
Supplementary Information

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

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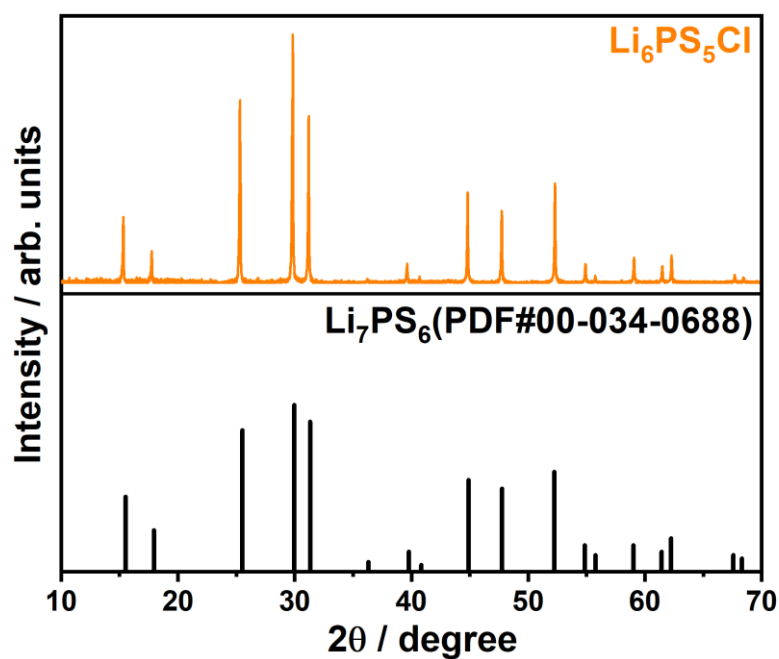
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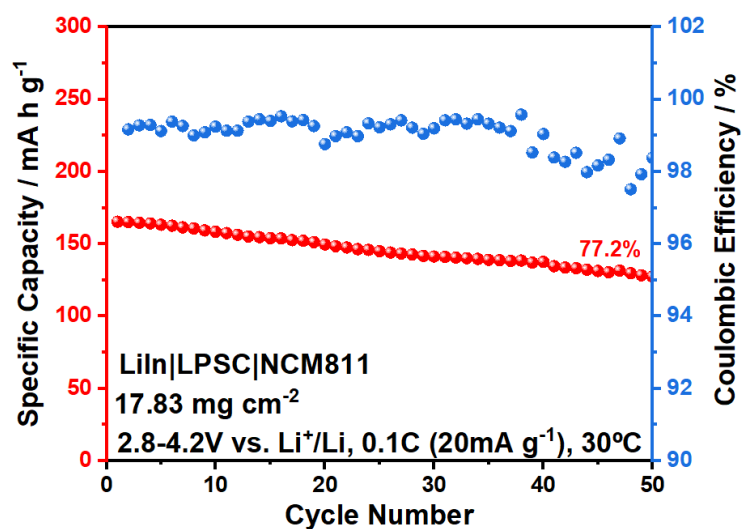
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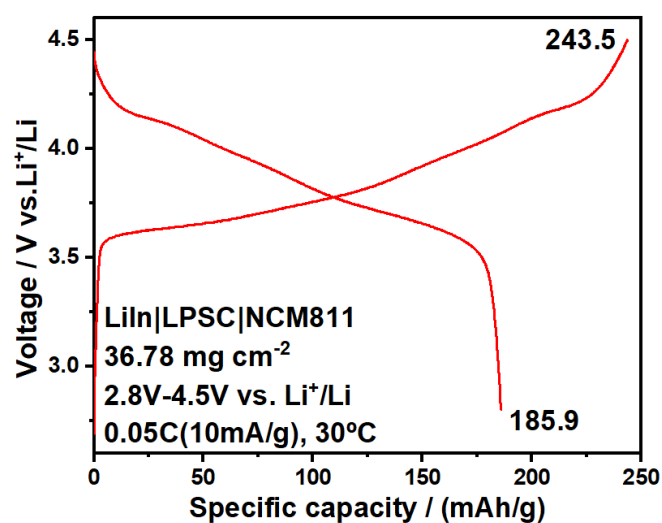
Supplementary Fig. 1 XRD patterns of the as-synthesized $\text{Li}_6\text{PS}_5\text{Cl}$ samples.

The as-synthesized $\text{Li}_6\text{PS}_5\text{Cl}$ samples are used as the electrolyte in ASSBs and as a conductive additive in the composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3).



Supplementary Fig. 2 Typical cycle performance and coulombic efficiency of LiIn|LPSC|NCM811 cells in the voltage range of 2.8–4.2 V (vs. Li^+/Li) at 0.1C (20 mA g^{-1}) and 30°C .

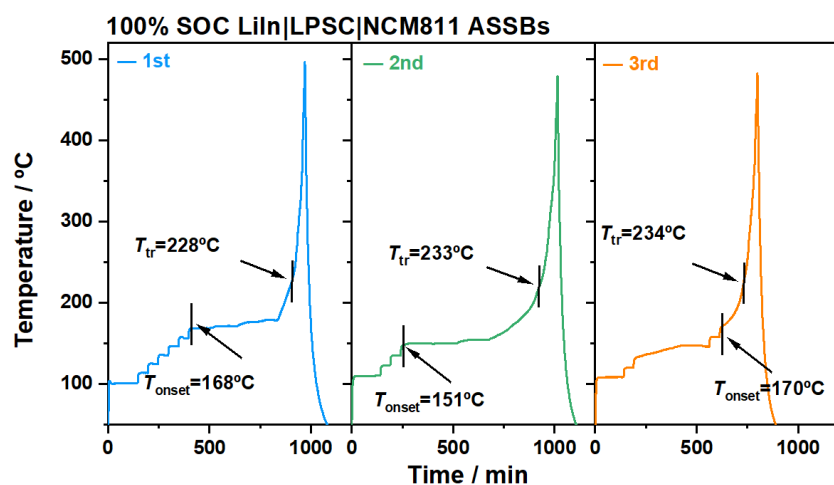
This experiment aims to evaluate the electrochemical performance of the self-assembled ASSBs. The as-obtained cells delivered considerable cycling performance, with an initial discharge specific capacity of $165.1 \text{ mAh} \cdot \text{g}^{-1}$ and a significant capacity retention of 77.2% after 100 cycles.



Supplementary Fig. 3 Typical charge-discharge profiles of LiIn|LPSC|NCM811 cells in the voltage range of 2.8–4.5 V (vs. Li⁺/Li) at 0.05C (10 mA g⁻¹) and 30 °C.

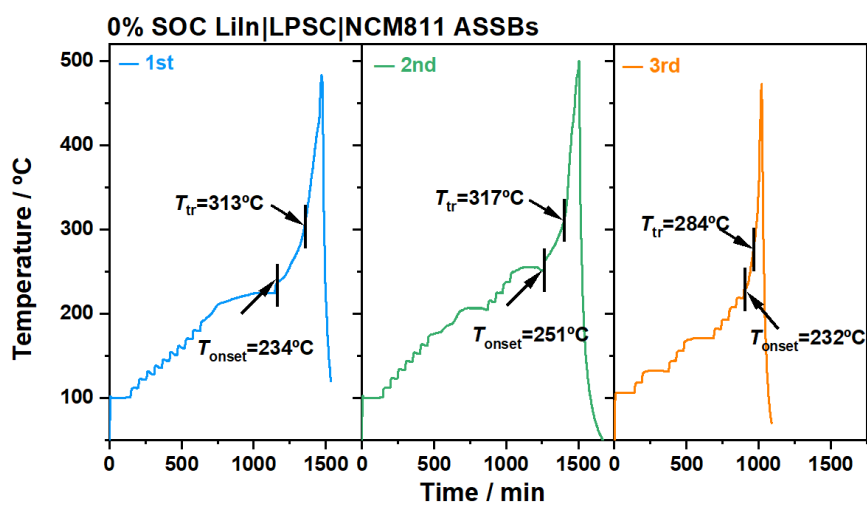
The ASSBs obtained from this experiment are used for thermal runaway testing.

The as-obtained cells delivered an initial charge capacity of 28.13 mAh (243.5 mAh·g⁻¹) and an initial discharge specific capacity of 21.47 mAh (185.9 mAh·g⁻¹).



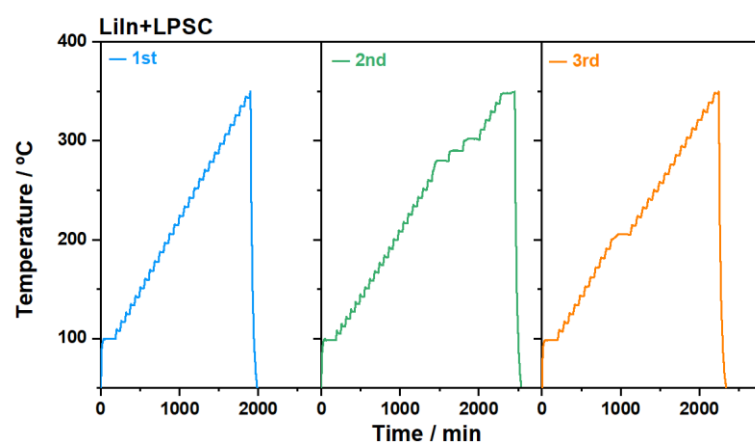
Supplementary Fig. 4 HWS curves of the 100% SOC LiIn|LPSC|NCM811 ASSBs (repeated three times under identical conditions).

$$T_{onset}=163.0\pm8.5\text{ }^{\circ}\text{C}; T_{tr}=231.7\pm2.6\text{ }^{\circ}\text{C}.$$

