GeS_4 , which has improved chemical stability with NCM, and demonstrate its higher thermal stability compared to other sulfide solid electrolytes. These findings provide novel insights into the thermal instability induced by the electrochemically formed interfacial species. Therefore, I would recommend the publication of this paper after addressing minor comments.

Response: We sincerely appreciate the reviewer's careful reading and positive evaluation of our work.

1. Rui et al. reported that thermal runaway between NCM and LPSC follows a solid-solid reaction (Energy Environ. Sci., 2023, 16, 3552-3563). This implies that the degree of contact between NCM and solid electrolytes has influence on thermal behavior. In addition, hand grinding of fully charged NCM and LPSC leads to violent burning even under inert atmospheres. How did the authors prepare the De-NCM/SE composites? Were the samples pelletized or loosely contacted?

Response: We sincerely thank the reviewer for raising this constructive question. The influence of interfacial contact between the cathode and solid electrolyte (SE) is indeed a crucial factor in the thermal behavior of the composite, as also highlighted in the work by Rui et al. Our findings further support the significant role of solid-solid interfacial reactions in the thermal runaway mechanism.

In this study, the delithiated NCM (De-NCM) material was scraped off from the current collector in an argon-filled glove box and then mixed with the solid electrolyte (SE). Specifically, De-NCM and SE were mixed at a mass ratio of 7:3, thoroughly hand-ground to ensure homogeneity, and then pressed under 312 MPa—the same pressure applied during the full cell assembly process. All compared samples in this study were prepared and tested under consistent pelleting conditions to ensure scientific rigor and comparability.

We have added a sentence in the [Materials characterization section \(paragraph 1, line 12-15\)](#) in Supplementary Information to clarify this point: “Samples (~10.0 mg) with an NCM-to-SE weight ratio of 7:3, prepared under the same pressure as the composite cathode, were placed in a 100 μ L stainless steel high-pressure sealed crucible (NETZSCH, Germany) for testing.”

2. Adiabatic ramp tests showed a rapid temperature increase of the 100% SOC composite cathode near 200 °C without further temperature rises, while several exothermic peaks appeared in DSC. Why is there a discrepancy between the two methods? In addition, the amounts of sample used for ARC and DSC were significantly different: 200 mg for ARC and 10 mg for DSC. Does this difference have influence on the thermal behavior?

Response: We thank the reviewer for these insightful questions regarding the differences between adiabatic ramp test at ARC and DSC results, as well as the influence of sample mass. These points are crucial for interpreting thermal runaway data correctly.

The apparent discrepancy between the ARC and DSC results is not due to inconsistent data, but rather arises from the fundamentally different operating principles and detection capabilities of the two techniques. The following table summarizes the key differences:

Table R1-1. Comparison of features between ARC and DSC tests.

Feature	Adiabatic Ramp test (ARC)	DSC
Principle	Adiabatic (Tries to hold $\Delta T = 0$, no heat loss). Measures self-heating rate (SHR)	Isothermal or Dynamic scanning with constant heat sink. Measures heat flow.
Condition	"Worst-case" scenario, simulating a large, insulated cell where heat cannot escape.	Small-scale, ideal for deconvoluting complex reactions under controlled heating.
Sample mass	Large (100 mg - several grams)	Small (~1-10 mg)
Key outcome	Identifies thermal runaway initiation and tracks its autocatalytic acceleration.	Identifies individual reaction steps and their onset temperatures & enthalpies.

Below are some specific reasons for the observed differences in our data:

Autocatalytic vs. Stepwise Behavior: In the ARC test, once the main exothermic reaction initiates near 200 °C, it generates heat so rapidly under adiabatic conditions that the temperature skyrockets in a single, uncontrollable thermal runaway event. The instrument's primary output is the temperature rise from this single catastrophic event; it does not resolve finer details once runaway

begins. Conversely, the DSC, with its high sensitivity to heat flow and non-adiabatic condition, excellently resolves the multiple, individual exothermic reactions that collectively contribute to the overall runaway process seen in the ARC. The several DSC peaks represent the deconvoluted reaction mechanism that is lumped together in the ARC trace.

Heat Accumulation: The large sample mass in the ARC promotes heat accumulation. The heat from one initial reaction (which might appear as a small, separate peak in DSC) is not lost and immediately contributes to heating the adjacent material, triggering the next reaction faster in a feedback loop. This leads to the observed single, sharp temperature rise.

In summary, the ARC result shows how thermal runaway propagates in a realistic, bulk scenario, while the DSC reveals the sequence of fundamental chemical reactions that cause it. The two methods are profoundly complementary, not contradictory.

Besides, the reviewer correctly identifies that the sample mass difference has a significant and intentional influence on the observed thermal behavior, and it is a critical factor in the design of these experiments.

ARC Requires a Large Sample Mass: For an adiabatic calorimeter like the ARC to function correctly and detect a self-heating rate (SHR), the heat generated by the sample must be sufficient to overcome inevitable minor heat losses to the sample container and thermocouples (phi-factor). A larger sample mass provides a higher thermal inertia and increases the total heat output, making it possible to accurately detect the onset of adiabatic thermal runaway. A 10 mg sample would be too small to be detected by most ARCs.

DSC Requires a Small Sample Mass: The DSC is designed for high-resolution thermal analysis with a small crucible. A small sample mass (~10 mg) ensures: Excellent thermal conductivity throughout the sample, minimizing internal temperature gradients. The recorded temperature is highly representative of the entire sample. The resolution of closely spaced thermal events is maximized.

Using a large amount sample in a DSC would likely result in poor resolution, broad peaks, and shifted onset temperatures due to significant thermal lag.

Therefore, the difference in sample mass is not an oversight but a deliberate choice to leverage the strengths of each instrument. The ARC with a large mass tells us if and when a full-scale runaway will occur, while the DSC with a small mass tells us why it occurs by breaking down the chemistry.

We have added a sentence in the [Materials characterization section \(paragraph 1, line 15-18\)](#) to clarify this point:

"The complementary use of ARC (with large sample mass to simulate bulk adiabatic runaway) and DSC (with small sample mass to resolve individual reactions) provides a complete picture of the thermal degradation mechanisms."

3. The authors claimed that thermal runaway mechanisms are divided into two stages. The initial heat generation is driven by reactions between delithiated NCM and electrochemically formed interfacial species. At elevated temperatures, sulfur-oxygen interdiffusion leads to bulk exothermic reactions. Although Li₄GeS₄ showed improved thermal stability, it is still unclear in which stage Li₄GeS₄ mitigated the detrimental reactions. Therefore, it would be helpful to clarify the role of Li₄GeS₄ by performing DSC and XPS on De-NCM/pristine LGS and De-NCM/4.5V- (LGS-VGCF) samples. In addition, NCM811-LGS ASSBs were cycled at 45 °C, which is higher than the operating temperature of NCM811-LPSC cells. This increased operating temperature could influence the electrochemical decomposition. Figure 5c shows a higher content of sulfate and sulfite products in the 100% SOC composite cathode compared to those in Figure 2d.

Response: We thank the reviewer for this insightful comment, which allows us to clarify the specific stage at which Li₄GeS₄ (LGS) improves thermal stability and to address the concerns regarding operating temperature and interfacial products.

As summarized in our study, thermal runaway occurs in two distinct stages:

The first exothermic stage is dominated by reactions between delithiated NCM and electrochemically formed interfacial species (e.g., –S–S–, thiophosphates), accompanied by O₂ and SO₂ release. The second stage involves direct solid–solid reactions between decomposed NCM and the bulk solid electrolyte.

Our results demonstrate that LGS primarily suppresses the first stage. As shown in Figure R1-1, the first exothermic peak is significantly reduced in the LGS-based composite (110.7 J/g) compared to the LPSC-based system (399.6 J/g). In contrast, the second-stage reaction was not markedly improved, indicating that LGS does not enhance the stability against bulk solid–solid reactions at higher temperatures.

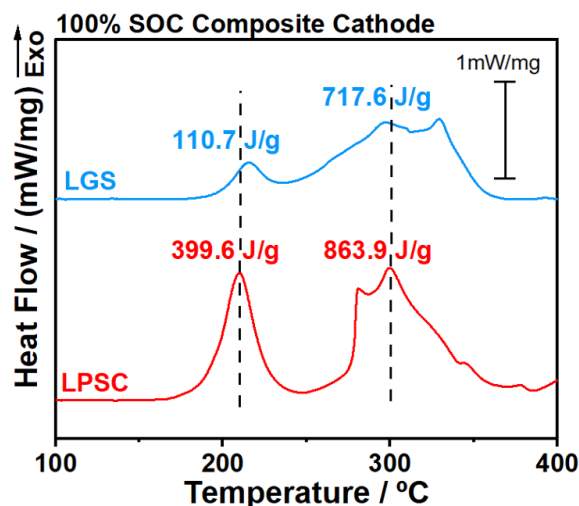


Figure R1-1. DSC curves of 100% SOC LPSC and LGS composite cathodes.

To further elucidate the function of LGS, we conducted additional experiments as suggested: XPS analysis of both De-NCM/pristine LGS and De-NCM/4.5V-(LGS-VGCF) composites (Figures R1-2) revealed that LGS undergoes notably less electrochemical decomposition than LPSC. Importantly, the formation of highly reactive species such as $-S-S-$ and $-Ge-S-Ge-$ was significantly suppressed.

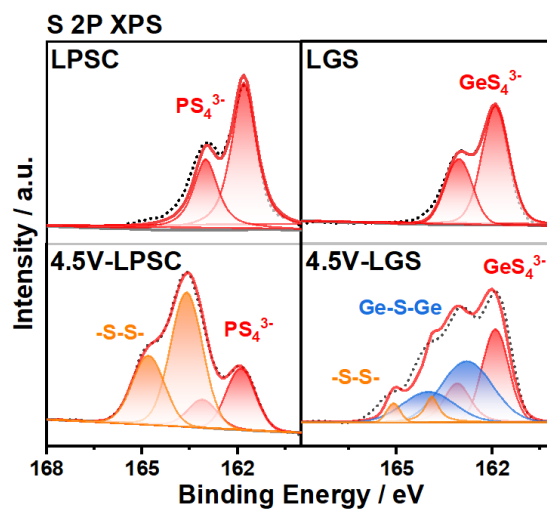


Figure R1-2. S 2p and P 2p XPS spectra for the LPSC/VGCF and LGS/VGCF before and after being charged to 4.5 V (vs. Li⁺/Li).

DSC measurements of these composites (Figure R1-3) further confirmed a marked reduction in heat release during the first stage in the LGS system, corroborating its role in inhibiting interfacial decomposition.

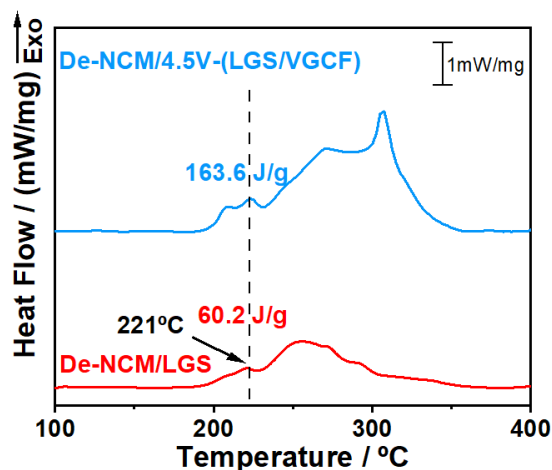


Figure R1-3. DSC curves of De-NCM/LGS and De-NCM/4.5V-(LGS/VGCF).

As to the difference in sulfate/sulfite content between Figure 5c and Figure 2d, we appreciate the reviewer's insightful observation. We agree that the elevated cycling temperature (45 °C) applied to the NCM811-LGS-based cells could promote electrochemical decomposition, leading to an increased amount of sulfate/sulfite species compared to the NCM811-LPSC cells cycled at room temperature. As rightly noted by the reviewer, we conducted additional XPS analyses on the cathode material from the NCM811-LGS cell cycled at room temperature. The results confirm that the LGS-based system exhibits a lower amount of decomposition products relative to the LPSC-based reference, which aligns with its improved thermal stability as demonstrated in our DSC and ARC tests.

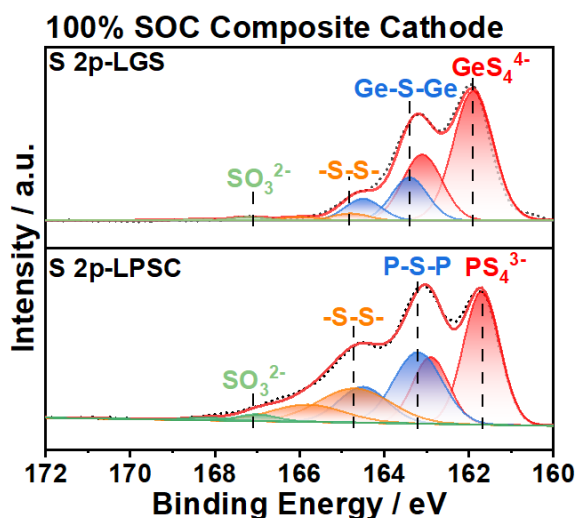


Figure R1-4. S 2p XPS spectra of the 100% SOC LGS and LPSC composite cathodes

Regarding the operating temperature used in different experiments:

All thermal safety tests (DSC and ARC) were conducted using materials harvested from cells

that were cycled under identical conditions (30 °C) and employing equivalent cell configurations (NCM-LPSC/LPSC/Li-In or NCM-LGS/LPSC/Li-In) to ensure comparability. The 45 °C cycling mentioned in the manuscript refers only to long-term electrochemical performance evaluations of full cells, and these conditions did not affect the thermal runaway tests conducted under standardized settings.

In summary, LGS enhances thermal stability mainly by suppressing the electrochemically driven interfacial decomposition at the first stage. We have incorporated these clarifications and new figures (S60-S61) into the revised manuscript (Section 2.3, Page 21): “XPS and DSC analysis of both De-NCM/pristine LGS and De-NCM/4.5V-(LGS-VGCF) composites revealed that LGS undergoes notably less electrochemical decomposition and smaller ΔH than LPSC (Figures S60-61).”

4. When the valence band edge of the solid electrolyte is above the Fermi level of the cathode, electron transfer from the solid electrolyte to the cathode leads to the oxidation of the solid electrolyte (ACS Appl. Energy Mater. 2022, 5, 2, 2045–2053).

Response: We apologize for the typographical error, it has been revised.

Manuscript (Section 2.2, Page 13): “According to solid-state band theory, the calculated valence band maximum (VBM) of LPSC was 1.47 eV higher than the Fermi level of NCM811, indicating that electron transfer from LPSC to NCM811 was energetically favorable (Figure S22).”

Supplementary Information (FigureS22): “This interfacial energy offset drives electron transferring from SE to cathode, leading to the oxidative degradation of LPSC.”

5. The sentences from line 346 to 352 need references to support it.

Response: We agree with the reviewer that the statements between lines 346 and 352 require supporting references. Appropriate citations have now been added to this section to substantiate our claims regarding the pDOS analysis.

“Furthermore, density of states (DOS) calculations revealed significant overlap between the S 3p orbitals of LPSC and the O 2p/Ni eg orbitals of NCM811 near the Fermi level (Figure S23). This overlap indicates a lower energy barrier for electron exchange, further supporting the hypothesis of strong chemical incompatibility between them. Moreover, the P 2p orbitals of LPSC also showed

considerable overlap with the O 2p/Ni eg orbitals of NCM811, suggesting a tendency for spontaneous chemical bonding (23, 24).” (Section 2.2, Page 13)

References

[23] Yanhao Dong and Ju Li. Oxide Cathodes: Functions, Instabilities, Self Healing, and Degradation Mitigations. Chemical Reviews 2023 123 (2), 811-833.

[24] Yizhou Zhu, Xingfeng He, Yifei Mo. Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations. ACS Appl. Mater. Interfaces 2015, 7, 42, 23685–23693

6. Please add a scale bar in DSC Figures and specify the carrier gas used for MS measurements.

Response: We apologize for these omissions. Scale bars have been added to all DSC figures (as shown in the representative figure listed below, others are revised in the manuscript and Supplementary Information).

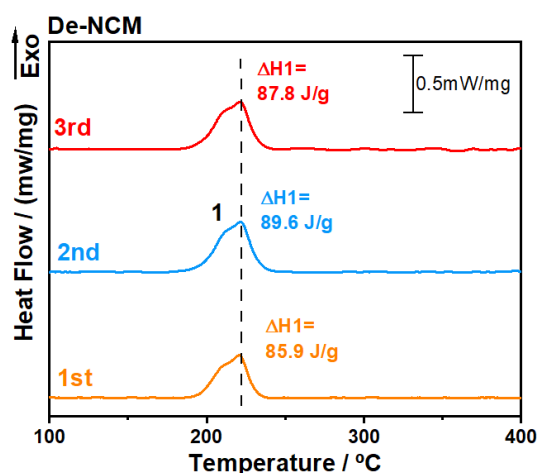


Figure R1-5. DSC of the De-NCM, repeated three times under identical conditions.
($\Delta H = 87.8 \pm 1.9 \text{ J/g}$)

Furthermore, the carrier gas used for the MS measurements has now been clearly stated in the Materials characterization section (paragraph 1, line 9-10): “All MS experiments were performed under an Ar flow at a rate of 5 mL/min.”

Reviewer #2 (Remarks to the Author):

This paper investigates thermal runaway mechanisms in sulfide-based all-solid-state batteries, focusing on NCM811/LPSC composite systems. It proposes a two-stage thermal degradation mechanism where early exothermic reactions arise from electrochemically formed interphase species, followed by bulk S-O interdiffusion at higher temperatures. Systematic thermal characterization reveals that charged cathodes (100% SOC) show greater thermal instability than discharged ones due to reactive interphase decomposition products like -S-S-, -P-S-P-, and Li₃PS₄. The study extends this to other sulfide electrolytes (LGPS, LSPSC) and suggests Li₄GeS₄ (LGS) for interface engineering, enhancing thermal safety by reducing thermodynamic driving forces for S-O exchange. DFT calculations support improved interfacial compatibility and experimental results indicate elevated thermal runaway temperatures, rising from 228°C to 312°C.

However, this paper has significant theoretical inconsistencies and methodological limitations that undermine its scientific rigor. The computational analysis focuses on pristine materials (0% SOC), while the critical experimental work centers on delithiated states (100% SOC), creating a mismatch between theory and experiment. The band theory explanation contains errors in the direction of electron transfer and inaccurately compares electronic properties without proper interface analysis. The electronic structure calculations overlook the actual reactive species crucial to the proposed mechanism, indicating a major gap in understanding. Experimental reproducibility is questionable, as thermal safety data are presented without statistical analysis, error bars, or multiple trials, which are vital for safety applications. The novelty of the Ge substitution approach is limited due to prior work by the same group, and practical validation is insufficient for real-world implementation. Furthermore, the paper exhibits numerical inconsistencies, inadequate figure descriptions, and unclear reaction energetics that further undermine its reliability. Due to these deficiencies and lack of completeness, I do not recommend this manuscript in its current form, published in Nature Communications.

Response: We sincerely thank the reviewer for their highly constructive suggestions. We acknowledge that our original manuscript did not clearly emphasize that both the AIMD and DOS calculations were performed on the delithiated NCM, same to the critical experimental situations, which may have led to misunderstanding. This point has now been clarified in the revised text. Furthermore, we have supplemented the band structure calculations with data for the delithiated

NCM to better corroborate our experimental findings. The inaccuracies regarding the direction of electron transfer have been corrected, and additional electronic structure calculations have been incorporated in response to the reviewer's comments. All relevant experiments have been repeated to ensure reproducibility. We have also included further comparative analysis regarding the Ge-substitution strategy to illustrate the differences between the two systems. Additionally, issues such as numerical inconsistencies, insufficient figure descriptions, and ambiguities in reaction energetics have been thoroughly addressed and corrected.

Below, we provide detailed responses to each specific point raised.

Comment 1) Figures 1a–1c present the ARC HWS and DSC traces for only one specimen, leaving the reproducibility of your thermal-safety metrics unclear. Please repeat the ARC-HWS and DSC tests at least three times under identical conditions (sample mass, cell pressure, HWS step length, purge gas, etc.) and report the mean $\pm$ standard deviation for the key parameters (T_{onset} , T_{tr} , and ΔH).

Response: We thank the reviewer for raising this important point regarding the reproducibility of our thermal safety data. We fully agree that demonstrating the repeatability of the ARC and DSC measurements is essential for validating the reported thermal-runaway characteristics.

In direct response to this comment, we have repeated both the ARC-HWS and DSC tests three times under identical experimental conditions—including sample mass, cell pressure, HWS step length, and purge gas. The new replicate data are listed below and provided in Supplementary (Figure S4-8, S12), which clearly displays all individual runs together with the original dataset.

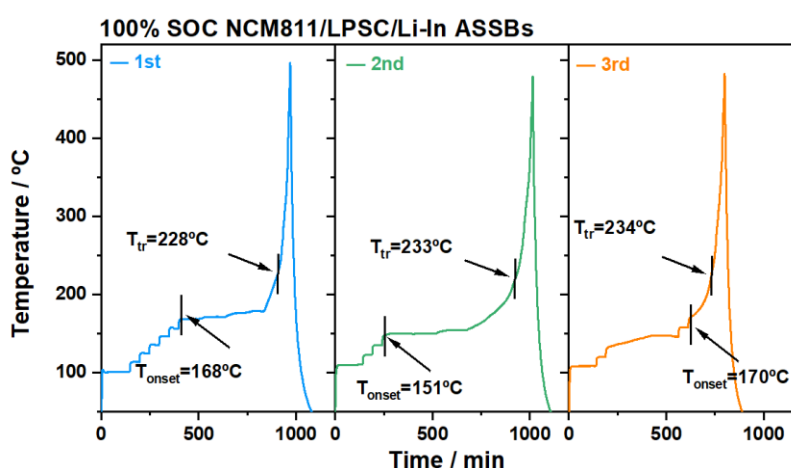


Figure R2-1. HWS curves of the 100% SOC NCM811/LPSC/Li-In ASSBs. ($T_{\text{onset}}=163.0\pm8.5^{\circ}\text{C}$; $T_{\text{tr}}=231.7\pm2.6^{\circ}\text{C}$)

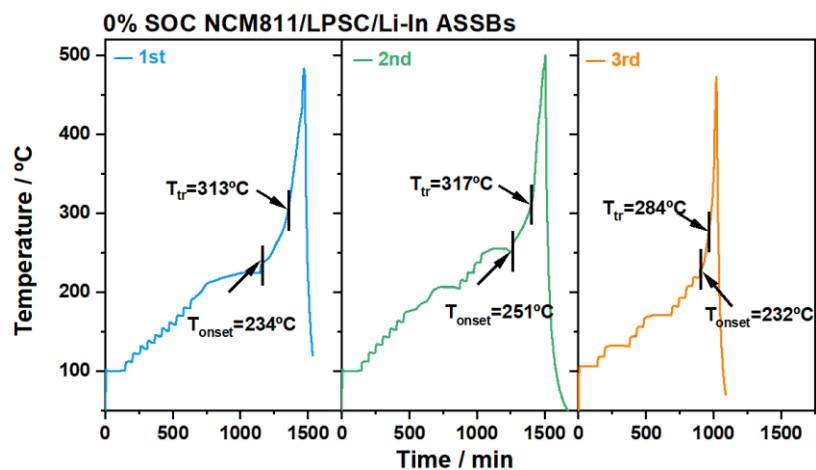


Figure R2-2. HWS curves of the 0% SOC NCM811/LPSC/Li-In ASSBs. ($T_{\text{onset}} = 239 \pm 8.5^{\circ}\text{C}$; $T_{\text{tr}} = 304.7 \pm 14.7^{\circ}\text{C}$)

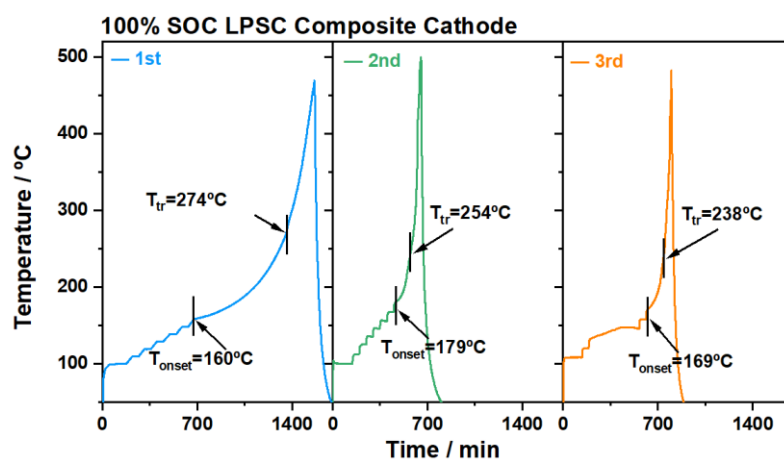


Figure R2-3. HWS curves of the 100% SOC LPSC composite cathode. ($T_{\text{onset}} = 169.3 \pm 7.8^{\circ}\text{C}$; $T_{\text{tr}} = 255.3 \pm 14.7^{\circ}\text{C}$)

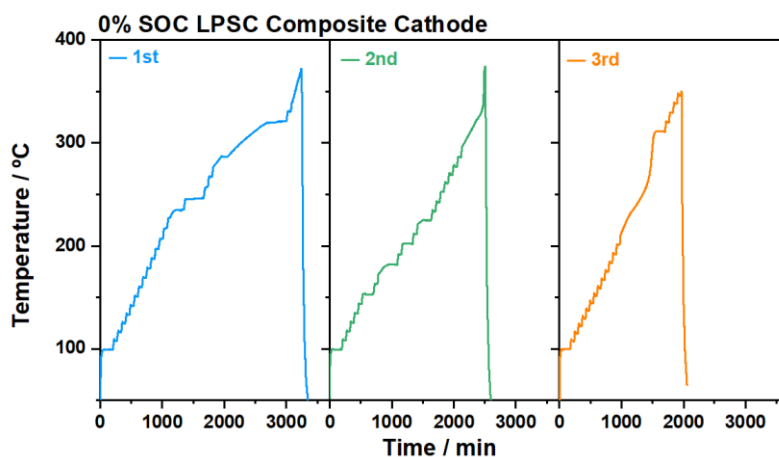


Figure R2-4. HWS curves of the 0% SOC LPSC composite cathode.

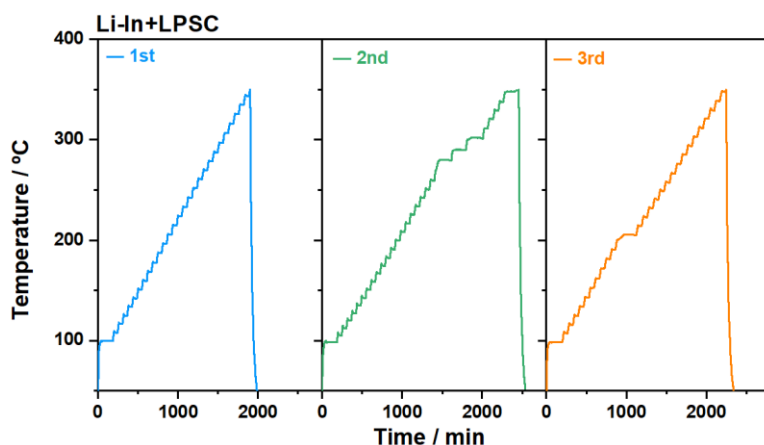


Figure R2-5. HWS curves of Li-In+LPSC.

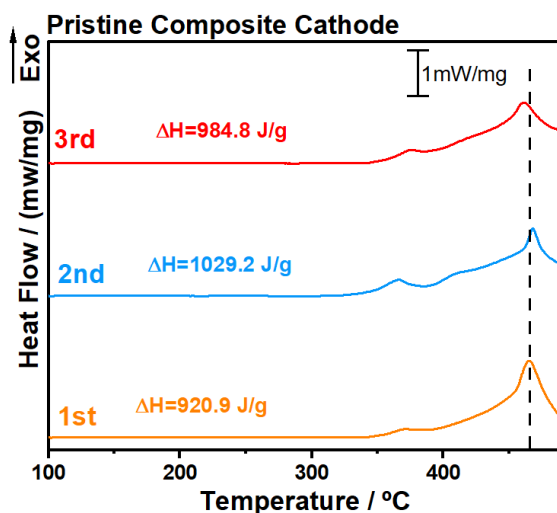


Figure R2-6. DSC of the pristine LPSC composite cathode. ($\Delta H=978.3 \pm 44.5$ J/g)

Moreover, beyond Figure 1, we have also conducted repeat experiments for **all other key thermal characterizations** presented in the study. These results, some of which are exemplarily shown in the figures below, consistently demonstrate high reproducibility and support the reliability of our conclusions.

All key thermal parameters—including onset temperature (T_{onset}), thermal runaway temperature (T_{tr}), and enthalpy change (ΔH)—are now reported as mean $\pm$ standard deviation derived from three independent measurements. These updates have been incorporated throughout the main text at the relevant locations ([S15](#), [S19](#), [S28-29](#), [S32](#), [S34-35](#), [S37](#), [S63-S65](#), and [S67](#)).

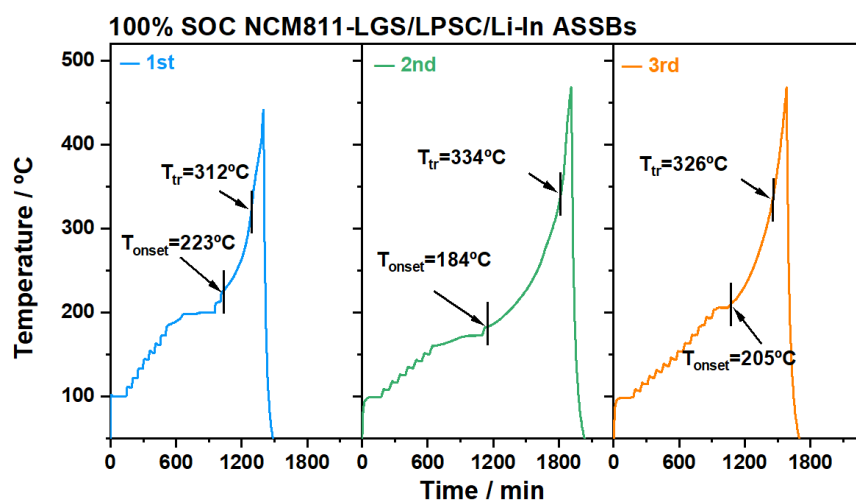


Figure R2-7. HWS curves of the 100% SOC NCM811-LGS/LPSC/Li-In ASSBs.
($T_{onset}=204.0\pm15.9^{\circ}\text{C}$; $T_{tr}=324.0\pm9.1^{\circ}\text{C}$)

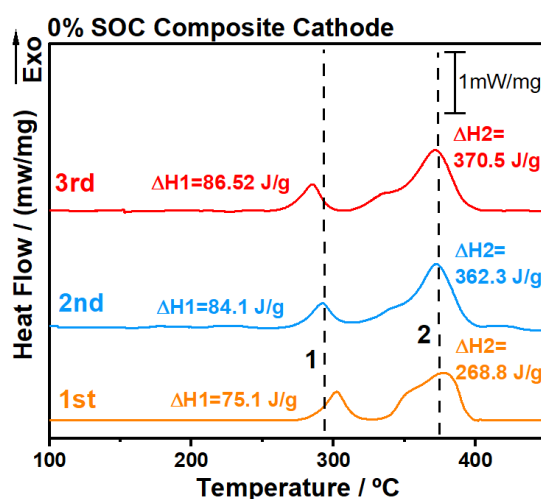


Figure R2-8. DSC of the 0% SOC LPSC composite cathode. ($\Delta H_1=81.9\pm4.9 \text{ J/g}$; $\Delta H_2=333.9\pm56.2 \text{ J/g}$)

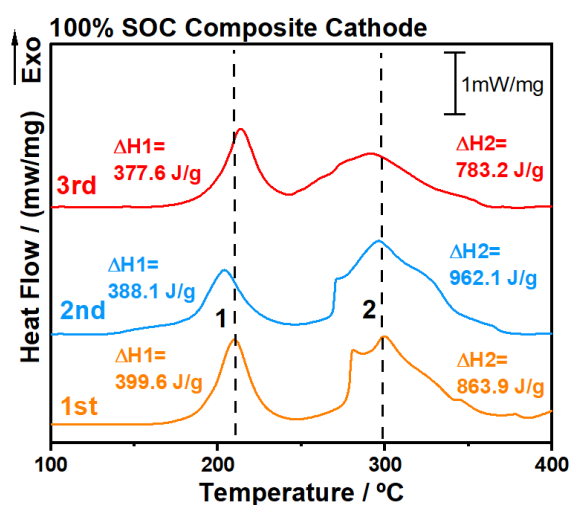


Figure R2-9. DSC of the 100% SOC LPSC composite cathode. ($\Delta H_1=381.8\pm16.4 \text{ J/g}$;
 $\Delta H_2=869.7\pm89.5 \text{ J/g}$)

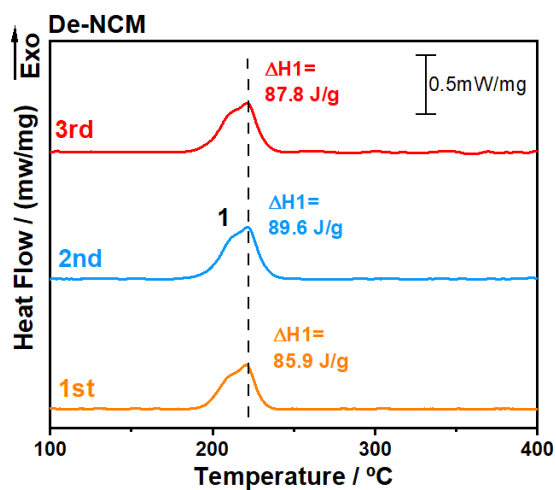


Figure R2-10. DSC of the De-NCM. ($\Delta H = 87.8 \pm 1.9 \text{ J/g}$)

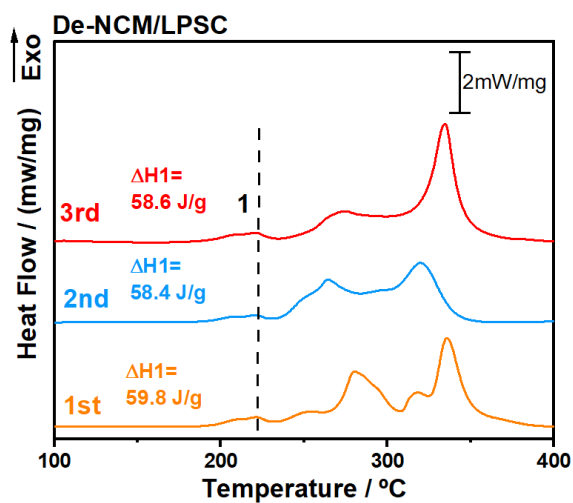


Figure R2-11. DSC of the De-NCM/LPSC. ($\Delta H_1 = 87.8 \pm 1.9 \text{ J/g}$)

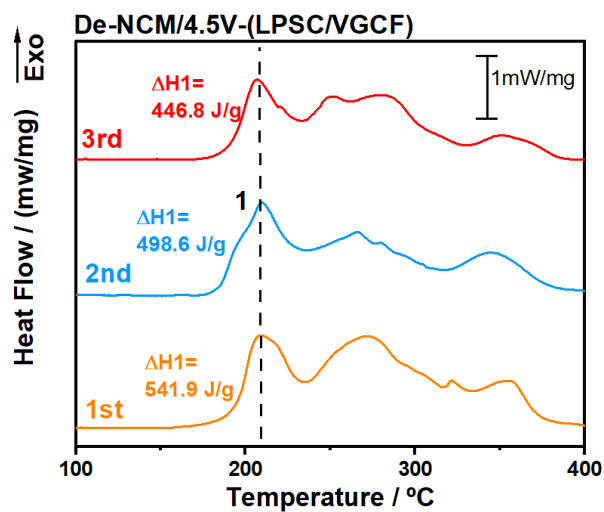


Figure R2-12. DSC of the De-NCM/4.5V-(LPSC/VGCF). ($\Delta H_1 = 495.8 \pm 47.6 \text{ J/g}$)

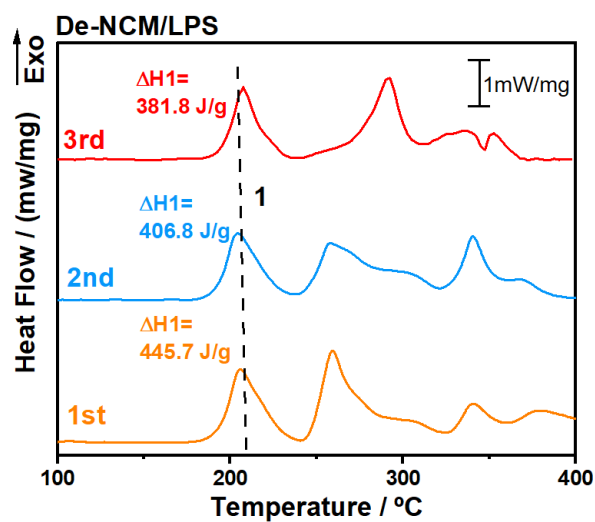


Figure R2-13. DSC of the De-NCM/LPS. ($\Delta H_f = 441.4 \pm 32.3 \text{ J/g}$)