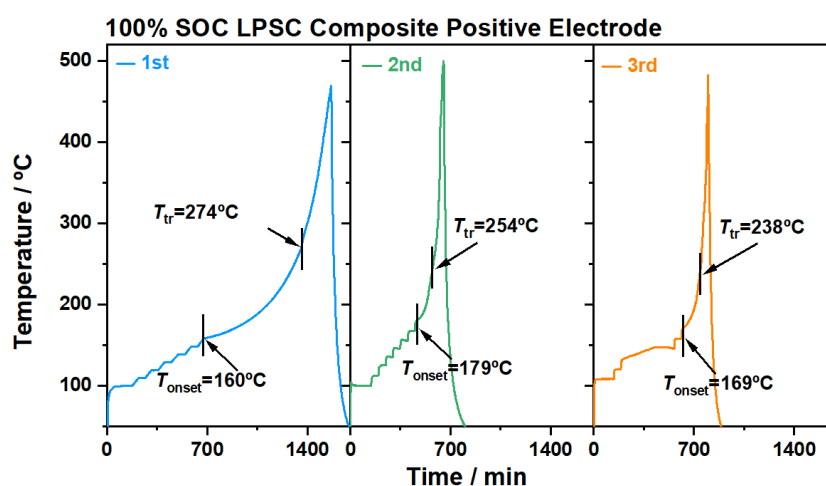


Supplementary Fig. 5 HWS curves of the 0% SOC LiIn|LPSC|NCM811 ASSBs (repeated three times under identical conditions).

$$T_{onset}=239\pm8.5\text{ }^{\circ}\text{C}; T_{tr}=304.7\pm14.7\text{ }^{\circ}\text{C}.$$

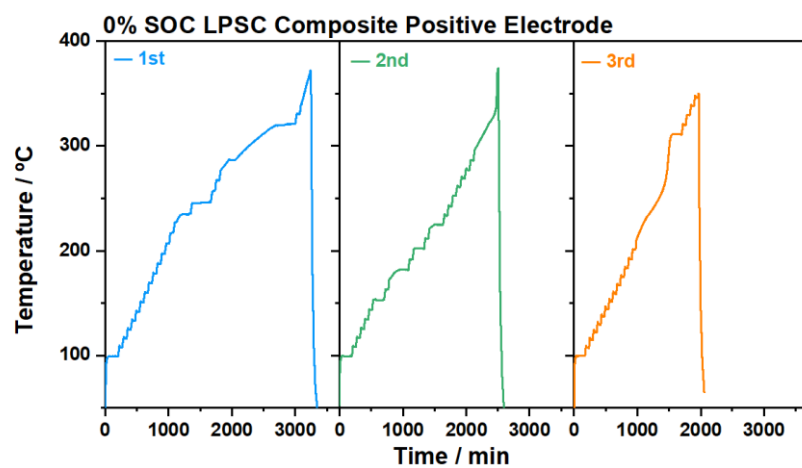


Supplementary Fig. 6 HWS curves of LiIn+LPSC (repeated three times under identical conditions).

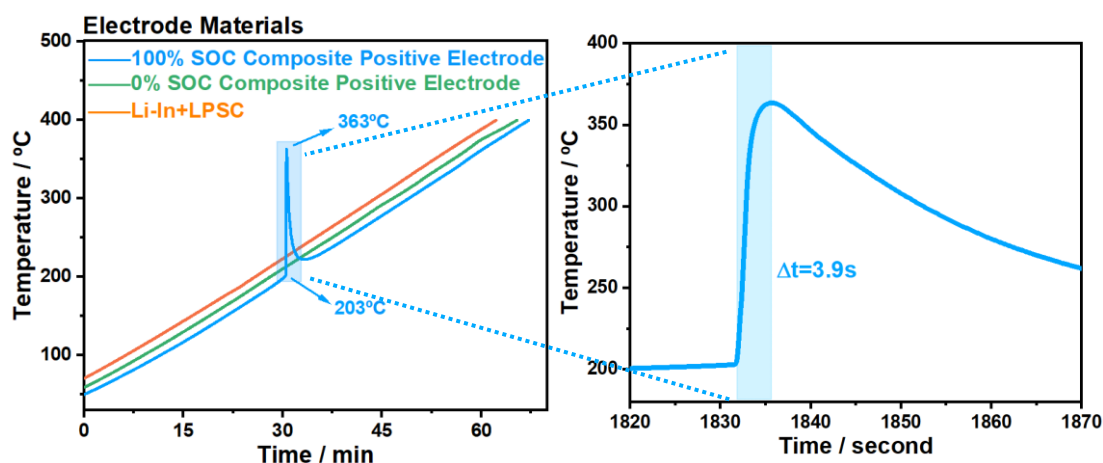


Supplementary Fig. 7 HWS curves of the 100% SOC LPSC composite positive electrode (repeated three times under identical conditions).

$$T_{onset}=169.3\pm7.8\text{ }^{\circ}\text{C}; T_{tr}=255.3\pm14.7\text{ }^{\circ}\text{C}.$$



Supplementary Fig. 8 HWS curves of the 0% SOC LPSC composite positive electrode (repeated three times under identical conditions).



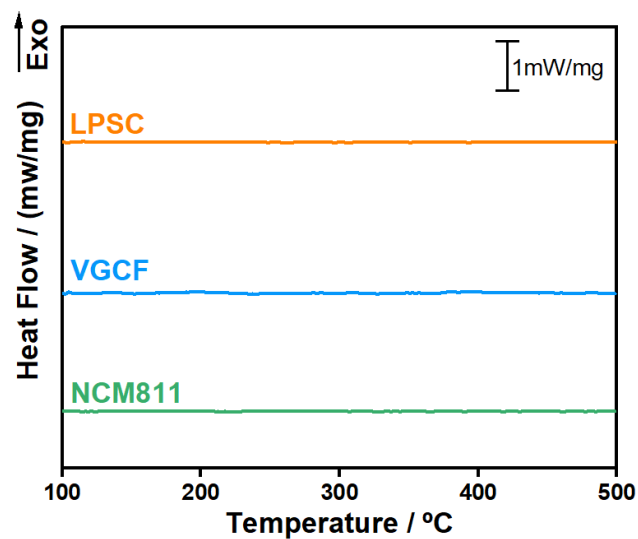
Supplementary Fig. 9 Adiabatic ramp test thermal profiles of electrode materials (negative electrode and positive electrode) at a scanning rate of $5\text{ }^{\circ}\text{C min}^{-1}$ in ARC.

This experiment aims to investigate the thermal runaway behavior of electrode materials under a constant heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. The 100% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) exhibited severe self-heating, with the sample temperature rapidly increases to $363\text{ }^{\circ}\text{C}$ within 3.9 seconds at $203\text{ }^{\circ}\text{C}$, indicating that thermal abuse can trigger thermal runaway in composite positive electrode.



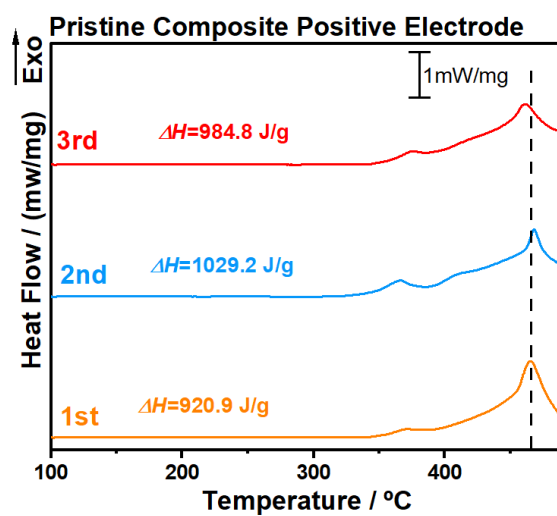
Supplementary Fig. 10 Typical images of the 100% SOC composite positive electrode pellets (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) for thermal runaway driven by mechanical abuse under inert atmospheres.

This experiment aims to investigate the thermal runaway of the 100% SOC composite positive electrode under mechanical abuse conditions. Grinding the 100% SOC composite positive electrode led to violent burning, demonstrating that mechanical abuse can also trigger thermal runaway.



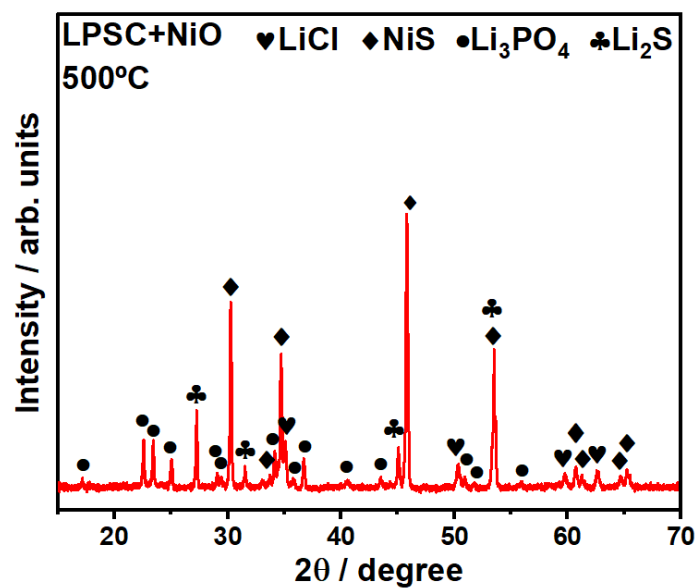
Supplementary Fig. 11 DSC profiles of LPSC, VGCF, and NCM811 samples.

This experiment aims to demonstrate that LPSC, VGCF, and NCM811 all exhibit excellent thermal stability. The three pristine samples without mixing exhibited no heat absorption or release, confirming their inherent high thermal stability.



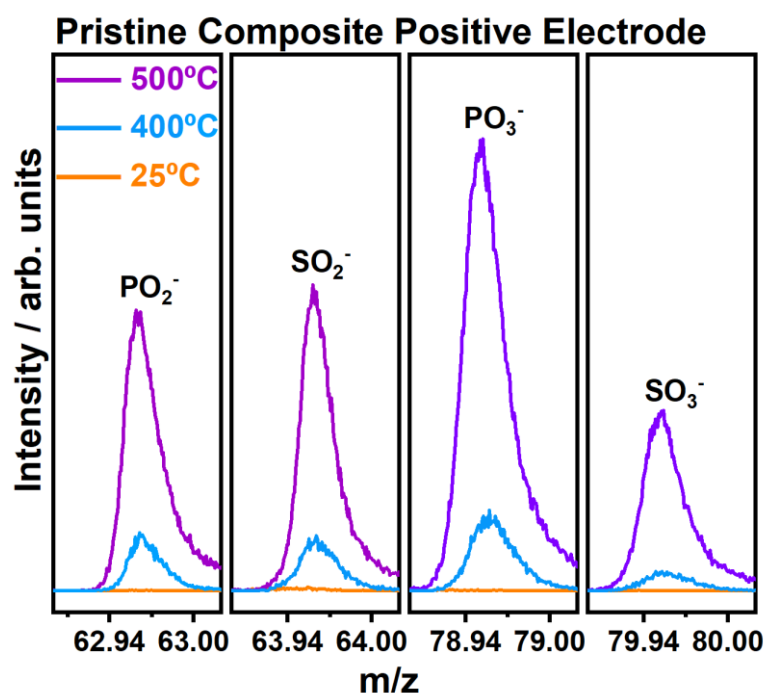
Supplementary Fig. 12 DSC of the pristine LPSC composite positive electrode (repeated three times under identical conditions).

$$\Delta H = 978.3 \pm 44.5 \text{ J} \cdot \text{g}^{-1}.$$



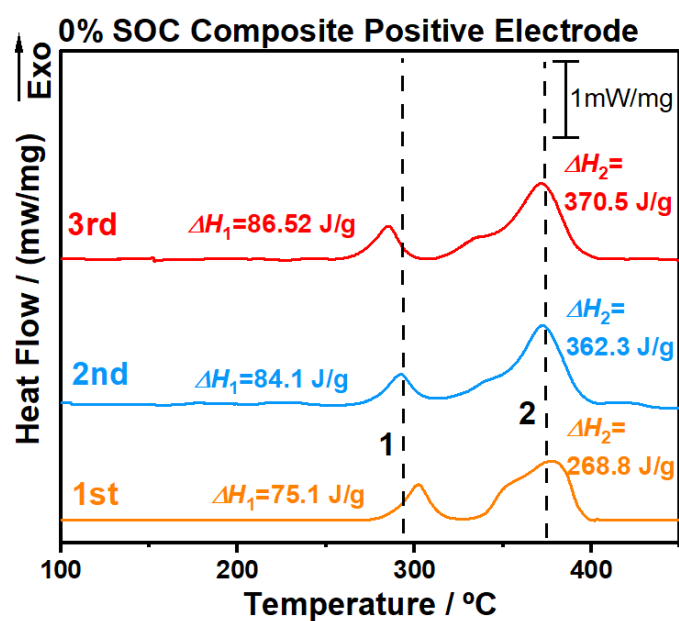
Supplementary Fig. 13 XRD patterns of LPSC with NiO in a 1:1 mass ratio after heating at 500 °C.

The aim of this experiment is to confirm that the second exothermic reaction in the pristine composite positive electrode involves the interactions between transition metal oxides and LPSC. The heating of LPSC with NiO resulted in the formation of NiCl, NiS, Li₃PO₄, and Li₂S. The formation of transition metal sulfides proved the validity of this conclusion.



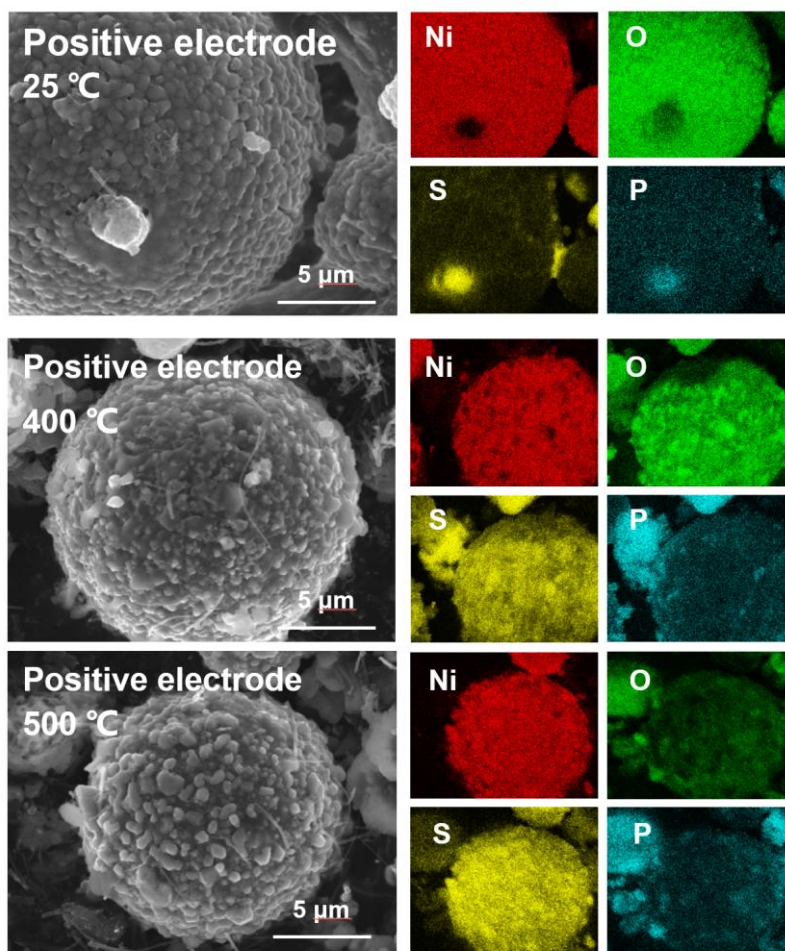
Supplementary Fig. 14 TOF-SIMS for the pristine composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) at 25 °C, 400 °C, and 500 °C.

To determine the exothermic reactions of NCM811 and LPSC in the pristine composite positive electrode, we conduct tests by heating the samples to various temperatures. The m/z at 62.96, 63.96, 78.95, and 79.95 correspond to PO_2^- , SO_2^- , PO_3^- , and SO_3^- . At 400 °C, the generation of PO_2^- , SO_2^- , PO_3^- , and SO_3^- indicated that the interfacial reactions are accompanied by the formation of P-O and S-O bonds. Upon further heating to 500 °C, the increased intensity of these signals suggested further generation of P-O and S-O bonds.



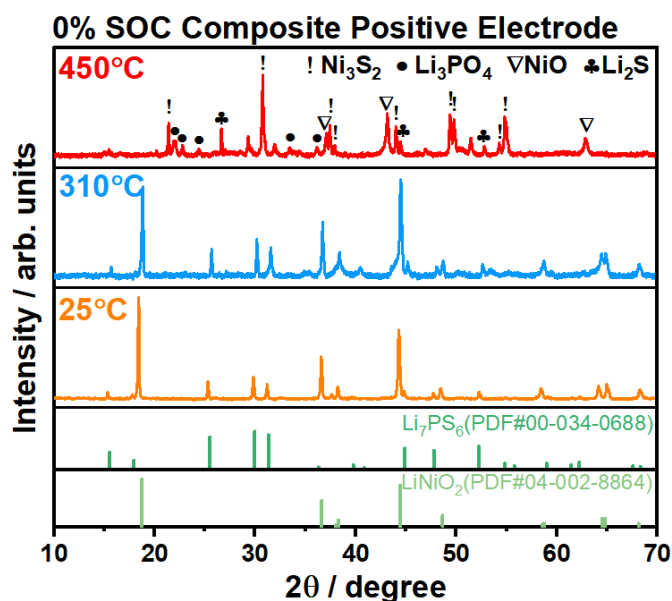
Supplementary Fig. 15 DSC of the 0% SOC LPSC composite positive electrode (repeated three times under identical conditions).

$$\Delta H_1 = 81.9 \pm 4.9 \text{ J} \cdot \text{g}^{-1}; \quad \Delta H_2 = 333.9 \pm 56.2 \text{ J} \cdot \text{g}^{-1}.$$



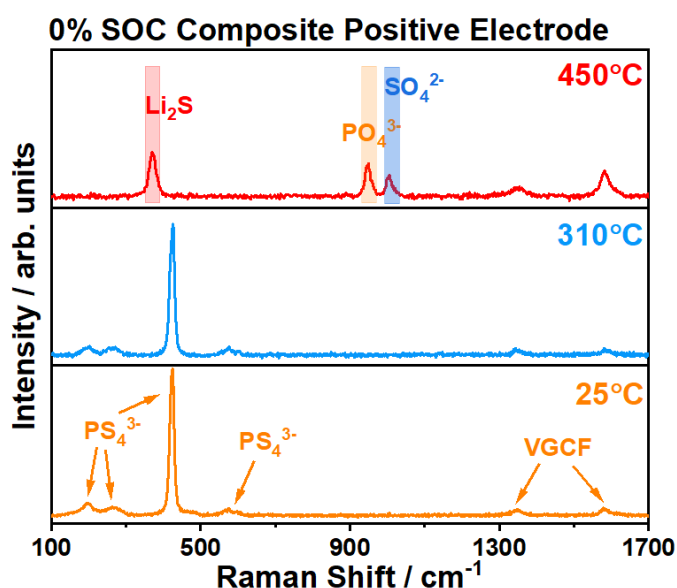
Supplementary Fig. 16 Typical surface SEM images and Ni, O, S, and P mapping results of the 0% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) at 25 °C, 310 °C, and 450 °C.

To determine the exothermic reactions of the 0% SOC composite positive electrode, we conduct tests by heating the samples to various temperatures. After heating at 310 °C, it was observed by SEM imaging that the diffusion of sulfur (S) into NCM811, indicating the decomposition of the interphase components. After heating at 450 °C, strong presence of Ni and S were observed in NCM811, while strong P and O were found in LPSC, indicating the complete occurrence of the interfacial reactions between NCM811 and LPSC.



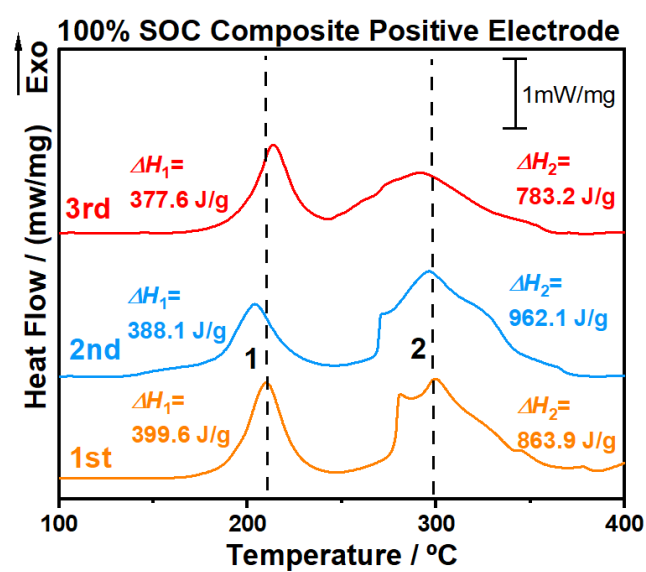
Supplementary Fig. 17 XRD spectra for the 0% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) measured at 25 °C, 310 °C, and 450 °C.