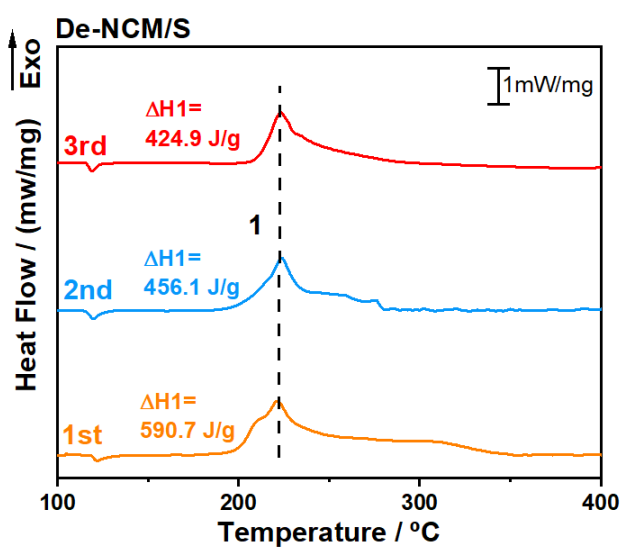


Figure R2-14. DSC of the De-NCM/S. ($\Delta H_f = 490.6 \pm 87.1 \text{ J/g}$)

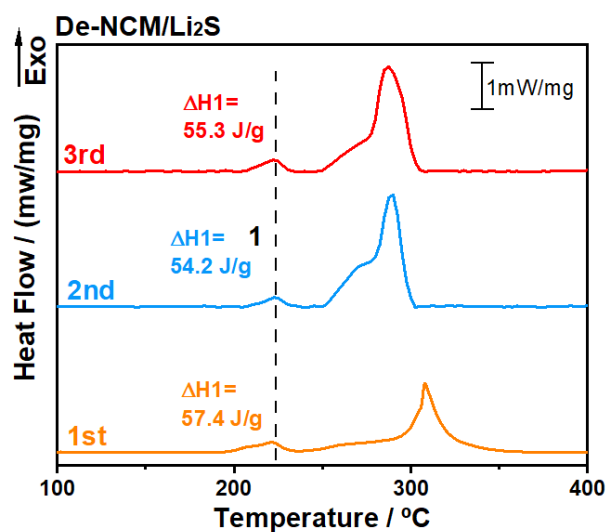


Figure R2-15. DSC of the De-NCM/Li₂S. ($\Delta H_f = 55.6 \pm 1.6 \text{ J/g}$)

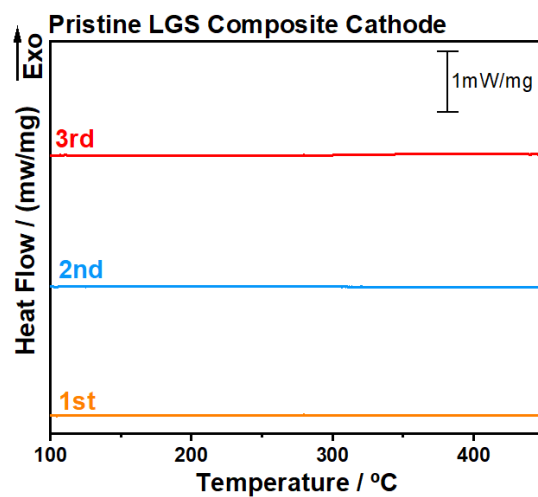


Figure R2-16. DSC of the pristine LGS composite cathode.

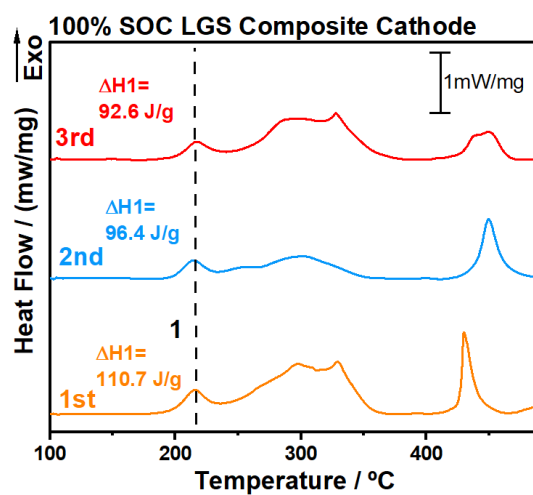


Figure R2-17. DSC of the 100% SOC composite cathode. ($\Delta H_f = 99.9 \pm 9.3 \text{ J/g}$)

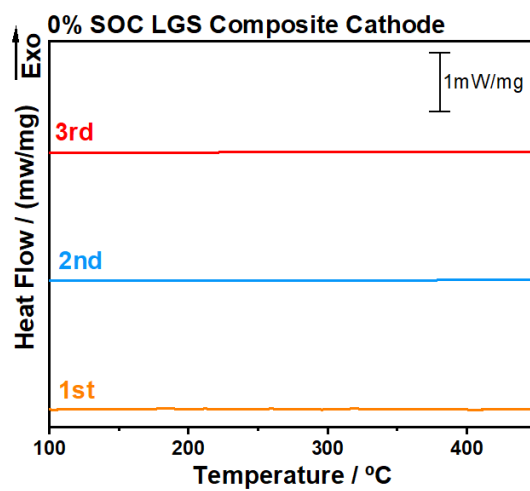


Figure R2-18. DSC of the 0% SOC LGS composite cathode.

Comment 2) There is a fundamental inconsistency between the computational and experimental approaches. The DFT calculations are performed on pristine materials representing 0% SOC conditions, while the critical thermal runaway analysis focuses on 100% SOC delithiated states. This mismatch severely undermines the theoretical justification for experimental observations, as the electronic properties of delithiated NCM811 differ significantly from the pristine state used in calculations.

Response: We thank the reviewer for raising this important concern regarding the consistency between our computational and experimental approaches. We sincerely apologize for the lack of clarity in the original manuscript, which may have led to a misunderstanding.

We would like to clarify that all AIMD and DOS calculations were in fact performed using structures representative of the delithiated NCM and LPSC, consistent with the composite cathode system studied in our thermal runaway analysis. The electronic structure analysis was conducted specifically for these delithiated states to ensure direct relevance to the experimental results.

We recognize that the figure captions did not explicitly state the delithiated state of NCM, which likely caused the misunderstanding. This has been corrected as shown below and corrected in the revised manuscript ([Figure 3g](#), [Figure S23](#)).

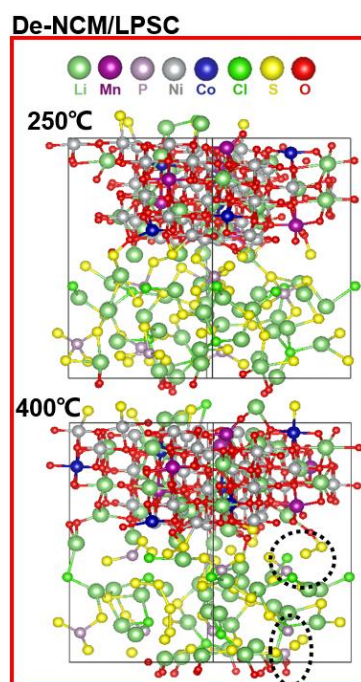


Figure 3g. AIMD simulations of the interfacial reactions between delithiated NCM811 and LPSC at 250°C, and 400°C.

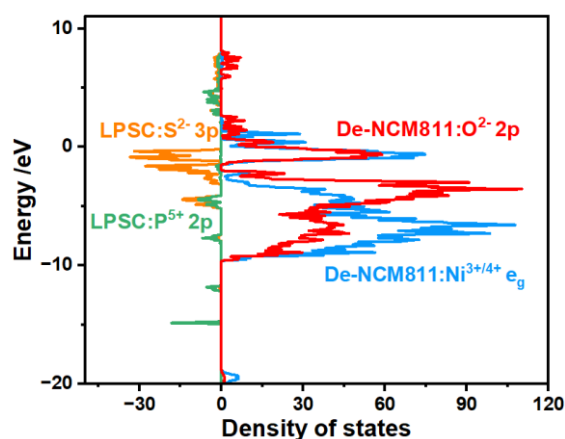


Figure R2-19. Densities of states (DOSs) of LPSC and De-NCM811.

Furthermore, to enhance consistency and clarity, we have supplemented the band alignment analysis with explicit inclusion of De-NCM, as shown in Figure R2-20 and R2-21. The results clearly indicate that the ΔE_f between LPSC and the delithiated cathode is significantly larger than that between LPSC and NCM, suggesting more severe interfacial instability between LPSC and the delithiated cathode. Moreover, the valence band maximum of LGS is lower than that of LPCL, and the corresponding ΔE_f values with both NCM and De-NCM are smaller than those of LPSC. This demonstrates that LGS exhibits improved interfacial stability compared to LPSC with both lithiated and delithiated cathodes, thus providing a more coherent connection between computational predictions and experimental observations. The new data are provided in Supporting Information (Figure S22 and S58).

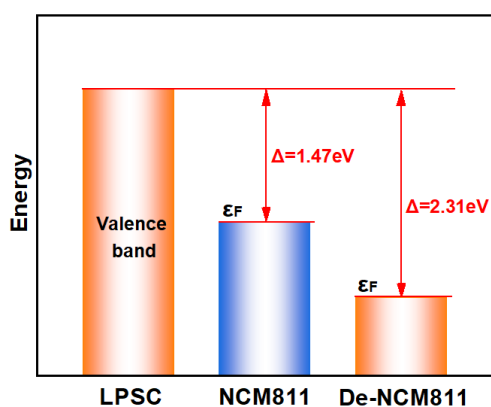


Figure R2-20. Schematic of oxidative degradation mechanism of a solid electrolyte in contact with a cathode active material based on band theory of solids.

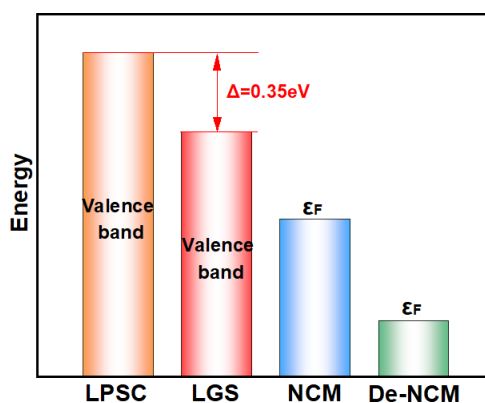


Figure R2-21. Schematic of oxidative degradation mechanism of sulfide SEs (LPSC and LGS) in contact with cathode active material (NCM811) based on band theory of solids.

These revisions affirm that our electronic structure calculations are well-aligned with the electrochemical state central to the thermal degradation study. Thank you again for prompting us to improve the presentation of our computational methodology.

Comment 3) Similar to Comment 2, there is ambiguity regarding the lithiation state of NCM811 used in the reaction energy calculations shown in Figure 5a. The authors do not specify whether the computational analysis employs delithiated NCM811 (relevant to 100% SOC conditions) or lithiated NCM811 (relevant to 0% SOC conditions). Given that the thermal runaway mechanism is critically dependent on the delithiation state, this specification is essential for the proper interpretation of the calculated energetics and their relevance to experimental conditions.

Response: We thank the reviewer for this important comment regarding the lithiation state of NCM811 in the reaction energy calculations in Figure 5a. We agree that clearly specifying the computational models is essential for interpreting the results in the context of state-of-charge-dependent thermal stability.

In the original Figure 5a, the reaction energy calculations were performed using lithiated NCM811 (0% SOC) to evaluate the intrinsic chemical compatibility between the pristine cathode and different solid electrolytes (LGS vs. LPSC). The results indicate that LGS exhibits superior interfacial stability with NCM compared to LPSC in the lithiated state.

To directly address the reviewer's question and eliminate any ambiguity, we have performed additional reaction energy calculations using delithiated NCM811 (100% SOC).

The reaction energies were analyzed using a convex hull diagram, which quantitatively evaluates the thermodynamic stability of interfaces between the cathode and solid electrolyte [1, 2].

In this approach, each interface is modeled as a pseudobinary system composed of end members A (electrolyte) and B (cathode). The x-axis represents the compositional ratio between A and B, denoted as x A + (1- x) B, while the y-axis represents the reaction energy (ΔE) of potential reaction products at various compositions. The convex hull (solid line) connects the most thermodynamically stable states across all compositions. The minimum point on each convex hull line reflects the most energetically favorable reaction pathway, and its value quantifies the thermodynamic driving force for interfacial reactions—more negative values indicate a stronger tendency for decomposition.

As shown in the new Figure R2-22, the results confirm that the reaction energy between delithiated NCM and LGS is significantly less exothermic (i.e., the reaction energy is less negative) than that between delithiated NCM and LPSC. This clearly indicates enhanced interfacial compatibility when LPSC is replaced by LGS, even under delithiated conditions.

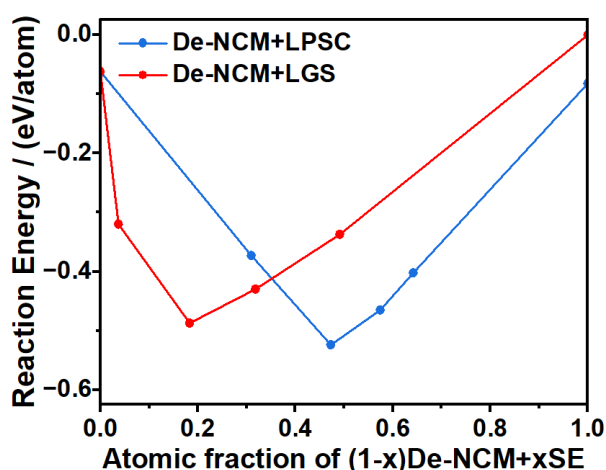


Figure R2-22. Reaction energies of De-NCM811/LPSC and De-NCM811/LGS by first-principles calculations.

We have updated this figure in the [Supplementary Information \(S57\)](#) to include both lithiated and delithiated state calculations, providing a complete picture across relevant electrochemical conditions. Thank you again for prompting us to improve the clarity and comprehensiveness of our computational analysis.

References

- [1] Nolan, A. M.; Liu, Y.; Mo, Y. Solid-state chemistries stable with high-energy cathodes for lithium-ion batteries. *ACS Energy Lett.* 2019, 4 (10), 2444–2451.
- [2] Zhu, Y.; He, X.; Mo, Y. First principles study on electrochemical and chemical stability of solid electrolyte–electrode interfaces in all-solid-state Li-ion batteries. *J. Mater. Chem. A* 2016, 4 (9), 3253–3266.

Comment 4) The electronic structure analysis is incomplete and fails to address the actual reactive species driving the thermal runaway mechanism. While the authors calculate band alignments between bulk NCM811 and LPSC, they ignore the Fermi levels and electronic properties of the key reactive intermediates (Li₃PS₄, Li₂S, Li₂S_x, -S-S-, -P-S-P-) that they identify as primary thermal runaway initiators. For a mechanism centered on electrochemical interphase decomposition, the electronic structure of these species is crucial for understanding electron transfer processes.

Response: We are deeply grateful to the reviewer for this critical and insightful comment. We fully agree that a thorough electronic structure analysis of the key reactive intermediates is essential to elucidate the electron transfer processes governing interphase decomposition and thermal runaway. Our initial submission overlooked this crucial aspect, and we sincerely apologize for the omission.

In direct response to this comment, we have conducted comprehensive first-principles calculations to determine the Fermi levels (E_f), electronic density of states (DOS), and band gaps of the major interfacial decomposition products identified in our study. The Fermi levels and band gaps of these species are summarized below:

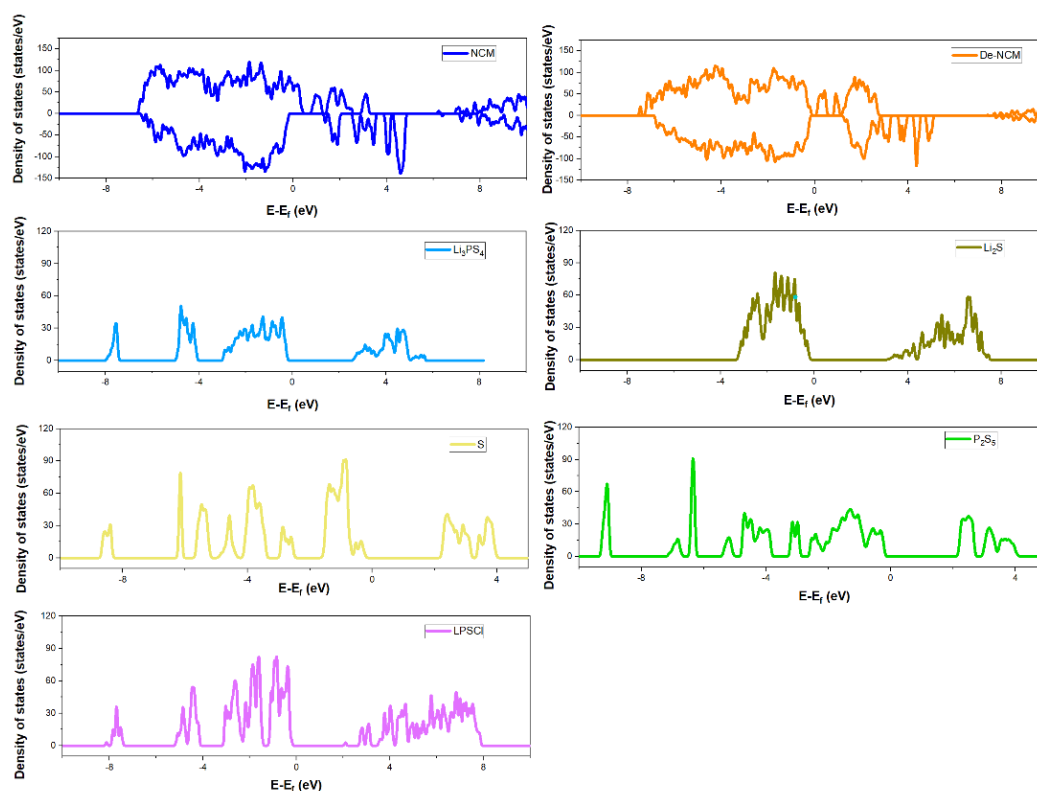


Figure R2-23. Density of states for varied reactive intermediates.

Thermodynamic Driving Force and Fermi Level Analysis

The Fermi level represents the highest occupied electronic energy level of a material. A higher E_f (vs. vacuum level set as 0 eV) indicates a stronger tendency to donate electrons, while a lower E_f signifies a stronger tendency to accept electrons. Our calculations reveal a clear hierarchy in E_f (from high to low): LPSC > Li₃PS₄ > Li₂S > NCM811 > –S–S– > P₂S₅ > De-NCM811.

This ordering is critically important: The highly oxidized sulfur intermediates (e.g., polysulfides, –P–S–P– motifs) possess higher E_f than both the delithiated cathode (De-NCM811) and stable Li₃PS₄. This creates a strong thermodynamic driving force for spontaneous electron transfer from these intermediates into the empty states of De-NCM811.

Notably, De-NCM811 has the lowest E_f (-6.13 eV), indicating it is a potent electron acceptor. This property, acquired upon delithiation, makes it prone to extracting electrons from other species, directly driving interfacial degradation.

Furthermore, the degradation product P₂S₅ has an extremely low E_f (-6.07 eV), making it a strong electron sink. Its formation from LPSC decomposition could create a vicious cycle, further accelerating interfacial reactions by "capturing" electrons.

Table R2-1. Summary of Fermi Level and Band Gap for key reactive intermediates

Species	Fermi Level (eV vs. Vacuum Level)	Band Gap (eV)
NCM	-5.2950	0.454
De-NCM	-6.1345	0.078
LPSC	-3.8207	2.320
Li ₃ PS ₄	-4.1658	2.803
Li ₂ S	-4.9028	3.348
Sulfur	-5.5304	2.434
P ₂ S ₅	-6.0734	2.378

Band Gap Analysis

The band gap (E_g), the energy difference between the valence band maximum and conduction band minimum, directly determines a material's electronic conductivity. The calculated E_g values (from small to large) are: De-NCM811 (0.078 eV) < NCM811 (0.454 eV) < LPSC (2.32 eV) < P₂S₅

(2.38 eV) < -S-S- (2.43 eV) < Li₃PS₄ (2.80 eV) < Li₂S (3.35 eV).

De-NCM811 exhibits a vanishingly small band gap (0.078 eV), indicating metallic character and facilitating rapid electron transport. This explains the high electronic conductivity of the decomposed cathode interface. In contrast, stable final products like Li₂S and Li₃PS₄ are wide-bandgap insulators, which would severely hinder electron flow and eventually passivate the interface. The initiating intermediates (e.g., polysulfides) have moderate band gaps, but their higher E_f and the conductive De-NCM811 surface enable rapid electron transfer kinetics.

The interfacial instability can be understood from the alignment: the large E_f difference between LPSC (-3.82 eV) and De-NCM811 (-6.13 eV), amounting to 2.31 eV, is a primary driver for electron transfer from the electrolyte to the cathode, leading to LPSC oxidation. The degradation of LPSC into intermediates with lower E_f (e.g., Li₃PS₄, P₂S₅) and the simultaneous formation of a metallic De-NCM811 surface create a perfect storm for a self-accelerating decomposition loop.

We acknowledge that the actual interface is a complex system influenced by factors like morphology, nanocrystallinity, and ion transport, which may cause deviations from our idealized calculations. However, by identifying the key electronic descriptors—Fermi level and band gap (thermodynamic driving force)—our analysis robustly identifies the species most likely to initiate catastrophic failure. This significantly strengthens our mechanistic proposal by directly linking material identity to electronic function.

We have added these new results, the table, and a detailed discussion to the revised manuscript (Section 2.2, Page 16) and Supporting Information (Table S2).

Table S2 Summary of Fermi Level and Band Gap for key reactive intermediates

Species	Fermi Level (eV vs. Vacuum Level)	Band Gap (eV)
NCM	-5.2950	0.454
De-NCM	-6.1345	0.078
LPSC	-3.8207	2.320
Li ₃ PS ₄	-4.1658	2.803
Li ₂ S	-4.9028	3.348
Sulfur	-5.5304	2.434
P ₂ S ₅	-6.0734	2.378

The Fermi level (E_f) shows how easily a material gives or takes electrons. A high E_f means it likes to donate electrons, while a low E_f means it accepts electrons. E_f (from highest to lowest): LPSC > Li₃PS₄ > Li₂S > NCM811 > -S-S- > P₂S₅ > De-NCM811. Highly oxidized sulfur intermediates have high E_f , while the delithiated cathode (De-NCM811) has the lowest E_f (-6.13 eV). This large difference drives electrons to spontaneously flow from the intermediates into De-NCM811, causing degradation. The band gap (E_g) shows how well a material conducts electricity. De-NCM811 has a very small band gap (0.078 eV), making it highly conductive. This helps electrons move quickly and speeds up reactions. In contrast, stable products like Li₂S have large band gaps and act as insulators, which would normally slow down reactions.

In short: the big difference in E_f drives electron transfer, and the small band gap of De-NCM811 allows fast electron movement. From a theoretical perspective, they together create a self-accelerating degradation cycle at the interface.

Comment 5) The band theory analysis contains fundamental conceptual errors in explaining electron transfer mechanisms. The authors state that "electron transfer from NCM811 to LPSC was energetically favorable" based on LPSC's VBM being 1.47 eV higher than NCM811's Fermi level. However, this interpretation is incorrect: electrons naturally flow from higher to lower energy levels, so if LPSC's VBM is higher than NCM811's Fermi level, electron transfer should occur from LPSC to NCM811, not the reverse. Furthermore, the authors inappropriately compare VBM (a material property of LPSC) with the Fermi level (a material property of NCM811) without a proper band alignment analysis that accounts for interface formation, band bending, and equilibrium conditions.

Response: We thank the reviewer for catching this critical conceptual error in our explanation of the electron transfer mechanism. The reviewer is absolutely correct: electrons transfer from a higher energy level to a lower one. We apologize for this error and have carefully revised the text to ensure the electron transfer direction is described accurately.

Manuscript (Section 2.2, Page 13): "According to solid-state band theory, the calculated valence band maximum (VBM) of LPSC was 1.47 eV higher than the Fermi level of NCM811, indicating that electron transfer from LPSC to NCM811 was energetically favorable (Figure S22)."

Supplementary Information (FigureS22): "This interfacial energy offset drives electron transferring from SE to cathode, leading to the oxidative degradation of LPSC."

As to the band alignment, we apologize for not clarifying in the article that the comparison of their valence band maxima (VBM) and Fermi levels was conducted after band alignment using the vacuum slab model [1, 2]. The Fermi levels of two materials obtained through VASP calculations cannot be directly compared due to the absence of a unified reference point. We employed a vacuum slab model to calculate the energy difference between the vacuum level and the Fermi level (i.e., the work function), selecting crystallographic planes with the lowest surface energy as our computational models. By aligning the vacuum levels of both materials under this vacuum slab model as a common reference benchmark and setting them as the energy zero point, we obtained and compared the numerical values of the materials' Fermi levels relative to the vacuum level. This approach enables a meaningful comparison of the Fermi levels or VBM between the two materials.

This clarification has been added to Supporting Information ([1.5. Calculation method](#)).

References

- [1] Swift, M. W.; Qi, Y. First-Principles Prediction of Potentials and Space-Charge Layers in All-Solid-State Batteries. *Phys. Rev. Lett.* 2019, 122 (16), 167701(167701–167706).
- [2] Swift, M. W.; Jagad, H.; Park, J.; Qie, Y.; Wu, Y.; Qi, Y. Predicting low-impedance interfaces for solid-state batteries. *Curr. Opin. Solid State Mater. Sci.* 2022, 26 (3), 100990.

Comment 6) The novelty of the proposed Ge substitution strategy is questionable given that the role of Ge in improving sulfide electrolyte stability has been previously established by the same research group's earlier publications, Kim et al. [13] The authors should clearly articulate what new insights or improvements their Li₄GeS₄ approach provides beyond existing Ge-based solutions and provide adequate differentiation from prior work.

Response: We thank the reviewer for raising this important point regarding the novelty of our Ge-substitution strategy. We fully acknowledge that previous studies have indicated the beneficial role of Ge in enhancing the stability of sulfide electrolytes. Nevertheless, our study introduces several conceptual and practical advances that extend significantly beyond prior Ge-containing systems such as LGPS (Li₁₀GeP₂S₁₂).

As the reviewer rightly noted, Kim et al. previously investigated Ge substitution within the LGPS structure, which still contains redox-active PS₄³⁻ units that are prone to electrochemical oxidation and thermal degradation. Although LGPS exhibits high ionic conductivity, it does not

fundamentally address the thermochemical instability at the cathode interface. This is corroborated by our experimental results, which show that the LGPS system still undergoes violent thermal runaway at the cathode/solid electrolyte interface.

In contrast, our approach utilizes Li_4GeS_4 (LGS), a phosphorus-free compound. Based on Hard-Soft Acid-Base principles, Ge^{4+} acts as a softer acid compared to P^{5+} , resulting in reduced reactivity toward oxygen released from delithiated NCM cathodes. This leads to markedly improved interfacial compatibility with oxide cathodes. Moreover, both our experimental results and theoretical calculations (Figure 5a, FigureS43) demonstrate that LGS effectively suppresses the initial exothermic reactions between the cathode and solid electrolyte.

Critically, we have developed an innovative cell architecture: LGS is deployed solely as a stabilizing additive within the composite cathode, while LPSC is retained as the bulk solid electrolyte. This design harnesses the high ionic conductivity of LPSC while avoiding the poor anode compatibility of LGS. It is well established that certain sulfide solid electrolytes (e.g., LGPS) react severely with lithium metal, forming mixed-conducting interphases (MCI) that lead to continuous decomposition and accelerated thermal failure [1-3]. Although LGS shows improved stability against oxide cathodes, it exhibits high impedance and poor compatibility when in direct contact with lithium metal anodes, as confirmed by our XPS analysis (Figure R2-24). The reduction of Ge species upon contact with lithium results in high interfacial resistance and rapid degradation. Precisely for this reason, we designed a hybrid architecture that confines LGS to the cathode side—preventing direct contact with the anode—while leveraging its ability to suppress cathode-side parasitic reactions.

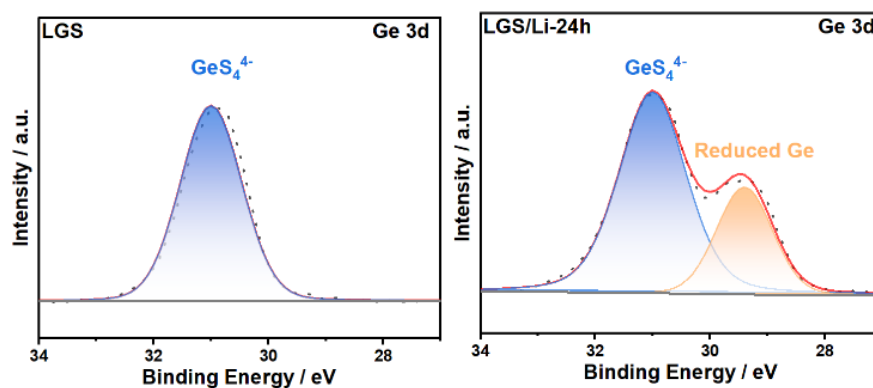


Figure R2-24. Ge 3d XPS spectra of LGS and LGS/Li pressed into tablets after 24 hours.

Thus, the novelty of our work lies not simply in the use of Ge, but in: (1) The application of phosphorus-free Li_4GeS_4 as an interfacial stabilizer; (2) A hybrid electrolyte design that decouples interface stabilization from bulk ion transport; (3) The explicit demonstration of suppressed early-stage exothermic reactions and enhanced overall safety, without compromising room-temperature electrochemical performance.

Moreover, the primary contribution of this work is not merely another Ge-substituted electrolyte, but a fundamental and detailed understanding of interfacial thermal failure mechanisms in sulfide-based all-solid-state batteries. This understanding informed a rational material and cell design strategy. The coating and electrolyte modifications presented serve as validations and applications of these insights, rather than constituting the central focus.

We have revised the manuscript to clarify these points and better emphasize the conceptual and practical advancements beyond earlier Ge-based systems (Figure S59).

Thank you once again for this insightful comment.

References

- [1] Zhao, J.; Zhao, C.; Zhu, J. et al. Size-Dependent Chemomechanical Failure of Sulfide Solid Electrolyte Particles during Electrochemical Reaction with Lithium. *Nano Lett.*, 2022, 22(1): 411-418.
- [2] Wenzel, S.; Randau, S.; Leichtweiß, T. et al. Direct Observation of the Interfacial Instability of the Fast Ionic Conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ at the Lithium Metal Anode. *Chem. Mater.*, 2016, 28(7): 2400-2407.
- [3] Yan, J.; Yao, J.; Zhao, J. et al. Revealing the Thermal Stability of the Li/Sulfide Solid Electrolyte Interface at Atomic Scale via Cryogenic Electron Microscopy. *Adv. Funct. Mater.*, 2025, 35: 2421918.

Comment 7) There is a numerical inconsistency in the reported Tonset. The authors state "Post-cycling 0% SOC LGS composites maintained stability to 450°C, contrasting with LPSC's 303°C exothermic initiation (Figure 5d vs 2a)" and "For the 0% SOC sample, two exothermic events were recorded at 303°C ($\Delta H=75.1$ J/g) and 379°C ($\Delta H=268.8$ J/g) (Figure 2a)." However, Figure 2a shows the onset temperature as 302°C, not 303°C as reported in the text. This discrepancy requires correction for accuracy.

Response: Thank you for highlighting this discrepancy. The value of 303°C mentioned in the text was a typographical error. The correct onset temperature, as clearly indicated in Figure 2a, is 302°C. This has been corrected in the revised manuscript and listed below to ensure full consistency between the text and the figure. We have further conducted a full-text review to ensure that no

similar errors are present. We appreciate your careful attention to the details.

“For the 0% SOC sample, two exothermic events were recorded at 302 °C ($\Delta H=75.1 \text{ J}\cdot\text{g}^{-1}$) and 379 °C ($\Delta H=268.8 \text{ J}\cdot\text{g}^{-1}$) (Figure 2a).” (Section 2.2, Page 9-10)

“Post-cycling 0% SOC LGS composites maintained stability to 450 °C, contrasting with LPSC's 302 °C exothermic initiation (Figure 5d vs 2a).” (Section 2.2, Page 21)

Comment 8) The manuscript contains inconsistent abbreviation usage. The authors define "valence band maximum (VBM)" on page 4, but subsequently use the full term again in "the calculated valence band maximum (VBM) of LPSC was 1.47 eV higher than the Fermi level of NCM811" (Figure S14). According to standard scientific writing conventions, once an abbreviation is defined, it should be used consistently throughout the manuscript rather than alternating between full terms and abbreviations.

Response: We thank the reviewer for this careful reading and for pointing out the inconsistent use of abbreviations. The reviewer is absolutely correct to highlight this deviation from standard scientific writing conventions.

We have now carefully reviewed the entire manuscript and standardized the terminology. The abbreviation "VBM" (valence band maximum) is now used consistently after its initial definition. The specific sentence in the caption of Figure S22 (or the relevant section in the main text) has been corrected to: “...the calculated VBM of LPSC was 1.47 eV higher than the Fermi level of NCM811.”

We apologize for this oversight and are grateful to the reviewer for helping us improve the clarity and professionalism of our manuscript.

Comment 9) Figure 4b lacks any description or discussion in the manuscript text. The authors present this figure without adequate explanation of its content, methodology, or relevance to the overall mechanism. This omission leaves readers unable to interpret the significance of the data presented, representing an incomplete presentation of the results.

Response: We thank the reviewer for pointing out this significant omission. We sincerely apologize for the lack of explanation for Figure 4b in the original manuscript, which hindered the readers' ability to interpret its significance.

In the revised manuscript, we have now added a comprehensive description and discussion of Figure 4b in the revised manuscript to fully explain its methodology, content, and critical role in

supporting the proposed mechanism, as presented below. (Section 2.2 Page 17-18)

The universal applicability of the thermal degradation mechanism across different sulfide solid electrolytes was systematically evaluated (Figure 4b). Specifically, we extended our investigation to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) and $\text{Li}_{9.54}\text{Si}_{11.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ (LSPSC) using the same methodology applied to LPSC. Composite cathodes were prepared in both the pristine state (De-NCM mixed with pristine SE) and the electrochemically decomposed state (De-NCM mixed with SE charged to 4.5 V within a VGCF composite). The thermal behavior of these systems was subsequently characterized using adiabatic calorimetry and gas analysis.

Both fully charged LGPS- and LSPSC-based composites exhibit significant self-heating initiating near 202 °C and 199 °C, respectively, closely matching the behavior of the LPSC system (199 °C) (Figure S43-S46). The first exothermic peak releases 395.5 J/g for the charged LGPS-VGCF composite and 419.9 J/g for the LSPSC-based counterpart. Crucially, the majority of this heat (246.3 J/g and 270.7 J/g, respectively) originates from the reaction between De-NCM and the electrochemically generated interphase species (e.g., oxidized sulfur and phosphorus compounds), rather than with the pristine electrolytes (Figure S47). This initial reaction stage is accompanied by significant SO_2 evolution, as confirmed by mass spectrometry (Figure S48). In stark contrast, control samples containing De-NCM mixed with the pristine (uncharged) LGPS or LSPSC powders showed negligible exothermic activity or gas release. These results universally confirm that the primary trigger for thermal runaway is the reaction between the delithiated cathode and the metastable decomposition products formed at the interface during high-voltage charging, not the reaction with the bulk, pristine solid electrolyte. This validates the generalizability of our proposed degradation roadmap across different sulfide electrolytes.

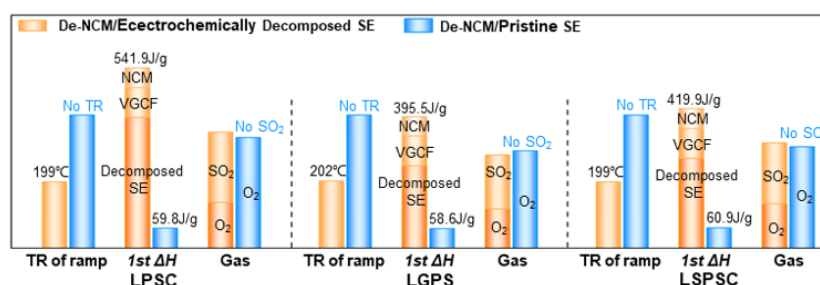


Figure 4b. Thermal behaviors between delithiated NCM811 (De-NCM) and sulfide SEs

Reviewer #3 (Remarks to the Author):

This manuscript investigates the thermal stability of sulfide-based all-solid-state batteries and elucidates the origin of thermal runaway, which is triggered by the interaction between the delithiated cathode and electrochemically decomposed LPSC. Furthermore, the authors provide insightful analysis on the role of VGCF in enhancing thermal safety, which is particularly meaningful for understanding how each component contributes to the overall thermal stability of ASSBs.