To determine the exothermic reactions of the 0% SOC composite positive electrode, we conduct tests by heating the samples to various temperatures. When heated to 310 °C, no significant changes occurred, suggesting that no reaction occurred between NCM811 and LPSC. Upon heating to 450 °C, the characteristic peaks of NCM811 and LPSC disappeared, while interfacial reactions products such as Ni_3S_2 , Li_3PO_4 , NiO , and Li_2S emerged. These findings indicate that the reactions between NCM811 and LPSC only occur during the second exothermic reaction, without involvement in the first exothermic event.



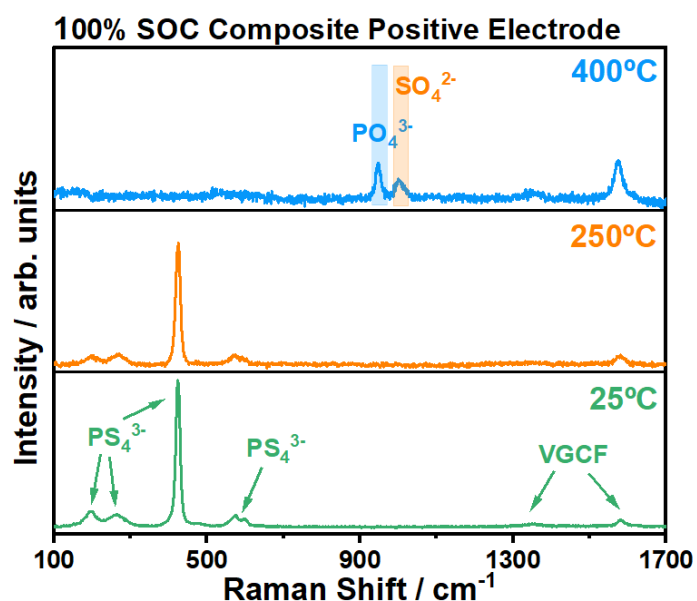
Supplementary Fig. 18 Raman profile of the 0% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) after heating at 25 °C, 310 °C, and 450 °C.

To determine the exothermic reactions of the 0% SOC composite positive electrode, we conduct tests by heating the samples to various temperatures. For the 0% SOC composite positive electrode, no significant changes were observed when heated to 310°C, indicating that no reaction occurred between NCM811 and LPSC. Upon heating to 450 °C, the characteristic peaks of NCM811 and LPSC disappeared, while interphase products such as Li₂S, PO₄³⁻, and SO₄²⁻ emerged. These findings indicate that the reactions between NCM811 and LPSC only occur during the second exothermic reaction, without involvement in the first exothermic event.



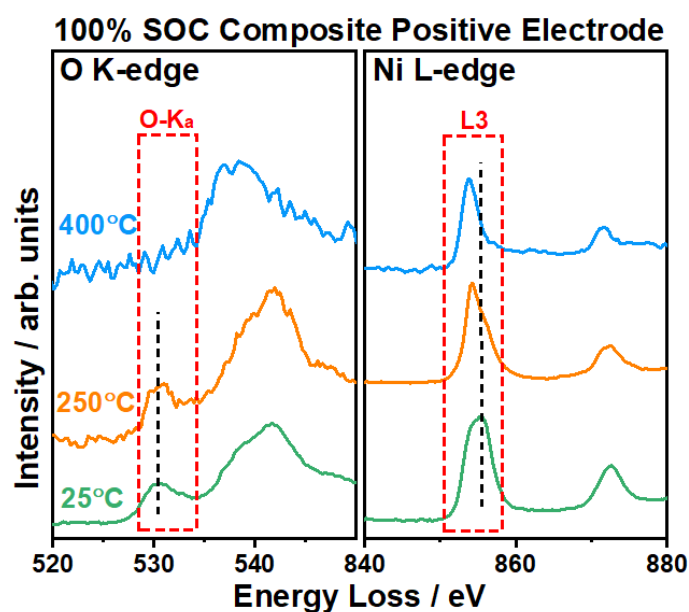
Supplementary Fig. 19 DSC of the 100% SOC LPSC composite positive electrode (repeated three times under identical conditions).

$$\Delta H_1 = 381.8 \pm 16.4 \text{ J} \cdot \text{g}^{-1}; \quad \Delta H_2 = 869.7 \pm 89.5 \text{ J} \cdot \text{g}^{-1}.$$



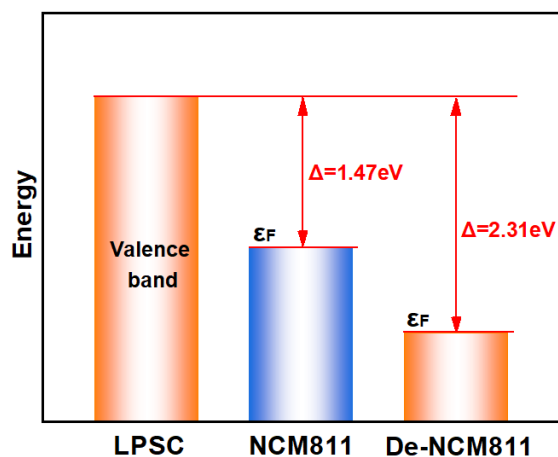
Supplementary Fig. 20 Raman profile of the 100% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) after heating at 25 °C, 250 °C, and 400 °C.

To determine the exothermic reactions of the 100% SOC composite positive electrode, we conduct tests by heating the samples to various temperatures. For the 100% SOC composite positive electrode, no significant changes were observed when heated to 250°C, indicating that no reaction occurred between NCM811 and LPSC. Upon heating to 450 °C, the characteristic peaks of NCM811 and LPSC disappeared, while interphase products such as Li_2S , PO_4^{3-} , and SO_4^{2-} emerged, indicating the complete occurrence of the interfacial reactions between NCM811 and LPSC.



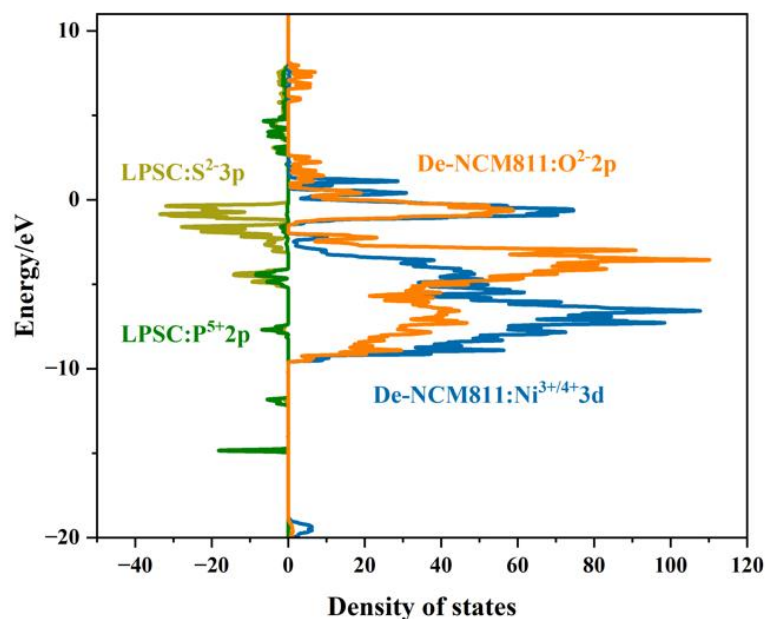
Supplementary Fig. 21 EELS spectrum of the 100% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) after heating at 25 °C, 250 °C, and 400 °C.

The aim of this experiment is to determine the exothermic reactions in the 100% SOC composite positive electrode by analyzing the changes in the valence states of transition metal elements. At 250 °C, the shift of the O *K*-edge pre-edge peak (527-534 eV, O-K_a) to higher energy loss and the Ni *L*-edge peak (852-858 eV, *L*3) to lower energy loss depicted the reduction of Ni^{3+/4+} and the release of reactive lattice oxygen, which accounted for the generation of various oxygen-containing gases during the first exothermic reaction. At 400 °C, the disappearance of the O *K*-edge pre-edge peak and the continuous shift of the Ni *L*-edge peak to lower energy loss corroborated the further reduction of Ni and the complete transformation of NCM811 into the rock-salt phase.



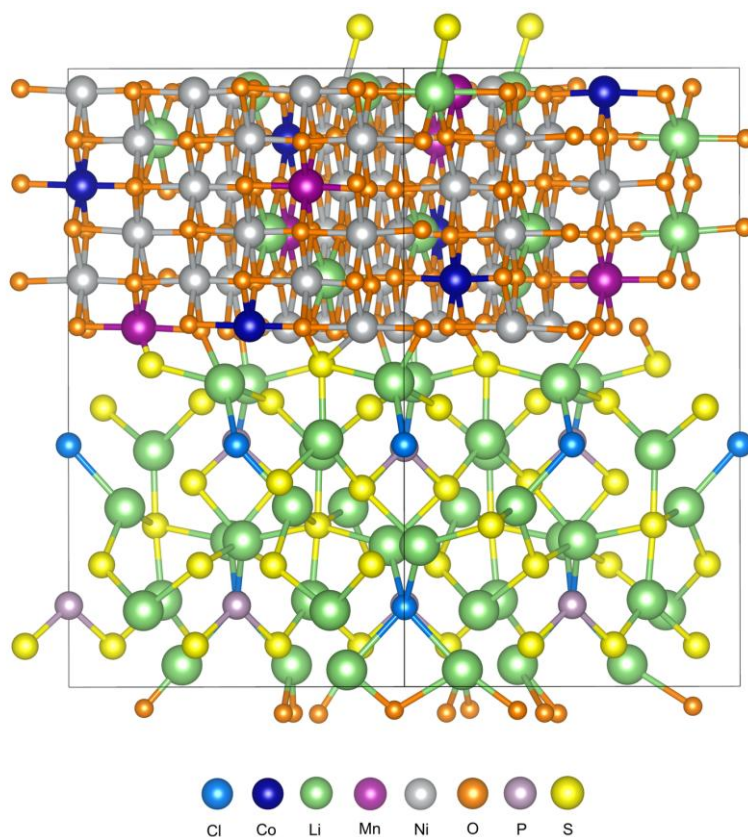
Supplementary Fig. 22 Schematic of oxidative degradation mechanism of a solid electrolyte in contact with a positive electrode active material based on band theory of solids.