The study offers valuable insight into the safety aspects of sulfide-based solid-state batteries and makes a significant contribution by demonstrating that electrochemical decomposition products of the solid electrolyte at the cathode interface play a critical role in determining thermal stability. I believe this work is highly meaningful and recommend it for publication, pending satisfactory responses to the following comments and questions.

Response: We sincerely thank the reviewer for their positive evaluation of our work and their supportive comments regarding the insights into thermal runaway mechanisms of sulfide-based all-solid-state batteries. Below we provide point-by-point responses to all comments raised.

Q1. If the thermal stability is mainly dependent on the cathode interfacial reaction as authors suggested, then, what is the origin of the difference of T_{tr} of SOC 100 between full cell and composite cathode as shown in Figure 1a and 1b. Additionally, even the HWS curve of SOC 0 between full cell and composite cathode is seems to be different. Is there any interaction between cathode or anode (like cross-talk)?

Response: We thank the reviewer for this insightful question regarding the differences in thermal behavior between the full cell and the composite cathode. We fully agree that the thermal stability of a full cell is influenced by multiple interrelated factors.

The observed differences in the thermal runaway trigger temperature (T_{tr}) and the Heat-Wait-Search (HWS) profiles between the full cell and the cathode composite (at both 0% and 100% SOC) can be attributed to several effects, with electrode crosstalk being a primary factor. As correctly noted by the reviewer and previously elucidated in liquid electrolyte systems [1,2], oxygen species (O_2) released from the delithiated NCM at elevated temperatures can migrate through solid state electrolyte to the anode and participate in highly exothermic reactions, thereby intensifying the

severity and altering the thermal runaway behavior in full cells, as also reported by Zhang Qiang et al in thermal runaways of solid state batteries [3]. Furthermore, our preliminary studies suggest that elemental sulfur present at the interface may also participate in cross-reactions with the anode [4]. Additional contributors include interfacial reactions between the anode and solid electrolyte, self-heating due to micro-shorts, and overall cell architecture.

Moreover, differences in experimental conditions between material-level and cell-level tests play a significant role. For material-level tests, the composite cathode was sealed in a small, confined vessel, representing a closed system. In contrast, during cell-level tests, the battery casing may rupture at high temperatures, effectively converting the system into an open one, which further influences gas release and heat accumulation.

Our study focuses specifically on the cathode interface because our data indicate that exothermic reactions originating from the cathode/electrolyte interface occur earlier and are more intense, serving as the primary trigger for the thermal runaway cascade. While crosstalk and anode-related reactions modulate the overall process, understanding and mitigating this initial cathode-driven exothermic event are crucial for improving overall cell safety. Therefore, we concentrate on decoupling the reaction pathways at the cathode to develop targeted safety strategies.

Reference

- [1] L. Huang, G. Xu, X. Du, et al., Uncovering LiH triggered thermal runaway mechanism of a high-energy LiNi_{0.5}Co_{0.2}Mn_{0.3} O₂/graphite pouch cell. *Advanced Science*, 2021, 8: 2100676.
- [2] X. Liu, D. Ren, H. Hsu, et al., Thermal runaway of lithium-ion batteries without internal short circuit. *Joule*, 2018, 2(10): 2047-2064.
- [3] Y. Li, X. Liu, L. Wang, et al., Thermal runaway mechanism of lithium-ion battery with LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ cathode materials. *Nano Energy*, 2021, 85: 105878.
- [4] L. Huang, T. Lu, G. Xu, X. et al., Thermal runaway routes of large-format lithium-sulfur pouch cell batteries. *Joule*, 2022, 6(4): 906-922.

Q2. According to the author's insists, the first exothermic reaction is due to the decomposition of interphase. Given the chemical composition of interphase is nearly same regardless of SOC (0 or 100) as shown in XPS (Fig 2b, d), can you explain the reason of decomposition temperature composite with SOC 100 is lower than composite with SOC 0? If the delithiated cathode participate in decomposition of interphase, what is the exact reaction mechanism? According to the references,

SOC 100 cathode can also evolve the O₂ gas from the cathode when it converts to the spinel phase from layered structure. Then, is the reaction between O₂ gas and interphase? In addition, the reason should be explained that gaseous product is evolved only at the first step of exothermic reaction not the second step of rock salt phase transition where the much more amount of O₂ gas can be evolved.

Response: We thank the reviewer for this insightful question regarding the difference in decomposition temperature between the 0% and 100% SOC composites and the specific role of the delithiated cathode.

The key reason for the lower decomposition temperature of the 100% SOC composite lies in the thermodynamic instability of the highly delithiated NCM cathode, which actively participates in the interfacial reactions. Although the chemical composition of the interphase is similar at both SOC (as shown by XPS in Fig. 2b, d), the delithiated NCM811 at 100% SOC acts as a strong oxidant, significantly reducing the activation energy required for the decomposition of interphase species.

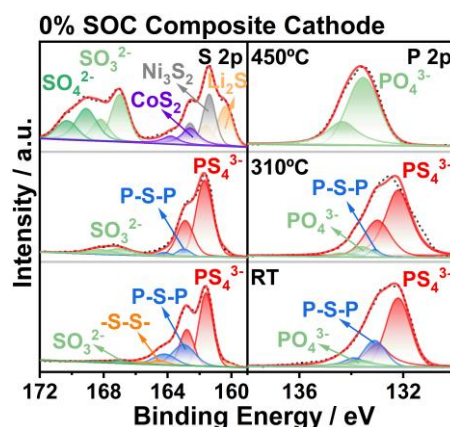


Figure 2b. S 2p and P 2p XPS spectra of the 0% SOC composite cathode at room temperature (RT, 25 °C), 310 °C, and 450 °C.

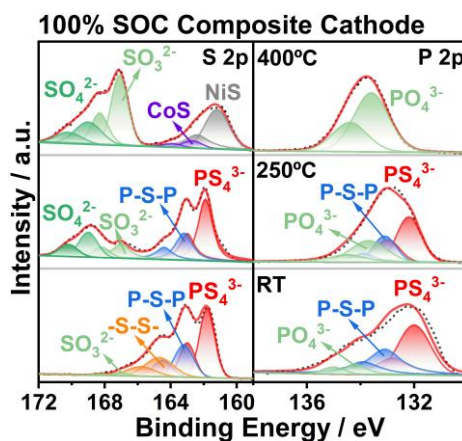


Figure 2d. S 2p and P 2p XPS spectra of the 100% SOC composite cathode at RT, 250 °C, and 400 °C.

The exact reaction mechanism involves reactive oxygen species (O) released from the delithiated NCM reacting with interphase compounds such as -S-S- , Li_3PS_4 , and -P-S-P- . This leads to the formation of sulfates, phosphates, and the release of SO_2 , as supported by our DSC and MS data (Figs. 3h–3i and R3-1).

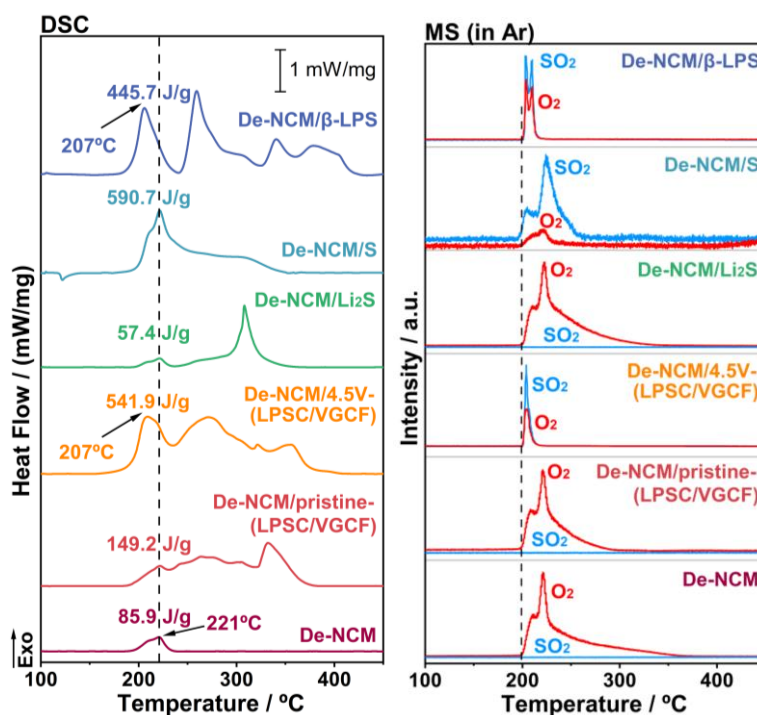


Figure 3h-3i. (h) DSC curves of different materials with delithiated NCM811 (De-NCM). (i) MS curves of different materials with delithiated NCM811.

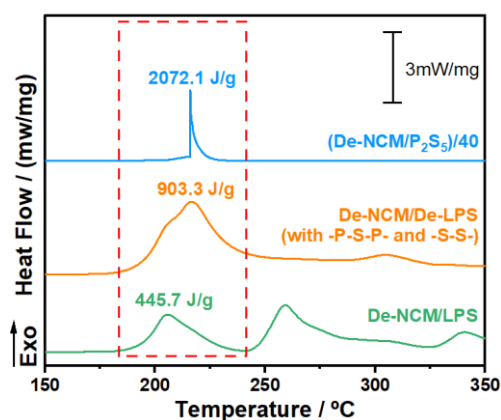


Figure R3-1. DSC profiles of β - Li_3PS_4 (LPS) and delithiated NCM811 (LPS and delithiated NCM811 in a weight ratio of 3:7); delithiated- β - Li_3PS_4 (De-LPS, including -P-S-P- and -S-S-) and delithiated NCM811 (De-LPS and delithiated NCM811 in a weight ratio of 3:7); P_2S_5 and delithiated NCM811 (P_2S_5 and delithiated NCM811 in a weight ratio of 3:7).

To unequivocally demonstrate that the oxygen source is lattice oxygen from NCM rather than gaseous O₂, we conducted an isotope labeling experiment: the 100% SOC composite was heated under an ¹⁸O₂ atmosphere, and the evolved gases were monitored in situ. The results showed that the SO₂ produced contained almost exclusively ¹⁶O, confirming that the oxygen originates from the NCM lattice and not from atmospheric O₂ (Fig. R3-2).

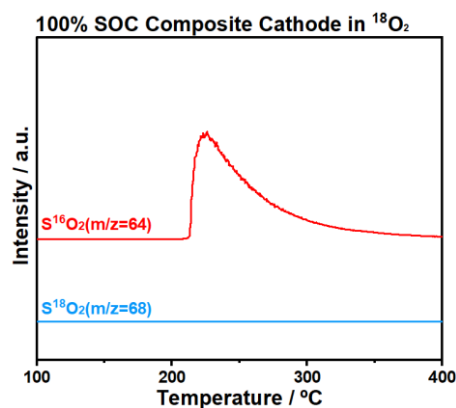


Figure R3-2. MS curves of the 100% SOC LPSC composite cathode in ¹⁸O₂.

In contrast, the lithiated NCM (0% SOC) does not release reactive oxygen species and therefore does not participate in such reactions. For the 0% SOC composite, we further explored the reaction mechanism through additional DSC tests. The results indicate that the exothermic reactions are initiated by the interaction between –P–S–P– species and lithiated NCM, as detailed in our response to Comment 4 below.

Regarding gas evolution during the two exothermic stages:

The first stage involves the oxidation of degraded sulfur species (e.g., disulfides (–S–S–) in the interphase) by atomic oxygen, leading to SO₂ release.

In the second stage, after the reactive sulfur species are depleted, the process transitions to a solid–solid interaction between decomposed NCM and LPSC, accompanied by sulfur–oxygen interdiffusion. This stage consumes lattice oxygen to form non-gaseous products such as sulfates and sulfites, explaining the absence of significant gas release. The difference in gas evolution between the two stages stems from the distinct chemical nature of the sulfur-containing reactants involved.

This mechanism aligns with the findings of Ouyang et al. [1], who also reported that crystalline sulfides primarily undergo solid–solid reactions at elevated temperatures. We have added these

clarifications to the revised manuscript (Section 2.2, Page 17) and Supporting Information (S41-S42) to provide a deeper mechanistic explanation.

Reference

[1] X. Rui, D. Ren, X. Liu, et al., Distinct thermal runaway mechanisms of sulfide-based all-solid-state batteries. *Energy Environ. Sci.* 2023, 16, 3552–3563.

Q3. The evaluation of the interaction between Li₂S, S, Li₃PS₄ and delithiated NCM is quite reasonable to investigate the effect of electrochemically degraded LPSC on thermal stability as interphase. Can you explain why the S or Li₃PS₄ can evolve the SO₂ gas evolution through the interaction with delithiated NCM? (in contrast to pristine LPSC).

Response: We thank the reviewer for this insightful question regarding the mechanism of SO₂ evolution during the interfacial reaction between degraded LPSC products (such as S and Li₃PS₄) and delithiated NCM. The difference in reactivity indeed stems from the thermodynamic instability and distinct chemical environments of sulfur in these species compared to pristine LPSC.

In pristine LPSC, sulfur exists primarily in the form of PS₄³⁻ tetrahedral units, where sulfur is in a reduced state and is stabilized by strong P–S bonds within a rigid anionic framework. This structure is both chemically and electrochemically stable within the operating window of the solid electrolyte, and does not readily release SO₂ under normal conditions.

However, upon electrochemical oxidation (e.g., during cycling or at high voltage), LPSC decomposes into products such as elemental sulfur (S⁰), Li₃PS₄, and polysulfides. These degradation products have distinctly different sulfur chemical environments: Elemental sulfur (S₈) contains S–S bonds that are highly susceptible to attack by nucleophiles or oxidants. Li₃PS₄ still contains PS₄³⁻ units but in a less structurally constrained environment compared to the crystalline LPSC, making it more reactive. When these species come into contact with delithiated NCM₈₁₁, which is a strong oxidant and can release atomic oxygen (O) at elevated temperatures, their interaction becomes thermodynamically favorable:

The driving force for SO₂ release is the high oxidation tendency of sulfur in S⁰ and weakly bound PS₄³⁻ in decomposition products, coupled with the strong oxidizing power of delithiated NCM.

By contrast, in pristine LPSC, the sulfur is already in a stable tetrahedral coordination with phosphorus. The energy required to break P–S bonds and oxidize S^{2-} to S^{4+} (in SO_2) is significantly higher, making SO_2 evolution less favorable both kinetically and thermodynamically. This was demonstrated in the work of Ouyang et al. [1], the thermal reaction mechanisms between De-NCM and sulfide electrolytes depend significantly on the crystallinity and composition of the electrolyte.

We have added a paragraph in the revised manuscript (Section 2.2, Page 16) to include this explanation and cited relevant literature on sulfur oxidation and solid electrolyte decomposition:

“Upon electrochemical oxidation (e.g., during cycling or at high voltage), LPSC decomposes into products such as elemental sulfur, Li_3PS_4 , and polysulfides. These degradation products have distinctly different sulfur chemical environments and are more reactive with oxygen.”

Thank you again for encouraging us to clarify this important mechanistic detail.

Reference

[1] X. Rui, D. Ren, X. Liu, et al., Distinct thermal runaway mechanisms of sulfide-based all-solid-state batteries. *Energy Environ. Sci.* 2023, 16, 3552–3563.

Q4. To emphasize the effect of interphase on thermal stability depending on the interaction with cathode, it is recommended to note the interfacial decomposition mechanism of SOC 0 also for comparison with SOC 100 (like as shown in Figure 4a).

Response: We sincerely thank the reviewer for this valuable suggestion. We agree that a comparative analysis of the interfacial decomposition mechanisms at both 0% and 100% SOC is essential for a comprehensive understanding of the state-of-charge-dependent thermal stability.

In direct response to this comment, we performed additional experiments to further elucidate the thermal reaction mechanism of the 0% SOC composite cathode. Specifically, we conducted DSC measurements on a mixture of electrochemically decomposed LPSC (obtained at 2.8 V vs Li^+/Li) and pristine NCM. A distinct exothermic peak was observed at 302 °C, which aligns perfectly with the first exothermic peak of the 0% SOC composite cathode (Figs. R3-3 and 2a). In contrast, no such exothermic behavior was detected at this temperature for the individual components (decomposed LPSC alone, pristine NCM, or a mixture of pristine NCM and pristine LPSC, Figs. R3-3 and R3-4).

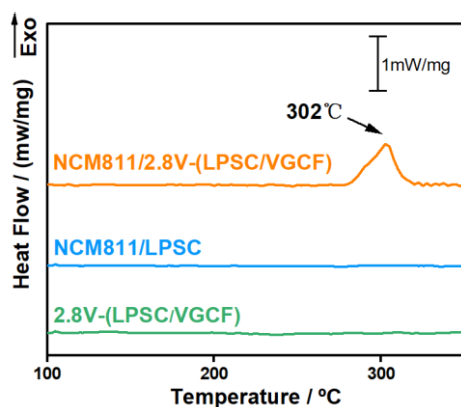


Figure R3-3. DSC profiles of NCM/2.8V-(LPSC/VGCF), NCM/LPSC, and 2.8V-(LPSC/VGCF).

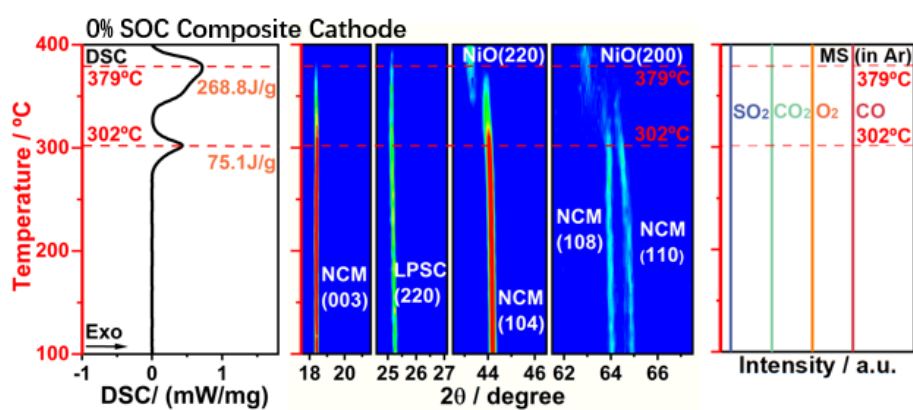


Figure 2a. In-situ heating DSC-XRD-MS analysis of the 0% SOC composite cathode.

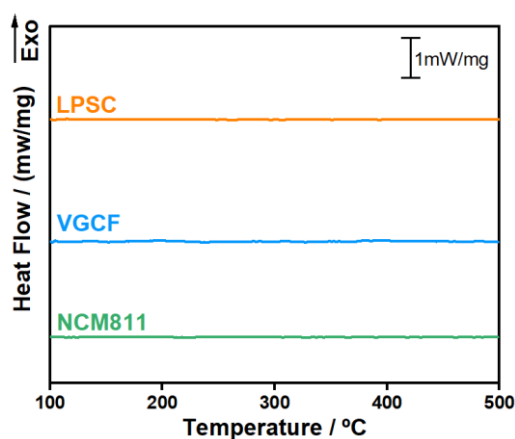


Figure R3-4. DSC profiles of LPSC, VGCF, and NCM811 samples.

Furthermore, systematic DSC tests combining pristine NCM with various electrochemical decomposition products (Li₂S, S, Li₃PS₄, and P₂S₅) revealed that only the mixture of NCM and P₂S₅ produced a sharp exothermic peak near 300 °C (Figs. R3-5). This strongly suggests that the first

exothermic event at 0% SOC is attributable to the reaction between NCM and phosphorus sulfide intermediates (such as -P-S-P- bridged structures) generated from LPSC decomposition.

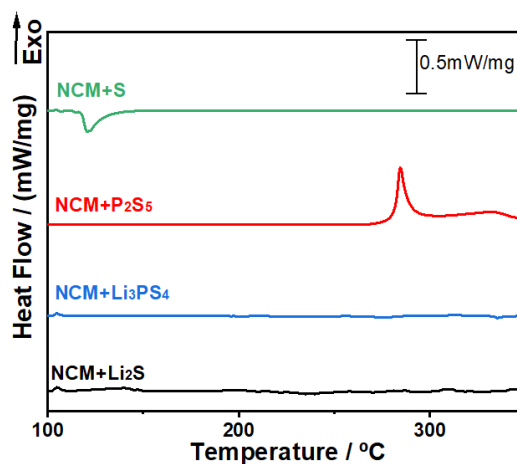


Figure R3-5. DSC profiles of NCM/S, NCM/P2S5, NCM/Li3PS4, and NCM/Li2S.

To probe the specific reaction pathway, we employed XPS to analyze the NCM/2.8V-(LPSC/VGCF) mixture before and after heating to 310 °C (Figs. R3-6). The spectra confirmed the consumption of -P-S-P- species and the simultaneous formation of oxidation products including SO_3^{2-} , SO_4^{2-} , and PO_4^{3-} . This evidence supports the proposed reaction pathway for the first stage:

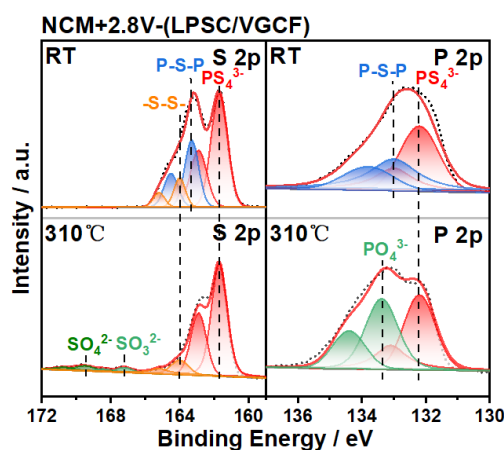


Figure R3-6. S 2p and P 2p XPS spectra of the NCM/2.8V-(LPSC/VGCF) at room temperature (RT, 25 °C) and 310 °C.

Regarding the second exothermic stage, in situ XRD results indicated the simultaneous disappearance of characteristic diffraction peaks from both NCM and LPSC, confirming that a direct

solid-solid reaction between the bulk materials occurs. The overall reaction can be summarized as:



These new findings, which have been added to the [revised manuscript \(Section 2.2, Page 17\)](#) and Supporting Information (S41-S42), provide a mechanistic parallel to the 100% SOC decomposition analysis already presented in Figure 4a. This comparison substantially strengthens our discussion on how the interfacial decomposition mechanism evolves with the state of charge.

Thank you again for this suggestion, which has helped us provide a more complete and mechanistic picture of the thermal degradation pathways in our system.

Reviewer #4 (Remarks to the Author):

The manuscript presents a comprehensive investigation into the thermal runaway behavior of sulfide-based all-solid-state batteries (ASSBs), emphasizing the role of electrochemically formed interphases and chemical cascade reactions at the cathode-electrolyte interface. The use of multiscale calorimetry, gas analysis, and advanced structural characterization to support a two-stage decomposition mechanism is novel. The authors correlate material-level interfacial reactions with cell-level thermal behavior and propose a paradigm shift from bulk stability to interfacial thermodynamics as the primary safety determinant. The following comments should be addressed.

Response: Thank you for this positive assessment of our work and for acknowledging its novelty and comprehensive nature. We greatly appreciate your constructive comments and have prepared a detailed point-by-point response to each of the specific points raised below.

1. While the authors attribute the first exothermic peak at 0% SOC to electrochemical interphase breakdown, it is unclear how such interphases persist or form under discharged conditions. Can the authors clarify whether residual sulfur species or kinetically trapped decomposition products contribute, and how this behavior is decoupled from active redox at 100% SOC?

Response: We thank the reviewer for raising this important question regarding the persistence and origin of reactive interphases under discharged (0% SOC) conditions. We agree that this point requires careful clarification.

As correctly noted by the reviewer and supported by prior literature [1,2], LPSC undergoes reversible electrochemical redox reactions during cycling. At high potentials, it is oxidized to species such as Li_3PS_4 , elemental S (or disulfide -S-S-), and phosphorus sulfides (e.g., P_2S_5 , containing -P-S-P- motifs). At low potentials, it is reduced to Li_2S and Li_3P . Part of this decomposition is reversible and contributes to the cycling capacity. However, not all decomposition products are electrochemically reversible. Kinetically trapped, metastable species—particularly phosphorus-rich sulfides like P_2S_5 (and its polymeric forms with -P-S-P- linkages)—persist at the interface even after full discharge. These residues are key to explaining the first exothermic peak at 302 °C at 0% SOC (Figs. 2a).

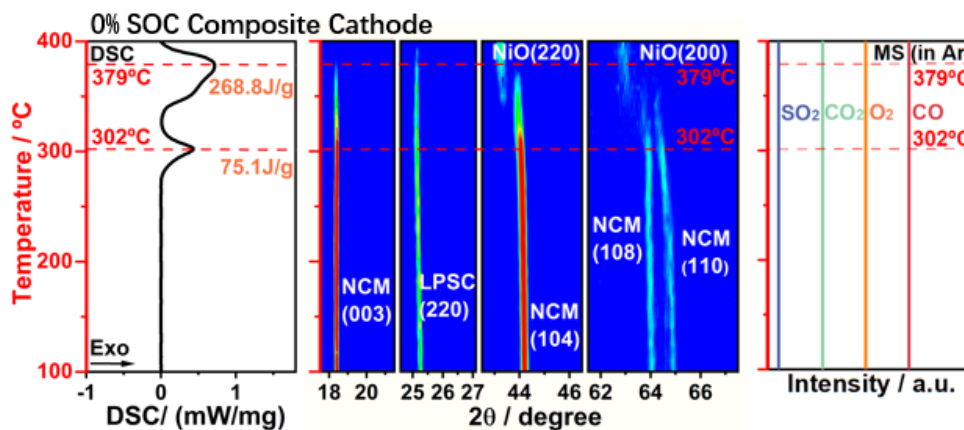


Figure 2a. In-situ heating DSC-XRD-MS analysis of the 0% SOC composite cathode.

To confirm that these residual species drive the exothermic reaction, we performed additional DSC experiments:

A mixture of electrochemically decomposed LPSC and pristine NCM exhibited a clear exothermic peak at 302 °C (Figs. R4-1). No such peak was observed for decomposed LPSC alone, pristine NCM alone, or a mixture of pristine NCM and pristine LPSC (Figs. R4-1 and R-2). Furthermore, systematic mixing of pristine NCM with individual decomposition products (Li_2S , S, Li_3PS_4 , and P_2S_5) revealed that only P_2S_5 produced a sharp exotherm near 300 °C (Figs. R4-3).

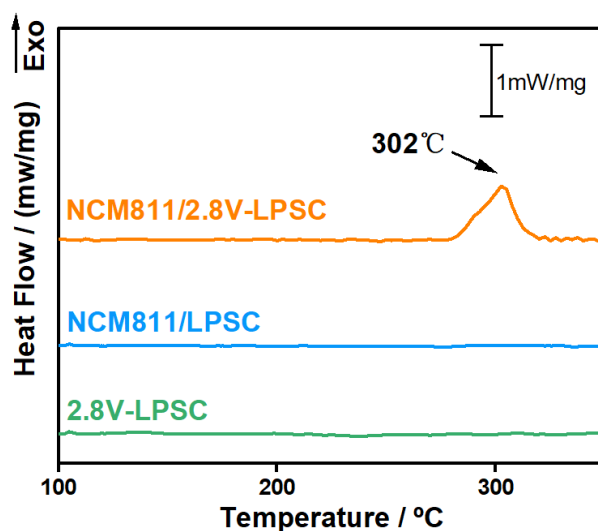


Figure R4-1. DSC profiles of NCM/2.8V-(LPSC/VGCF), NCM/LPSC, and 2.8V-(LPSC/VGCF).

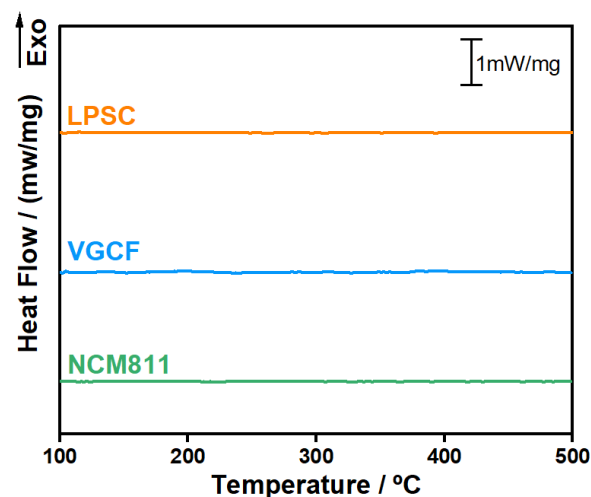


Figure R4-2. DSC profiles of LPSC, VGCF, and NCM811 samples.

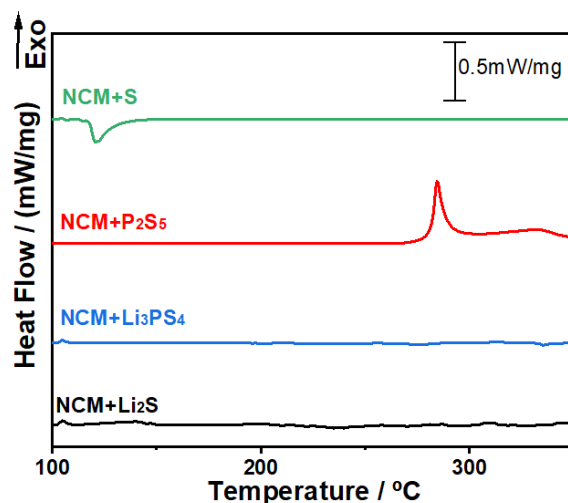


Figure R4-3. DSC profiles of NCM/S, NCM/P₂S₅, NCM/Li₃PS₄, and NCM/Li₂S.

This indicates that the thermal decomposition of these irreversible, kinetically trapped phosphorus-sulfide intermediates is responsible for the initial heat release at 0% SOC.

We further probed the reaction pathway via XPS analysis of the NCM/decomposed-LPSC mixture before and after heating to 310 °C (Figs. R4-4). The spectra showed the disappearance of the -P-S-P- signal and the formation of SO₃²⁻, SO₄²⁻, and PO₄³⁻, supporting the following pathway:



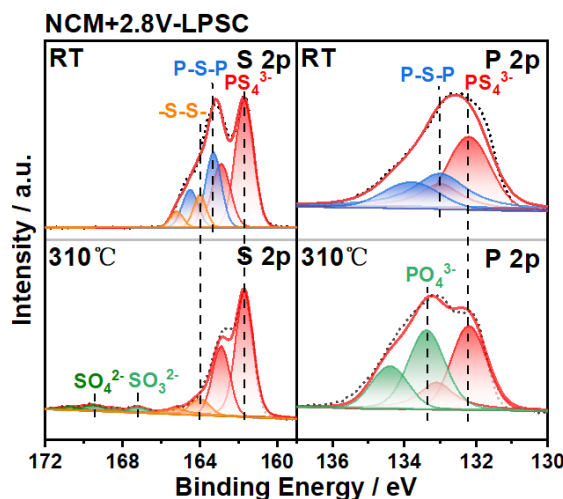


Figure R4-4. S 2p and P 2p XPS spectra of the NCM/2.8V-(LPSC/VGCF) at room temperature (RT, 25 °C) and 310 °C.

In contrast, at 100% SOC, the delithiated NCM is highly oxidizing and actively drives the decomposition of LPSC, generating a thicker interphase containing -S-S-, Li_3PS_4 , and more -P-S-P- species. These can all react with oxygen released from NCM, leading to more intense heat release and SO_2 generation.

Thus, the behavior is decoupled: at 0% SOC, the exotherm is caused by thermal breakdown of irreversibly formed interfacial residues; at 100% SOC, it is intensified by combined electrochemical and thermal instability.

We have added this discussion and the supporting data to the revised manuscript (Section 2.2 Page 17) and Supporting Information (S41-S42) to provide a clearer mechanistic picture. Thank you for this insightful comment.

Reference

- [1] Tan, D. H. S.; Wu, E. A.; Nguyen, H. et al. Elucidating Reversible Electrochemical Redox of $\text{Li}_6\text{PS}_5\text{Cl}$ Solid Electrolyte. *ACS Energy Lett.*, 2019, 4(10): 2418-2427.
- [2] Schwietert, T. K.; Arszewska, V. A.; Wang, C. et al. Clarifying the Relationship between Redox Activity and Electrochemical Stability in Solid Electrolytes. *Nat. Mater.*, 2020, 19: 428–435.

2. The author states that there is a sequential progression from interphase breakdown to bulk NCM-LPSC reactions but does not define the temperature boundaries or timing clearly. Could the authors specify more definitively when LPSC becomes actively involved?

Response: We thank the reviewer for this comment, which helps us clarify the temperature boundaries that define the transition from interphase-driven to bulk electrolyte-driven reactions.

Based on our in situ high-temperature XRD results of the 100% SOC composite cathode (Figure R4-5), the active involvement of bulk LPSC in the decomposition reaction begins at approximately 280 °C, coinciding with the onset of the phase transition of NCM from a spinel to a rock-salt structure (NiO) and the gradual attenuation of LPSC diffraction peaks. The reaction continues until around 350 °C, at which point all characteristic peaks of LPSC completely disappear, indicating full consumption of the solid electrolyte.

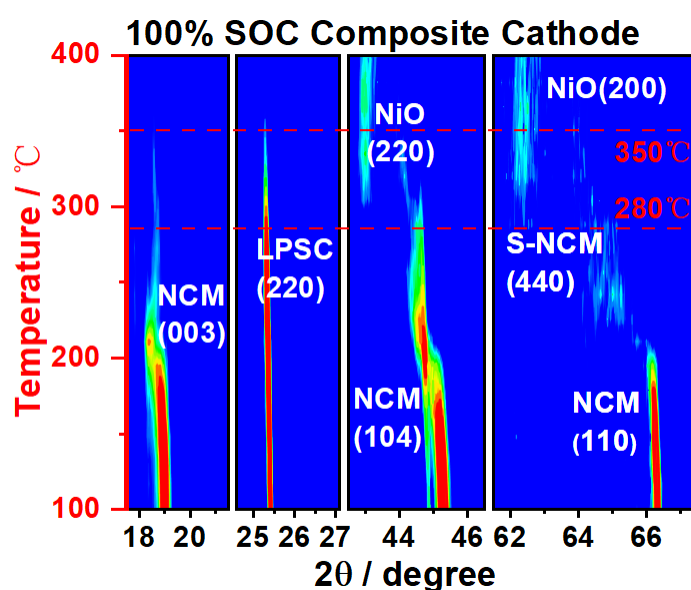


Figure R4-5. In-situ heating XRD analysis of the 100% SOC composite cathode.

This temperature range is strongly supported by our DSC analysis (see Figure R4-6). The second exothermic peak, which we have previously attributed—via a combination of EBSD, MS, and XPS—to the reaction between bulk LPSC and delithiated NCM, is observed to start at approximately 280 °C and conclude near 350 °C. The excellent agreement between the DSC and in situ XRD data provides robust and consistent evidence for the temperature window (~280–350 °C) within which bulk LPSC becomes actively involved in the exothermic solid-solid reaction.

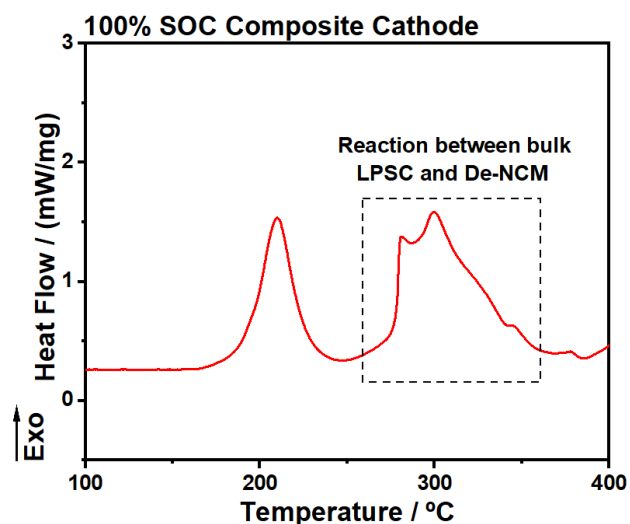


Figure R4-6. DSC of the 100% SOC LPSC composite cathode.

Therefore, the sequential progression is clearly demarcated: the first exothermic stage (lower temperature) corresponds to the decomposition of the electrochemically formed interphase, while the second stage (initiating around 280 °C) marks the participation of bulk LPSC.

We have added this clarification along with the corresponding references to Figure R4-4 and the DSC result (Figure R4-5) in the revised manuscript (Section 2.2, Page 10-11) to more precisely delineate the reaction stages.

“In-situ heating XRD analysis revealed structural evolution during these events: the first peak corresponded to phase transformation of delithiated NCM811 from layered to spinel structure, while the second marked transition to rock-salt phase alongside progressive LPSC signal attenuation (Figure 2c). These observations confirm delithiated cathode-driven initiation of thermal decomposition, with bulk solid electrolyte involvement restricted to later stages (280 °C-350 °C).”