The objective of this experiment is to demonstrate the inherent interfacial incompatibility between LPSC and NCM811. The VBM of LPSC lied energetically above the Fermi level of NCM811 and De-NCM811. This interfacial energy offset drives electron transferring from SE to positive electrode, leading to the oxidative degradation of LPSC. These findings highlight the intrinsic incompatibility at the NCM811/LPSC interface.



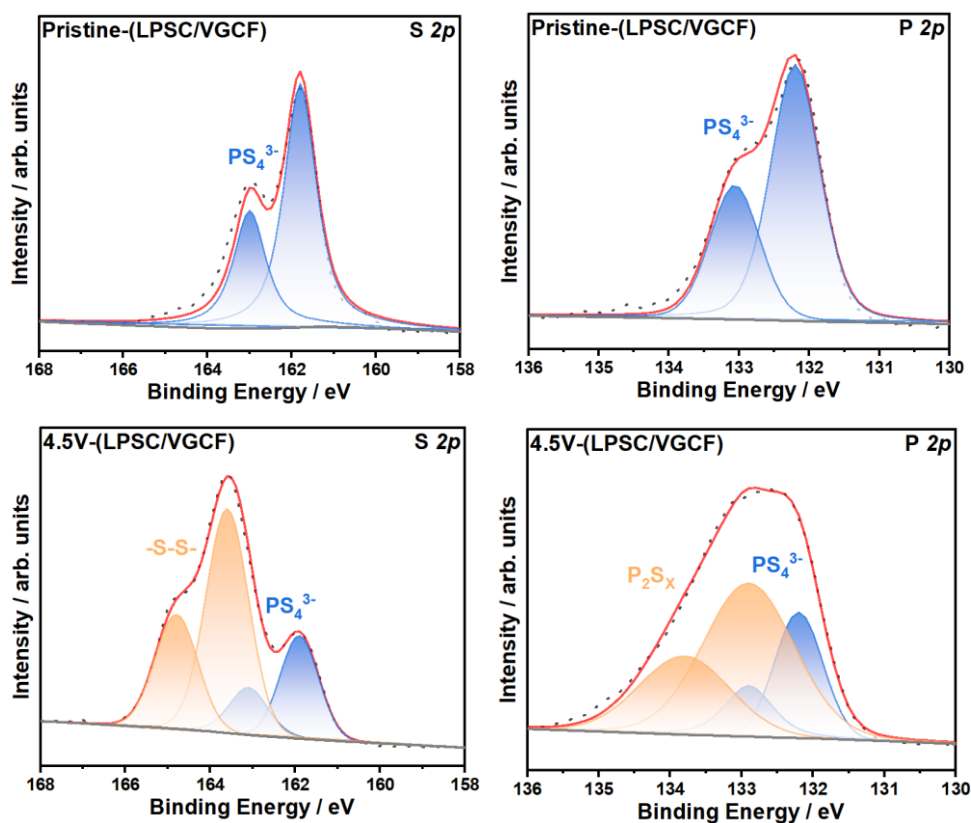
Supplementary Fig. 23. Densities of states (DOSs) of LPSC and De-NCM811.

The objective of this experiment is to demonstrate the inherent interfacial incompatibility between LPSC and De-NCM811. DOS calculations revealed significant overlap between the S 3*p* orbitals of LPSC and the O 2*p*/Ni *e_g* orbitals of De-NCM811 near the Fermi level. This overlap indicates a lower energy barrier for electron exchange, further supporting the hypothesis of strong chemical incompatibility between them. Furthermore, the P 2*p* orbitals of LPSC also showed considerable overlap with the O 2*p*/Ni *e_g* orbitals of De-NCM811, suggesting a tendency for spontaneous chemical bonding.



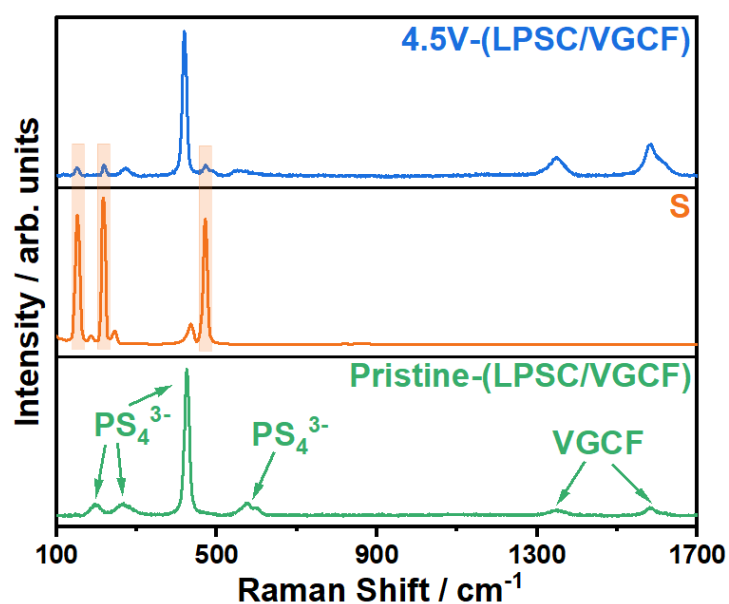
Supplementary Fig. 24 Delithiated NCM811 with LPSC at 25 °C simulated by AIMD.

The aim of this experiment is to investigate the interfacial reactions between delithiated NCM811 and LPSC. The delithiated NCM811 and LPSC were chemically incompatible, resulting in the formation of S-O and S-Ni at the positive electrode/SE interface. However, the relatively slow interfacial reaction kinetics at room temperature contributed to the stability of the majority of the PS_4^{3-} structure.



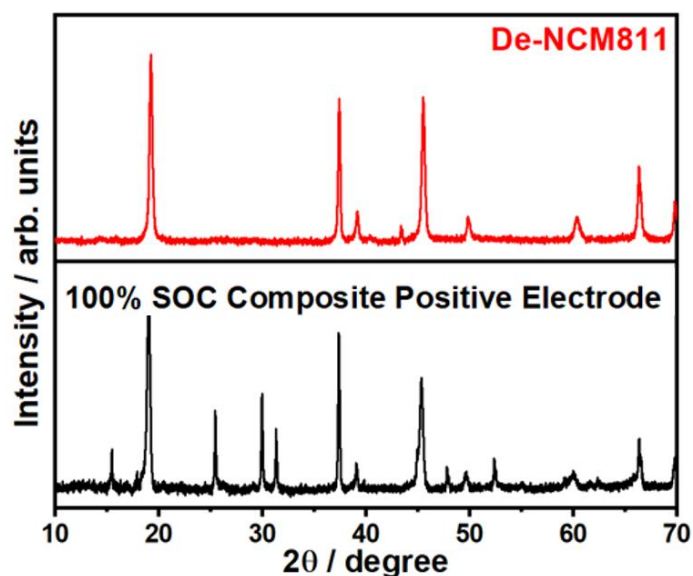
Supplementary Fig. 25 S 2*p* and P 2*p* XPS spectra for the LPSC/VGCF (LPSC and VGCF in a weight of 9:1) before and after being charged to 4.5 V (vs. Li⁺/Li).

This experiment aims to obtain the electrochemically decomposed LPSC and demonstrate that its decomposition products align with the interphase composition of the 100% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3). S 2*p* and P 2*p* XPS spectra revealed that after electrochemical decomposition, LPSC formed an interphase containing components such as -S-S- and -P-S-P-, consistent with the interphase composition of the 100% SOC composite positive electrode.



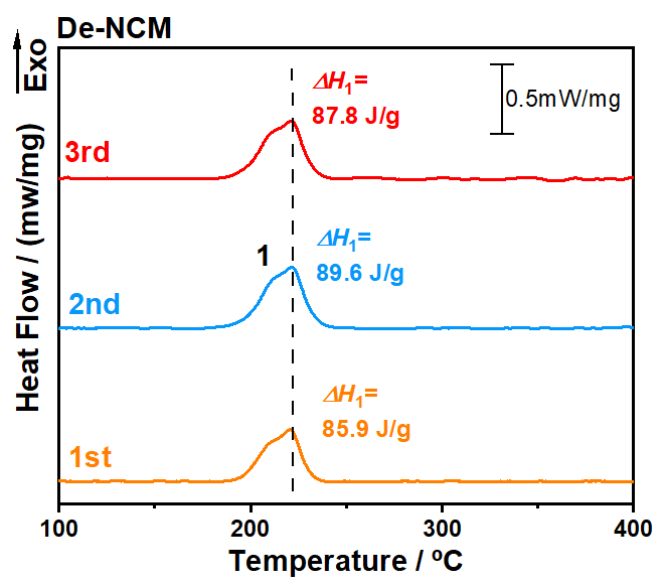
Supplementary Fig. 26 Raman spectra of LPSC/VGCF (LPSC and VGCF in a weight of 9:1) before and after being charged to 4.5 V (vs. Li⁺/Li).

This experiment aims to obtain the electrochemically decomposed LPSC and demonstrate that its decomposition products align with the interphase composition of 100% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3). The characteristic peaks observed at 152 cm⁻¹, 217 cm⁻¹, and 471 cm⁻¹ in Raman spectra confirmed the presence of S, which was a product of the electrochemical decomposition of LPSC under high voltage conditions. The decomposition product is consistent with the interphase composition of the 100% SOC composite positive electrode.



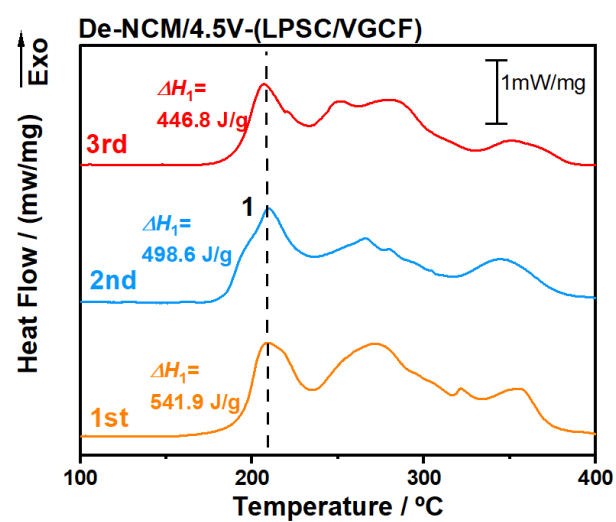
Supplementary Fig. 27 XRD patterns of the 100% SOC composite positive electrode (NMC811, LPSC, and VGCF in a weight ratio of 70:30:3) and the delithiated NCM811 (named as De-NCM) from LIBs.

The aim of this experiment is to obtain a large quantity of delithiated NCM811 from LIBs for subsequent testing. The NCM811/LE/Gr LIBs were charged to 4.5 V (vs. Li^+/Li) at 0.05C (10mA g^{-1}) and 30 °C. After soaking in EC and thorough cleaning, the electrode was dried in an argon atmosphere. Finally, the positive electrode powders were gently scraped off the current collector and collected for subsequent testing. The delithiated NCM811 obtained from LIBs exhibited a structure similar to that of ASSBs. Therefore, it is feasible and reasonable to use this delithiated NCM811, isolated from LIBs, to investigate the interfacial reactions between it and various sulfur-containing substances (such as sulfide SEs and their electrochemical decomposition products).



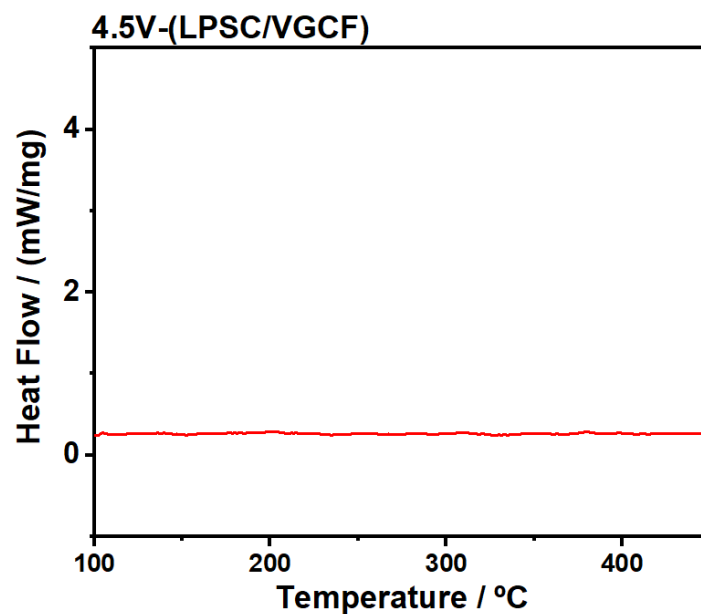
Supplementary Fig. 28 DSC of the De-NCM (repeated three times under identical conditions).

$$\Delta H_1 = 58.9 \pm 0.6 \text{ J} \cdot \text{g}^{-1}.$$



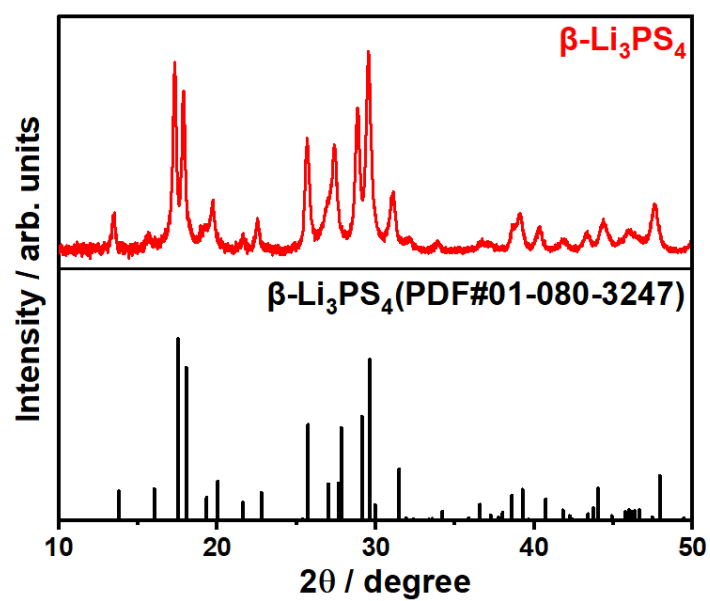
Supplementary Fig. 29 DSC of the De-NCM/4.5V-(LPSC/VGCF) (repeated three times under identical conditions).

$$\Delta H_1 = 495.8 \pm 47.6 \text{ J} \cdot \text{g}^{-1}.$$



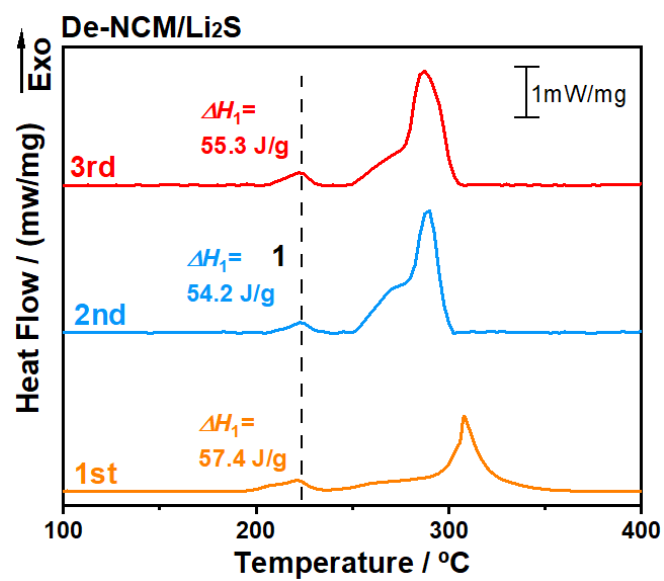
Supplementary Fig. 30 DSC profiles of LPSC/VGCF (LPSC and VGCF in a weight of 9:1) after being charged to 4.5 V (vs. Li^+/Li).

The aim of this experiment is to demonstrate that the heat contribution from the first exothermic peak of De-NCM/4.5V-(LPSC/VGCF) is unrelated to the decomposition reaction of 4.5V-(LPSC/VGCF) itself. The absence of endothermic or exothermic peaks in 4.5V-(LPSC/VGCF) proved the validity of the conclusion.



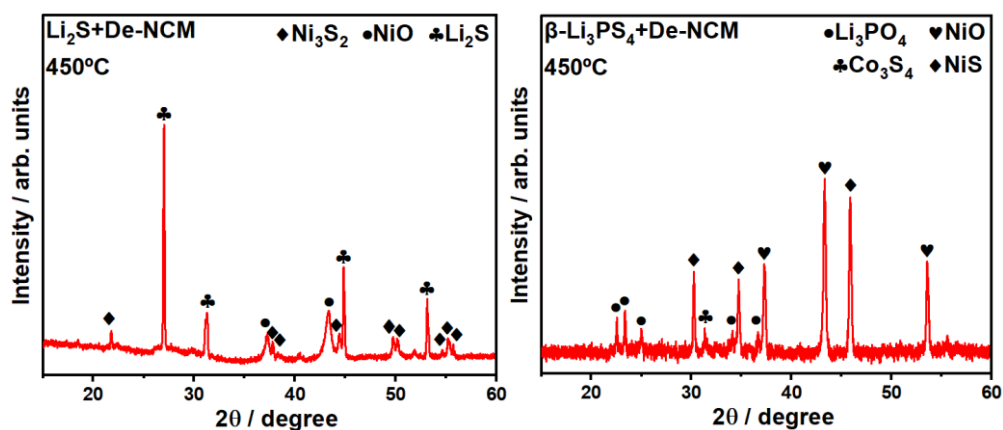
Supplementary Fig. 31 XRD patterns of the as-synthesized $\beta\text{-Li}_3\text{PS}_4$ samples.

The as-synthesized $\beta\text{-Li}_3\text{PS}_4$ samples are used to investigate the impact of the electrochemical decomposition products of LPSC on the exothermic behavior.



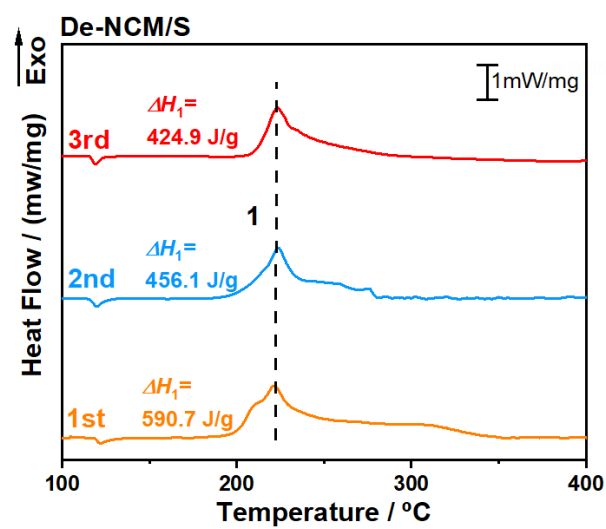
Supplementary Fig. 32 DSC of the De-NCM/Li₂S (repeated three times under identical conditions).

$$\Delta H_1 = 55.6 \pm 1.6 \text{ J} \cdot \text{g}^{-1}.$$



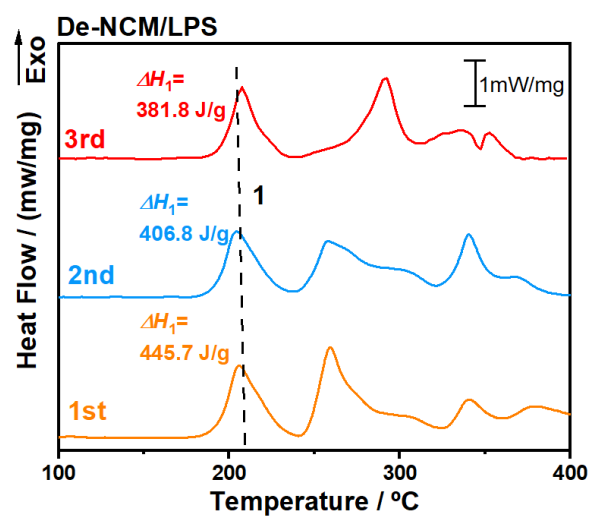
Supplementary Fig. 33 XRD patterns of electrochemical decomposition products of LPSC (Li₂S (left) and β-Li₃PS₄ (right)) with delithiated NCM811 (named as De-NCM) after heating at 450 °C.