3. While the authors report multiple exothermic peaks, there are no normalized quantitative comparisons of reaction enthalpies (ΔH) across pristine, uncycled, and cycled cathodes. This makes it difficult to rank or compare thermal risk attributed to specific interfacial chemistries across states of charge. Can the authors elaborate on this to allow a clearer comparison?

Response: We thank the reviewer for raising this important point. We agree that a quantitative comparison of the reaction enthalpies (ΔH) is essential for objectively evaluating the thermal hazards associated with different interfacial states. We apologize for this omission in the original

manuscript.

In response to this comment, we have now calculated and normalized the total exothermic heat release (ΔH , in J g^{-1}) for all tested conditions—including the pristine, uncycled, and cycled cathodes at various states of charge (SOC). The quantitative results are summarized in the table below and have been added to the revised manuscript as a new table (Figure R4-7). The results clearly indicate that the delithiated (100% SOC) cathode composites exhibit the highest exothermic heat release, confirming the critical role of the degraded cathode-electrolyte interphase in accelerating thermal decomposition. In contrast, the pristine material and composites at 0% SOC show notably lower enthalpies.

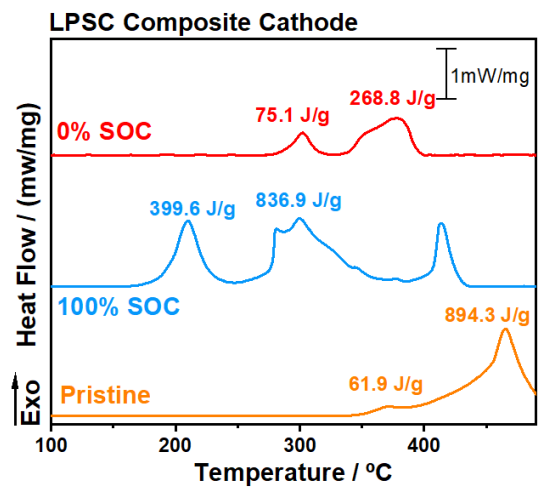


Figure R4-7. DSC of the pristine, 0% SOC and 100% SOC LPSC composite cathodes.

Table R4-1. DSC Parameters of the Pristine, 0% SOC, and 100% SOC LPSC Composite Cathodes

Composite sample	1st peak	ΔH of 1st peak ($\Delta H1$)	2nd peak	ΔH of 2nd peak ($\Delta H2$)
Pristine	348-389 °C	61.9 J/g	389-500 °C	894.3 J/g
0%SOC	280-322 °C	75.1 J/g	335-400 °C	268.8 J/g *
100%SOC	171-246 °C	399.6 J/g	263-383 °C	863.9 J/g

* The reduced heat release in the 0% SOC sample compared to the pristine sample may be attributed to the presence of inert substances in its interface layer, which hinder the solid-solid reaction between NCM and SE.

Furthermore, to ensure data reliability, the thermal stability of each sample was tested three times using the identical method. As shown in the figure below, the DSC curves exhibit excellent reproducibility, thus confirming the repeatability and reliability of our measurements.

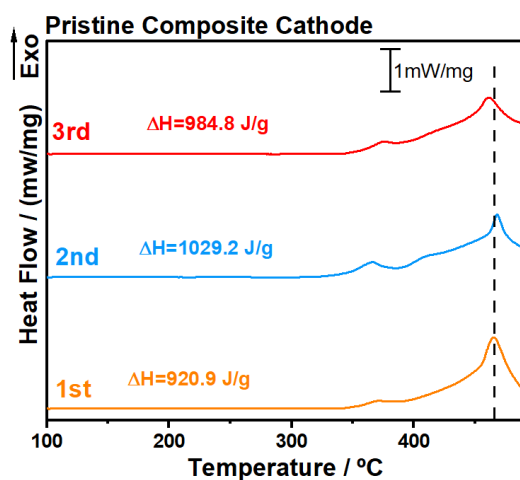


Figure R4-8 DSC of the pristine LPSC composite cathode ($\Delta H = 978.3 \pm 44.5 \text{ J/g}$).

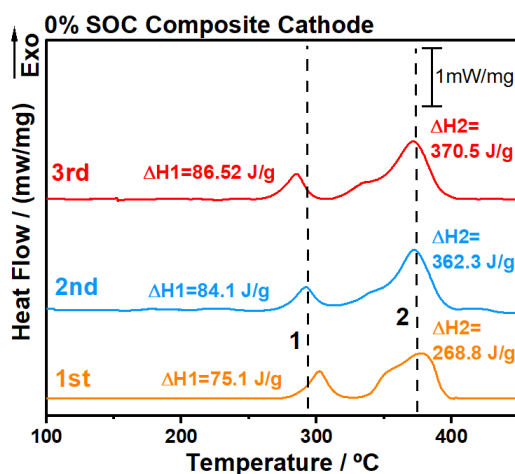


Figure 4-9. DSC of the 0% SOC LPSC composite cathode ($\Delta H_1 = 81.9 \pm 4.9 \text{ J/g}$; $\Delta H_2 = 333.9 \pm 56.2 \text{ J/g}$).

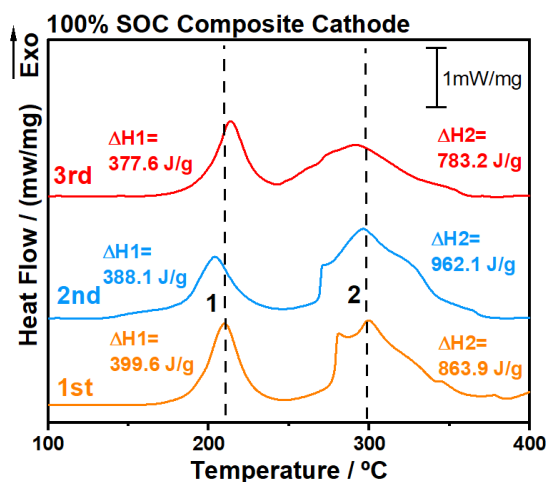


Figure R4-10. DSC of the 100% SOC LPSC composite cathode ($\Delta H_1 = 381.8 \pm 16.4 \text{ J/g}$;

$\Delta H_2 = 869.7 \pm 89.5 \text{ J/g}$).

We have also included these normalized ΔH values to offer readers a clearer basis for comparing the contributions of specific interfacial reactions in the revised manuscript (Section 2.2,

Page10): “Notably, the 100% SOC composite cathode displayed significantly enhanced interfacial reactivity under thermal stress, characterized by two sharp exothermic peaks at 209 °C and 299 °C (Figure 2c and S19). This process was accompanied by a markedly greater heat release ($\Delta H_1 = 381.8 \pm 16.4 \text{ J}\cdot\text{g}^{-1}$, $\Delta H_2 = 869.7 \pm 89.5 \text{ J}\cdot\text{g}^{-1}$) compared to the pristine and 0% SOC counterparts (Table S1).” Thank you again for this suggestion, which has greatly improved the rigor and clarity of our thermal safety analysis.

4. The authors present in-situ heating XRD and identify NiO formation, but it is unclear whether NiO arises from lattice oxygen evolution, sulfur-induced destabilization, or both. Can the authors clarify this? NiO is typically associated with the oxidative decomposition of NCM cathodes, whereas sulfur-rich environments tend to reduce transition metals.

Response: We thank the reviewer for this insightful question regarding the origin of NiO formation during the thermal decomposition process. We agree that the formation of NiO involves a complex interplay between oxygen release from the cathode and reduction by sulfur species, and our experimental data provide clear evidence for both mechanisms occurring concurrently.

Our in-situ heating XRD results reveal that the formation of NiO is synchronized with the disappearance of crystalline LPSC, indicating a direct thermochemical reaction between the delithiated NCM and the solid electrolyte (Figure R4-11). Several key observations help clarify the dual origin of NiO:

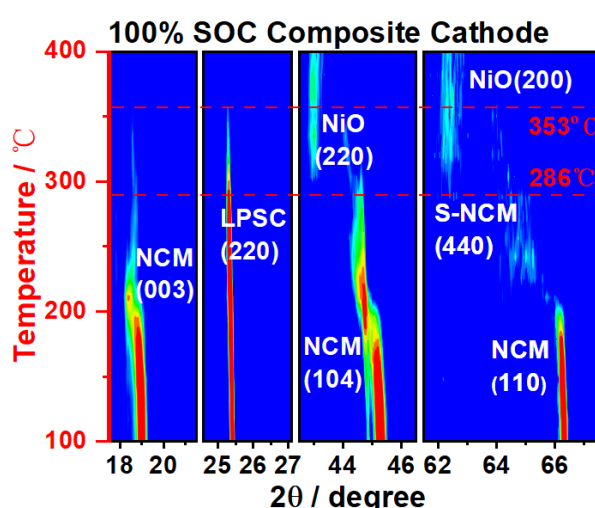


Figure R4-11. In-situ heating XRD analysis of the 100% SOC composite cathode.

Sulfur-Induced Destabilization: 0% SOC NCM alone remains stable and does not form NiO below 400 °C (Figure R4-12). However, when mixed with LPSC (Figure R4-13), NiO formation is

observed near 350 °C, confirming that sulfur-containing species from LPSC destabilize the NCM structure and facilitate its reduction to NiO.

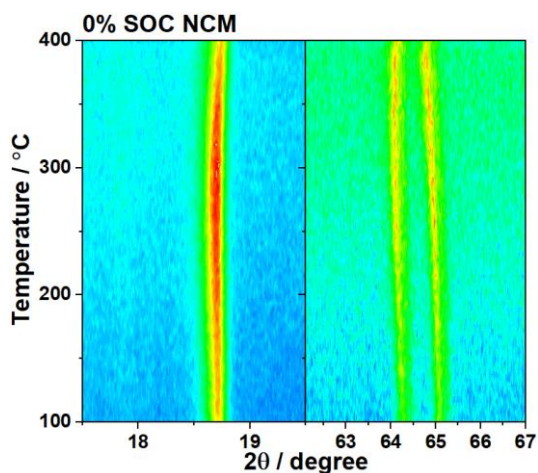


Figure R4-12. In-situ heating XRD analysis of the 0% SOC NCM811.

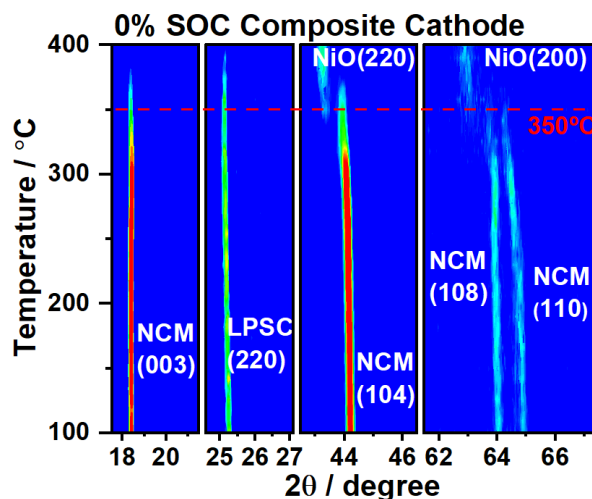


Figure R4-13. In-situ heating XRD analysis of the 0% SOC composite cathode.

Lattice Oxygen Participation: Post-reaction characterizations (XPS and Raman spectroscopy) confirm the presence of sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and nickel sulfide (NiS). The increase in sulfur oxidation state (e.g., $\text{S}^{2-} \rightarrow \text{S}^{4+}/\text{S}^{6+}$) and the reduction of nickel (e.g., $\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$) strongly suggest that sulfur-containing species derived from LPSC act as reducing agents, facilitating the reduction of transition metals in NCM and leading to NiO formation.

Lattice Oxygen Release: Concurrently, the generation of oxygen-containing anions (SO_3^{2-} , SO_4^{2-} , PO_4^{3-}) implies that lattice oxygen released during the phase transition of NCM (from a layered/spinel structure to a rock-salt NiO phase) participates in the oxidation of sulfur and phosphorus species.

Thus, NiO formation in our system arises from a cooperative process:

- (1) Sulfur-induced reduction of nickel, destabilizing the NCM structure, and
- (2) Subsequent release and involvement of lattice oxygen in oxidizing sulfur/phosphorus species.

This mechanism has been clarified in the revised manuscript (“The formation of NiO occurred alongside the initial reaction of LPSC, suggesting a synergistic promotion driven by the combined effects of lattice oxygen release from the cathode and destabilization by sulfur species” (Section 2.2, page 10-11) to provide a more definitive explanation. We thank the reviewer for prompting this important discussion.

5. In section 2.3, the authors use NCM811 cathodes with a 4 nm coating, but do not explore whether this thickness is optimal. Given prior literature showing non-linear effects of coating thickness on both ionic conductivity and interfacial stability, can the authors comment on why 4 nm was chosen and whether thicker or thinner coatings were evaluated?

Response: We sincerely thank the reviewer for raising this critical point regarding coating thickness optimization. We agree that the thickness of a coating layer can non-linearly influence both ionic transport and interfacial stability, and we appreciate the opportunity to clarify our experimental design and expand on the implications of our findings.

In this study, a 4 nm Al_2O_3 coating was selected not as an optimized thickness, but as a representative and widely reported benchmark for constructing a physical barrier between NCM811 and LPSC. As correctly noted by the reviewer, the primary role of such coating is to mitigate (electro)chemical reactions and suppress the space-charge layer effect at the cathode–sulfide electrolyte interface. Numerous coating materials—such as LiNbO_3 , Li_2ZrO_3 , and LiAlO_2 —have been investigated with the aim of enhancing interfacial stability while maintaining satisfactory ionic conductivity, as highlighted in the literature [1,2].

Although our results indicate that the 4 nm Al_2O_3 coating delayed the initial exothermic reaction and reduced heat release to some extent, it could not fully prevent the electrochemical degradation of LPSC. This is consistent with the inherent limitations of coating strategies: even an ideally uniform nanoscale coating may exhibit pinholes or insufficient electronic insulation, and it cannot entirely suppress all parasitic reactions under high voltages.

In direct response to the reviewer’s comment, we conducted additional experiments using a

thinner Al_2O_3 coating (2 nm) to preliminarily probe the thickness dependence. The results confirm that the 2 nm coating offers inferior suppression of the first exothermic peak compared to the 4 nm version (heat reduction of 80.8 J/g vs. 69.4 J/g), supporting the role of coating thickness in moderating interfacial reactions.

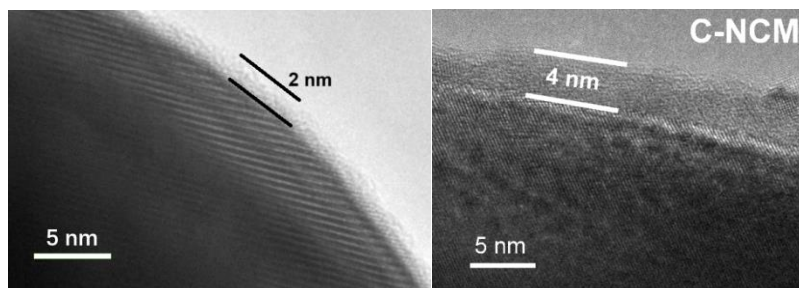


Figure R4-14. Typical surface TEM images of 2nm- Al_2O_3 and 4nm- Al_2O_3 coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (named as C-NCM) samples.

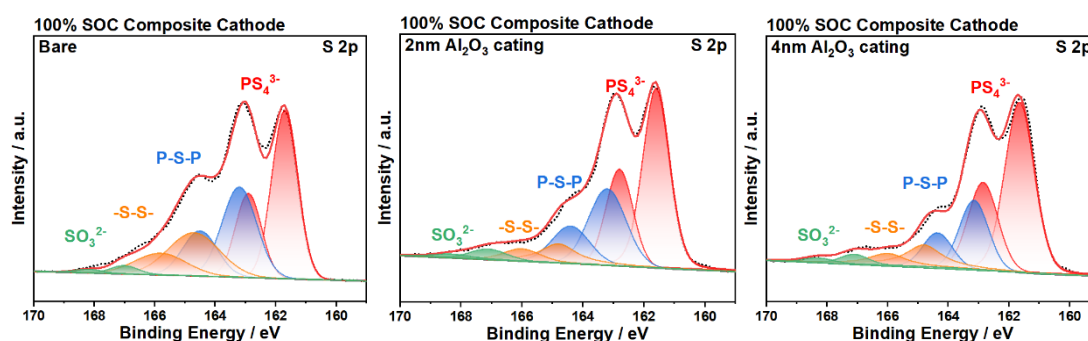


Figure R4-15. S 2p and P 2p XPS spectra of the 100% SOC composite cathode (layered oxide cathode, LPSC, and VGCF in a weight ratio of 70:30:3) with 2nm- Al_2O_3 and 4nm- Al_2O_3 coated NCM811 and uncoated NCM (bare NCM811).

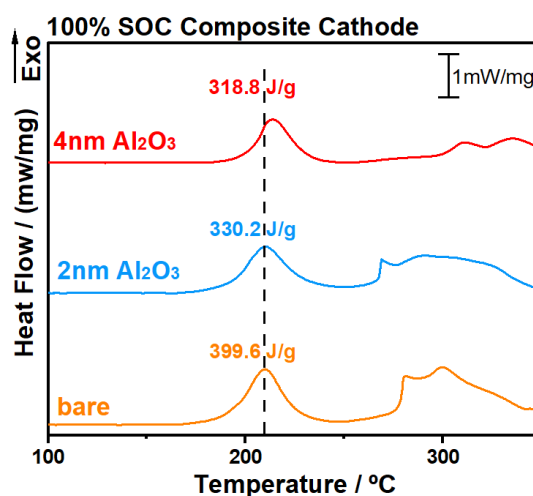


Figure R4-16. DSC of the 100% SOC composite cathode (layered oxide cathode, LPSC, and VGCF in a weight ratio of 70:30:3) with 2nm- Al_2O_3 and 4nm- Al_2O_3 coated NCM811 and NCM (bare NCM811).

Nevertheless, both coated samples eventually underwent significant thermal decomposition, underscoring a fundamental limitation: extrinsic coating layers may improve interfacial stability only within a narrow operational window. Moreover, practical challenges—such as uniformity, scalability, and cost—further complicate the large-scale application of coated cathodes.

Therefore, while coating can offer partial improvement, we concur that future efforts should focus not only on optimizing coating materials and thickness but, more importantly, on developing intrinsically more stable sulfide electrolytes. Such materials would alleviate the need for complex interfacial engineering and facilitate the realization of high-energy, long-life all-solid-state batteries.

We thank the reviewer again for this insightful suggestion, which has significantly enriched our analysis.

Reference

- [1] Banerjee A, Tang H, Wang X, et al. Revealing nanoscale solid-solid interfacial phenomena for long-life and high-energy all-solid-state batteries. *ACS Applied Materials & Interfaces*, 2019, 11(46): 43138-43145
- [2] Liu B, Wang D, Avdeev M, et al. High-throughput computational screening of Li containing fluorides for battery cathode coatings. *ACS Sustainable Chemistry & Engineering*, 2020, 8(2): 948-957.