The aim of this experiment is to identify the exothermic reaction products of electrochemical decomposition products of LPSC (Li₂S and β-Li₃PS₄) with delithiated NCM811. After heating at 450 °C, β-Li₃PS₄ combined with delithiated NCM811 yielded NiO, NiS, Li₃PO₄, and Co₃S₄, while Li₂S combined with delithiated NCM811 produced NiO and Ni₃S₂.



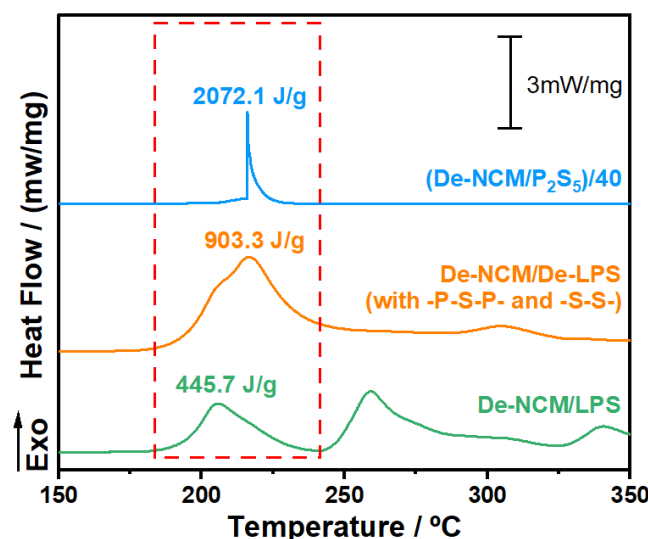
Supplementary Fig. 34 DSC of the De-NCM/S (repeated three times under identical conditions).

$$\Delta H_1 = 490.6 \pm 87.1 \text{ J} \cdot \text{g}^{-1}.$$



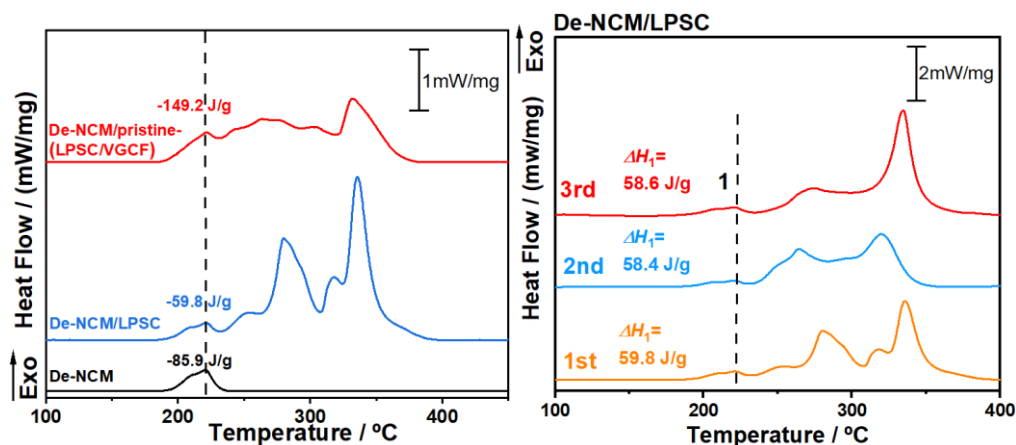
Supplementary Fig. 35 DSC of the De-NCM/LPS (repeated three times under identical conditions).

$$\Delta H_1 = 441.4 \pm 32.3 \text{ J/g.}$$



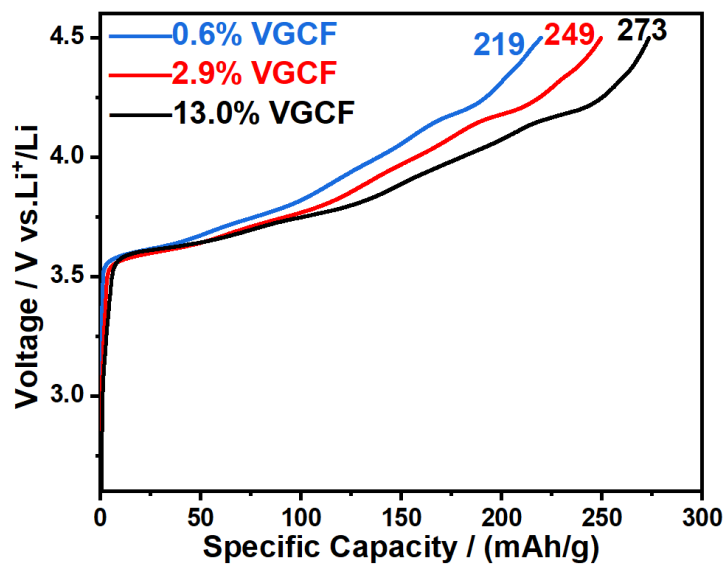
Supplementary Fig. 36 DSC profiles of β -Li₃PS₄ (LPS) and delithiated NCM811 (LPS and delithiated NCM811 in a weight ratio of 3:7); delithiated- β -Li₃PS₄ (De-LPS, including -P-S-P- and -S-S-) and delithiated NCM811 (De-LPS and delithiated NCM811 in a weight ratio of 3:7); P₂S₅ and delithiated NCM811 (P₂S₅ and delithiated NCM811 in a weight ratio of 3:7).

The aim of this experiment is to investigate the effect of -P-S-P- species on early-stage exothermic reactions. Prior studies have shown that electrochemical decomposition of LPS generates -S-S- and -P-S-P- structures (such as P₂S₇⁴⁻, P₂S₆²⁻, and P₂S₅).^[1-3] When the electrochemically decomposed LPS was mixed with delithiated NCM811, the observed enthalpy change reached 903.3 J·g⁻¹, larger than those for the De-NCM/S and De-NCM/ β -LPS mixtures (590.7 J·g⁻¹ and 445.7 J·g⁻¹, respectively). This indicates that the degraded -P-S-P- species are involved in early-stage exothermic reactions with the delithiated NCM, resulting in a considerably higher heat release. Meanwhile, the De-NCM/4.5V-(LPSC/VGCF) system exhibits higher early-stage heat release (541.9 J·g⁻¹) than De-NCM/ β -LPS blends and De-NCM/sulfur composites, directly linking this phenomenon to interfacial electrochemical activity. This is further corroborated by the substantial enthalpy change (2072.1 J·g⁻¹) measured in De-NCM/P₂S₅ mixtures, which establishes the dominant role of -P-S-P- moieties in initiating exothermic cascades during thermal runaway.



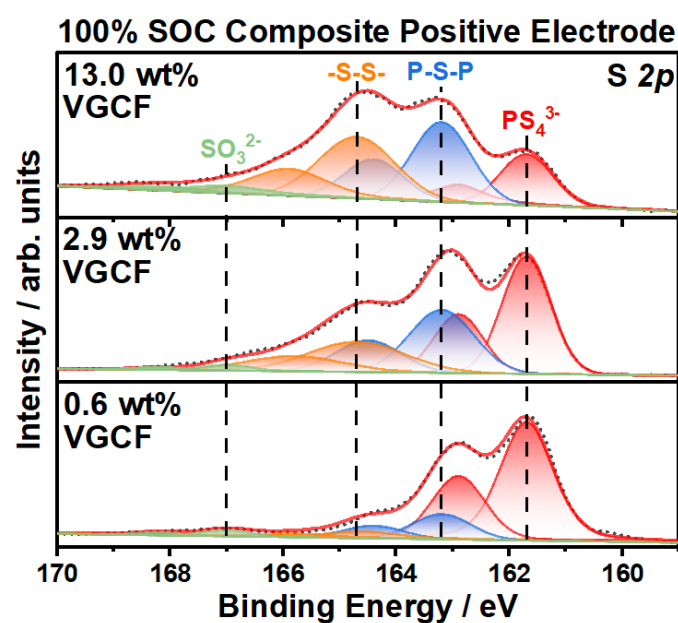
Supplementary Fig. 37 DSC profiles of delithiated NCM (named as De-NCM), De-NCM/LPSC (De-NCM and LPSC in a weight ratio of 7:3), and De-NCM/pristine-(LPSC/VGCF) (De-NCM, LPSC, and VGCF in a weight ratio of 70:30:3).

The purpose of this experiment is to quantify the heat contribution from the reaction between VGCF with De-NCM. For the De-NCM, an exothermic peak was observed at 221 °C with a total enthalpy change of 85.9 J·g⁻¹. In the case of De-NCM/LPSC, the first exothermic peak observed at 221 °C was nearly identical to that of the NCM phase transition, with a heat release of 59.8 J·g⁻¹ (58.9±0.6 J·g⁻¹). The heat generated by the delithiated NCM in De-NCM/LPSC was calculated as 85.9 × 0.7 = 60.1 J·g⁻¹, which was almost identical to the observed 59.8 J·g⁻¹. These findings indicate that LPSC and delithiated NCM do not react during the first exothermic process. For De-NCM/(LPSC/VGCF), the first exothermic peak remained unchanged at 221 °C, but the enthalpy change increased to 149.2 J·g⁻¹. Here, the NCM contributes 58.4 J·g⁻¹ (85.9×70 / 103 J·g⁻¹), while the remaining 90.8 J·g⁻¹ could be attributed to the heat released by VGCF during the generation of CO₂ and CO.