6. While LGS shows good interfacial stability with NCM811 on the cathode side, the authors employ a Li-Si anode in full-cell validation without evaluating its interfacial compatibility with LGS or LPSC. Given known issues of volume expansion and potential interfacial reactivity in Si-based alloys, the absence of any post-mortem analysis or thermal characterization at the anode-SE interface limits the comprehensiveness of the system-level safety claims. Can the authors provide a discussion on whether the LGS impacts long-term anode stability or interacts chemically?

Response: We thank the reviewer for this insightful comment regarding the anode-side interfacial compatibility of LGS. We agree that a comprehensive safety evaluation must consider all cell components, and we appreciate the opportunity to clarify our experimental design and provide further justification.

Firstly, we would like to emphasize that all thermal safety evaluations—including ARC and DSC tests for both LPSC and LGS-based cells—were performed using Li-In anodes. This ensures consistency in the variable under investigation (the cathode/electrolyte interface) and allows for a

direct and fair comparison of the thermal behavior between different solid electrolytes. The Li-Si anode was employed only in long-term electrochemical cycling tests of the LGS-based full cell, as it offers superior cycling performance compared to Li-In, thereby enabling a more meaningful evaluation of the cell's capacity retention over time.

We acknowledge the well-known challenges of Si-based anodes, including substantial volume changes. To mitigate this, a constant stack pressure was applied throughout the cycling tests to maintain mechanical integrity and interfacial contact, which contributed to the stable cycling performance observed.

It is well documented in the literature that certain sulfide solid electrolytes (such as LGPS) exhibit severe reactivity with lithium metal, forming mixed-conducting interphases that lead to continuous decomposition and accelerated thermal failure [1-2]. Although LGS shows improved stability with oxide cathodes, it demonstrates high impedance and poor compatibility when in direct contact with lithium-based anodes, as confirmed by our own XPS analysis (Figure R4-17). LGS reacts with lithium metal to form reduced Ge species, leading to high impedance and rapid degradation. This is precisely why we designed a hybrid cell architecture: LGS is used only as a stabilizing additive within the composite cathode, while LPSC is retained as the bulk separator. This strategy successfully prevents direct contact between LGS and the anode, thereby circumventing its inherent instability while still leveraging its beneficial role in suppressing cathode-side parasitic reactions.

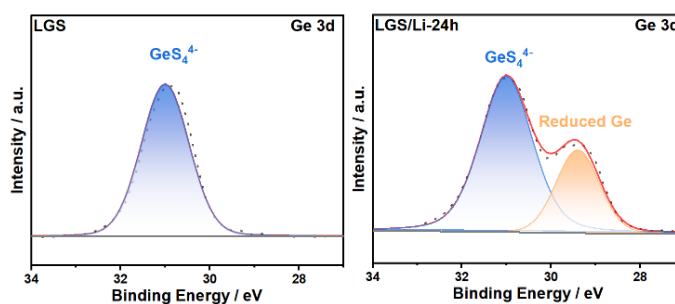


Figure R4-17. Ge 3d XPS spectra of LGS and LGS/Li pressed into tablets after 24 hours.

Moreover, regarding the thermal stability at the anode interface: we conducted supplementary DSC tests of LPSC with both Li-In and Li-Si. The results exhibit their excellent thermal compatibility with LPSC, showing no exothermic reactions below 350 °C (Figure R4-18). This

indicates that the anode is not the primary source of thermal instability in our system.

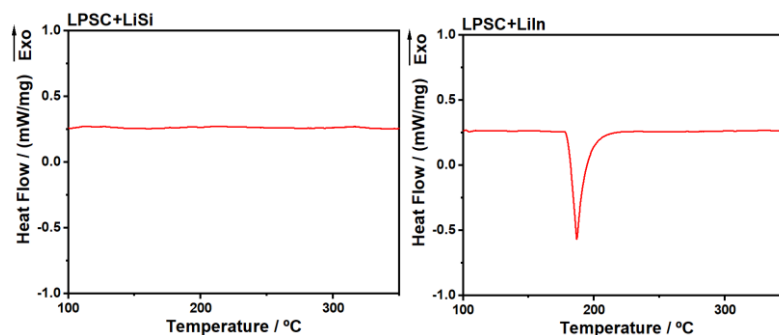


Figure R4-18. DSC of LPSC/LiSi and LPSC/LiIn.

In conclusion, while LGS is unstable against lithium metal, our cell design isolates it from the anode. We have added a discussion on this design rationale and the supporting anode compatibility data to the revised [Supporting Information \(S59\)](#) to provide a more comprehensive perspective. We thank the reviewer for raising this important point regarding anode-electrolyte interfacial compatibility, which is indeed critical for evaluating the overall safety and stability of all-solid-state batteries.

Reference

- [1] Wenzel, S.; Randau, S.; Leichtweiß, T. et al. Direct Observation of the Interfacial Instability of the Fast Ionic Conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ at the Lithium Metal Anode. *Chem. Mater.*, 2016, 28(7): 2400-2407.
- [2] Yan, J.; Yao, J.; Zhao, J. et al. Revealing the Thermal Stability of the Li/Sulfide Solid Electrolyte Interface at Atomic Scale via Cryogenic Electron Microscopy. *Adv. Funct. Mater.*, 2025, 35: 2421918.

Reviewer #1:

Comment: The manuscript has been revised based on the reviewers' previous comments. However, the interpretation of the computational and experimental results still remains questionable. The authors argue that the strong overlap of S and O in their DOS calculations indicates the feasibility of a bond exchange. Nevertheless, the XRD results after heat treatment suggest that it is not simply the delithiated NCM reacting with LPSCl to form NiS₂ while maintaining the oxidation state of Ni. Instead, the results imply that Ni⁴⁺ is reduced and NiS is formed. This suggests that the reaction is not a simple S–O exchange, but rather that S²⁻ transfers electrons to Ni and becomes oxidized, which could also result in the formation of gaseous species such as SO₂.

In addition, the crystallographic data used for the DOS calculations need to be clearly provided. To perform DOS calculations, the initial crystal structures are required, but it is not specified whether these were obtained from databases such as Materials Project or derived from experimental XRD results. If refined XRD structures were used, then the corresponding refined XRD patterns together with the crystallographic information tables should be included to ensure reproducibility and reliability of the computational results.

Response: We sincerely thank the reviewer for this insightful comment, which has drawn our attention to a key aspect of the reaction mechanism between delithiated NCM and LPSCl. We agree that the process is more complex than a simple S–O exchange, and the reduction of Ni⁴⁺ along with NiS formation, as revealed by XRD, is a critical observation.

In our original discussion, the pronounced S and O orbital overlap identified in the DOS was interpreted as an indicator of favorable chemical interaction that may facilitate interfacial co-diffusion. We acknowledge, however, that these calculations do not fully capture the complexity of the interfacial process, particularly the subsequent redox reactions that occur under high-temperature conditions.

During thermal treatment, multi-stage reactions take place between delithiated NCM and LPSCl. The structural collapse of delithiated NCM results in oxygen release and reduction of Ni⁴⁺. The resulting NiO could further react with LPSCl to form NiS, as experimentally confirmed in **Figure S13** in our original Supporting Information. Simultaneously, under high-temperature conditions, S²⁻ in the PS₄³⁻ tetrahedral units can also be oxidized through reaction pathways governed by the local chemical environment. In the presence of metal oxides (e.g., NCM) and lithium sources, this process preferentially yields sulfate species, as supported by prior studies [1]. Collectively, these findings confirm that the interfacial reactions involve complex multi-step chemistry beyond a simple S–O exchange, encompassing both anion diffusion and coupled redox processes.

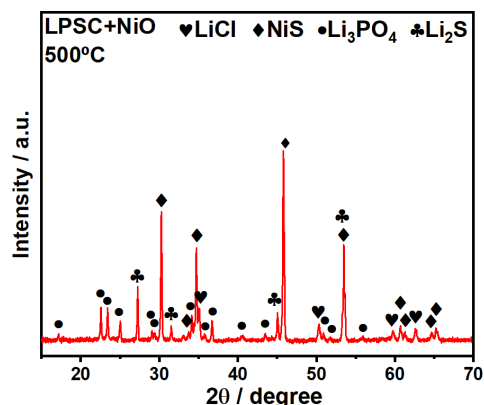


Figure S13. XRD patterns of LPSC with NiO in a 1:1 mass ratio after heating at 500 °C.

To address this point, we have revised the relevant descriptions in the manuscript to more accurately reflect the complexity of the process. The term "S–O exchange" has been replaced with "cathode-SE interaction involving both anion exchange and redox chemistry" to avoid ambiguity and to better represent the multi-step nature of the reaction. We believe this revised interpretation better aligns the computational and experimental results and provides a more accurate description of the interfacial reaction.

Besides, the crystal structures of $\text{Li}_6\text{PS}_5\text{Cl}$, Li_2S , Li_3PS_4 , P_2S_5 and Li_4GeS_4 were sourced from the Materials Project database. For NCM811, its crystal structure was constructed based on our experimental XRD results (Figure S27), which confirm that all diffraction peaks correspond to the $\alpha\text{-NaFeO}_2$ -type hexagonal structure with the $R\text{-}3m$ space group, a well-established model widely reported in the literatures [2-6]. The NCM model for DFT calculations was constructed based on the LiNiO_2 structure from the Materials Project by substituting Ni atoms with Co and Mn in the appropriate stoichiometric ratio. The 80% delithiated structure was then generated by removing a corresponding number of Li atoms from the pristine model. The final structure used for DOS calculations was determined as the lowest-energy configuration after DFT relaxation.

We have revised the computational methods section ([1.5. Calculation method](#)) to explicitly state the data source for all compounds studied. This amendment will allow other researchers to easily retrieve the same structures and verify our calculations.

Reference

- [1] Rui, X.; Ren, D.; Liu, X.; Wang, X.; Wang, K.; Lu, Y.; Li, L.; Wang, P.; Zhu, G.; Mao, Y.; et al. Distinct Thermal Runaway Mechanisms of Sulfide-Based All-Solid-State Batteries. *Energy Environ. Sci.* 2023, 16, 3552–3563.
- [2] Dixit, M.; Kosa, M.; Lavi, O. S.; Markovsky, B.; Aurbach, D.; Major, D. T. Thermodynamic and Kinetic Studies of $\text{LiNi}_0.5\text{Co}_0.2\text{Mn}_0.3\text{O}_2$ as a Positive Electrode Material for Li-Ion Batteries Using First Principles. *Phys. Chem. Chem. Phys.* 2016, 18, 6799–6812.
- [3] Kuo, L.-Y.; Guillon, O.; Kaghazchi, P. Origin of Structural Phase Transitions in Ni-Rich $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with Lithiation/Delithiation: A First-Principles Study. *ACS*

Sustainable Chem. Eng. 2021, 9, 7437–7446.

[4] Dai, Z.; Zhao, H.; Chen, W.; Zhang, Q.; Song, X.; He, G.; Zhao, Y.; Lu, X.; Bai, Y. In Situ Construction of Gradient Oxygen Release Buffer and Interface Cation Self-Accelerator Stabilizing High-Voltage Ni-Rich Cathode. *Adv. Funct. Mater.* 2022, 32, 2209075.

[5] Hsieh, I. T.; Wu, Y.; Li, B.; Qi, Y. First-Principles Study of the Structures and Redox Mechanisms of Ni-Rich Lithium Nickel Manganese Cobalt Oxides. *Solid State Ion.* 2024, 411, 116562.

[6] Lowe, J. S.; Hafiz, H.; Jr, L. G. H. First Principles Method for Predicting Lithiation Induced Volume Change and Open Circuit Voltage of NCM Cathode Materials. *J. Electrochem. Soc.* 2025, 172, 083504.

Reviewer #2:

The author addressed the reviewers' comments to improve the completeness of the research. First, they clarified ambiguities in the experimental conditions by thoroughly analyzing the reactivity of NCM811 under 100% SOC conditions, which means fully delithiated NCM811, and is directly linked to thermal runaway phenomena. Additionally, by examining the Fermi levels of key reaction intermediates, the author strengthened the explanation of the electron transfer mechanism at the interface. They also corrected a conceptual error in the description comparing the VBM of LPSC and the Fermi level of NCM811 and provided the accurate direction of electron transfer based on energy levels, increasing the analysis's reliability. Through these revisions, the author has carefully addressed the reviewers' questions and further bolstered the paper's main arguments.

Despite revisions to several sections, this is an additional comment that a critical issue remains unresolved. The author's DFT calculations were based on pristine materials in their initial state (0% SOC), but the thermal runaway phenomenon, the main focus of analysis, occurs in a fully delithiated state corresponding to 100% SOC. This fundamental mismatch between the material state used in the calculations and the actual conditions of analysis makes the theoretical basis supporting the experimental results insufficient. The electronic properties of delithiated NCM811 differ significantly from those in the initial state, so the current calculation results alone have limitations in explaining the actual phenomenon.

Comment 1) The fundamental discrepancy between calculations and experimental conditions remains unresolved. While DFT calculations seem to assume the material is in its initial state (0% SOC), the critical thermal runaway analysis focuses on a fully delithiated state at 100% SOC. This inconsistency risks undermining the theoretical basis needed to support the experimental findings. Specifically, the cathode shown in Figure 3g appears to contain a considerable amount of lithium, raising doubt on the claim that it is fully delithiated. If the structure used by the authors is not a fully delithiated but instead represents a state where lithium is removed to the maximum extent possible while maintaining structural stability, then the exact chemical formula for this state must be clearly stated in the Computational Method section to ensure the model's accuracy and reproducibility.

Response: We sincerely thank the reviewer for this insightful comment regarding the alignment between our computational models and experimental conditions. We acknowledge that the original description lacked precision and have now provided the following clarification.

The reviewer correctly points out that a fully delithiated state is neither experimentally attainable nor computationally stable. In our work, the focus is on the fully charged state (defined as 100% SOC at 4.5 V, [Result and Discussion](#) section, line 6), which

corresponds to a highly delithiated, but not completely lithium-free, state of the NCM cathode. Our DFT calculations were therefore conducted on a structural model that closely mirrors this realistic, highly delithiated experimental state. Specifically, the model used corresponds to an **80% degree of delithiation**, as referenced in our original Supporting Information (Figure S24). This choice was based on the following experimental and practical considerations:

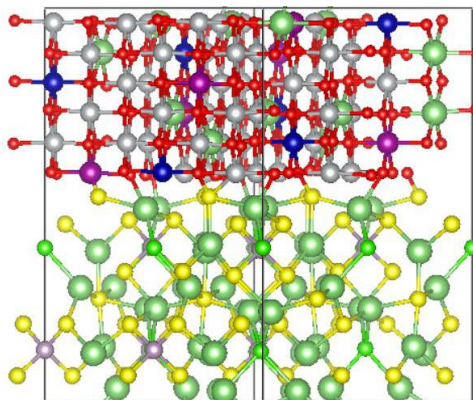


Figure S24. Initial atomic configuration of the 80% delithiated NCM811 | LPSCl interface from AIMD simulation at 25 °C.

(1) Experimental Capacity Analysis: When charged to 4.5 V, the full cell delivered a specific capacity of 243.5 mAh/g (Figure S3). Based on the theoretical capacity of NCM811 (~280 mAh/g), this would correspond to a theoretical delithiation degree of ~87%. However, the measured capacity includes a minor contribution from the electrochemical decomposition of the sulfide solid-state electrolyte. Therefore, the actual degree of delithiation from the NCM cathode is slightly lower than 87%. To accurately reflect the realistic delithiation level while avoiding the severe structural degradation associated with higher voltages, we adopted a conservative and representative 80% delithiation model for our simulations. This approach ensures that our computational results are pertinent to the actual interfacial state under investigation.

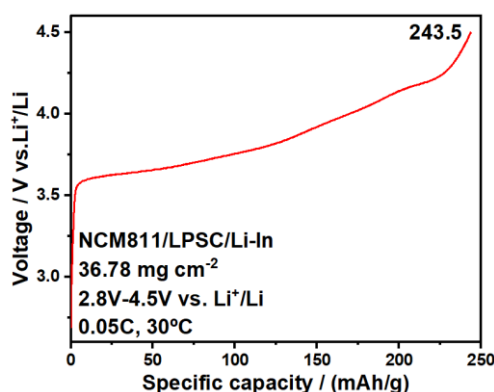


Figure S3. Typical charge-discharge profiles of NCM811/LPSC/Li-In cells in the voltage range of 2.8–4.5 V (vs. Li⁺/Li) at 0.05C.

(2) Computational Stability: Furthermore, this 80% delithiation degree represents a

highly delithiated yet structurally stable configuration, making it suitable for meaningful and reliable DFT simulations of the high-SOC reactivity relevant to thermal runaway scenarios.

We agree with the reviewer on the importance of clarity and reproducibility. In response, we have explicitly stated the specific delithiation degree of 80% in the revised computational methods section (**1.5. Calculation method**).

Regarding the presence of lithium in the cathode in **Figure 3g**, it originates from two sources: **(1)** Residual lithium in the delithiated cathode, consistent with the 80% delithiation level. **(2)** Lithium migration from the $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte into the cathode vacancies during heating, as part of the interfacial reaction, a phenomenon also supported by previous studies (e.g., Adv. Funct. Mater., 2404806, 2024).

In response to the reviewer's comment on clarity and reproducibility, we have explicitly provided the chemical formula of the 80% delithiated model ($\text{Li}_{0.2}\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) in the revised computational methods section (**1.5. Calculation method**), along with the rationale for selecting this specific delithiation degree. We believe these clarifications resolve the apparent discrepancy and strengthen the alignment between our computational models and experimental conditions. Thank you again for this valuable suggestion.

Reference

[1]. T. Kim, H. Chang, G. Song, S. Lee, K. Kim, S. Lee, J. Moon, K. T. Lee, Critical Factors Contributing to the Thermal Runaway of Thiophosphate Solid Electrolytes for All-Solid-State Batteries. Adv Funct Materials, 2404806 (2024).

Reviewer #3:

Authors successfully addressed the questions and comments that I have raised. Regarding the reply for the question 1 (difference of Ttr of SOC100 for full cell and composite cathode), it is recommended to add the discussion. After that, I would recommend the publication of this manuscript in Nature Communications.

Response: We sincerely thank the reviewer for their positive feedback and for acknowledging our responses. As recommended, we have now added the discussion in the Discussion section of the revised manuscript as shown below:

“The differing thermal runaway behaviors between full cells and cathode composites are primarily attributed to electrode crosstalk, where reactive species from the cathode migrate to the anode and undergo exothermic reactions, alongside other architectural factors.”