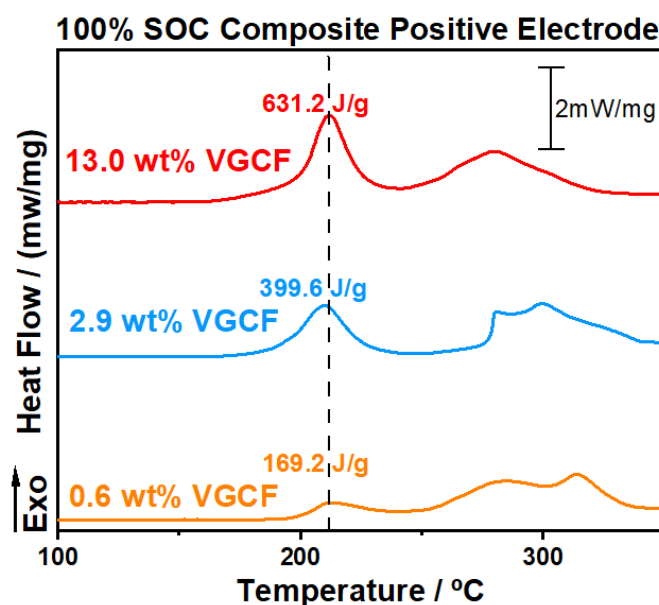
Supplementary Fig. 38 Typical charge curves of the cell of NCM811/LPSC/Li-In with different wt% of VGCF (carbon additive) after charging to 4.5 V (vs. Li⁺/Li) at 0.1C and 30 °C.

The aim of this experiment is to prepare three 100% SOC composite positive electrodes with different VGCF wt% for thermal runaway testing, in order to investigate the influence of VGCF on thermal propagation mechanisms.



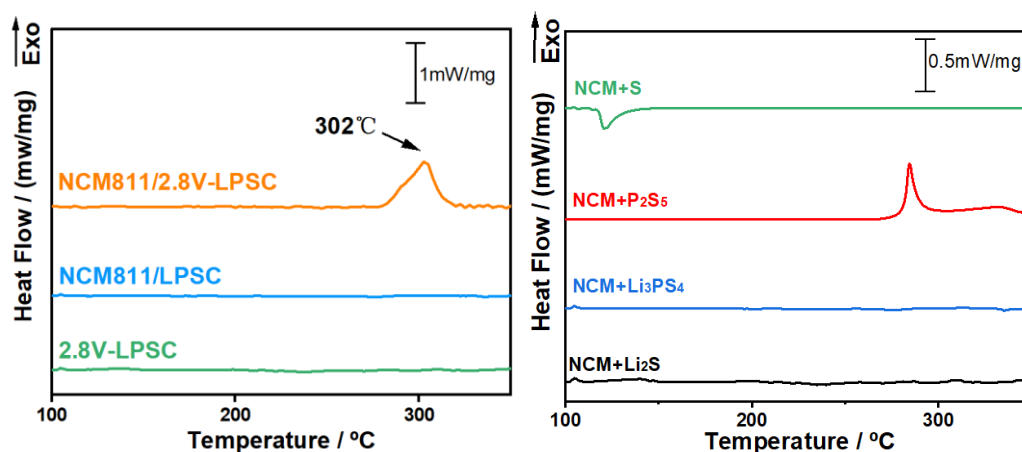
Supplementary Fig. 39 S 2p XPS spectra of the 100% SOC composite positive electrodes with different wt% of VGCF (carbon additive).

The aim of this experiment is to demonstrate that the presence of VGCF can promote the electrochemical decomposition of LPSC. As the VGCF content increased, the intensity of -S-S- and -P-S-P- also increased in the 100% SOC composite positive electrode, indicating that VGCF promoted the decomposition of LPSC to form -S-S- and bridge sulfur species.



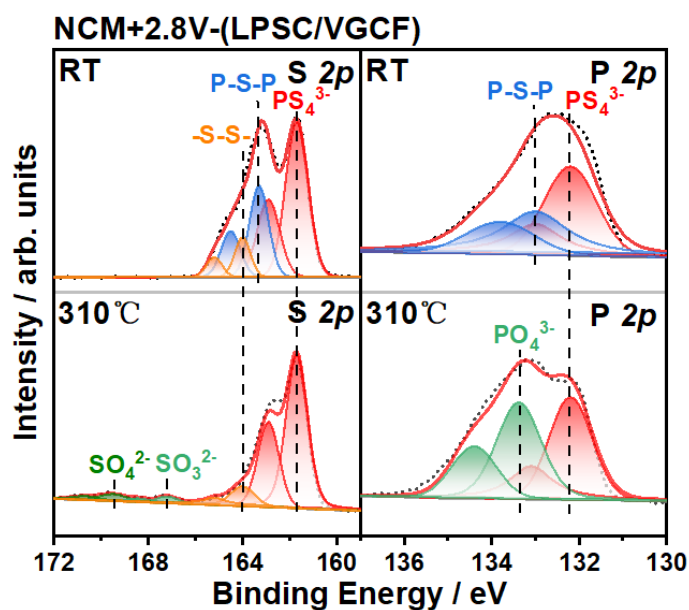
Supplementary Fig. 40 DSC curves of the 100% SOC composite positive electrodes with different wt% of VGCF (carbon additive).

The aim of this experiment is to investigate the impact of the presence of VGCF on the exothermic reactions. As the VGCF content increased, enthalpy changes of the first exothermic peak increased to $169.2 \text{ J}\cdot\text{g}^{-1}$, $399.6 \text{ J}\cdot\text{g}^{-1}$, and $631.2 \text{ J}\cdot\text{g}^{-1}$. These findings confirm two synergistic thermal pathways: (1) direct exothermic carbon-positive electrode reactions generating CO/CO₂, and (2) catalytic acceleration of LPSC decomposition that amplifies subsequent interfacial exothermicity. This dual mechanism establishes conductive carbon as both reactant and reaction promoter in thermal runaway initiation.



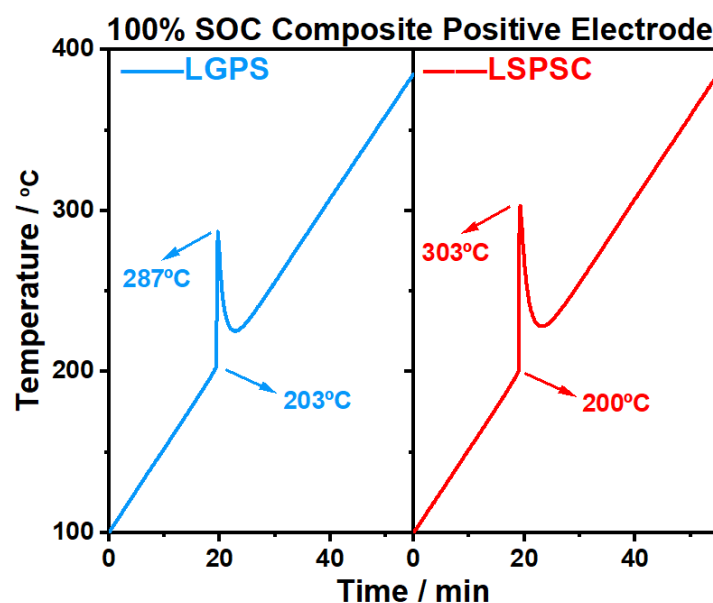
Supplementary Fig. 41 DSC profiles of NCM/2.8V-(LPSC/VGCF), NCM/LPSC, 2.8V-(LPSC/VGCF), NCM/S, NCM/P₂S₅, NCM/Li₃PS₄, and NCM/Li₂S.

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 positive electrode. 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). 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. This strongly suggests that the first exothermic event at 0% SOC is attributed to the reaction between NCM and phosphorus sulfide intermediates (such as -P-S-P- bridged structures) generated from LPSC decomposition.



Supplementary Fig. 42 S 2p and P 2p XPS spectra of the NCM/2.8V-(LPSC/VGCF) at 25 °C and 310 °C.

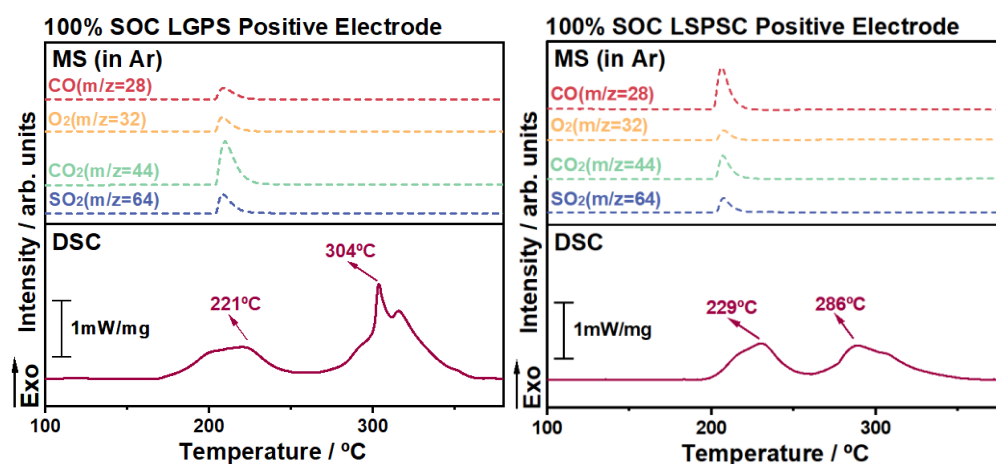
To probe the specific reaction pathway, we employed XPS to analyze the NCM/2.8V-(LPSC/VGCF) mixture before and after heating to 310 °C. The spectra confirmed the consumption of -P-S-P- species and the simultaneous formation of oxidation products including SO₃²⁻, SO₄²⁻, and PO₄³⁻. This evidence supports the proposed reaction pathway for the first stage: $\text{-P-S-P-} + \text{NCM} \rightarrow \text{SO}_3^{2-} + \text{SO}_4^{2-} + \text{PO}_4^{3-}$



Supplementary Fig. 43 Adiabatic ramp test thermal profiles of the 100% SOC LGPS and LSPSC composite positive electrodes (NMC811, SE, and VGCF in a weight ratio of 70:30:3) at a scanning rate of 5 °C min⁻¹ in ARC.

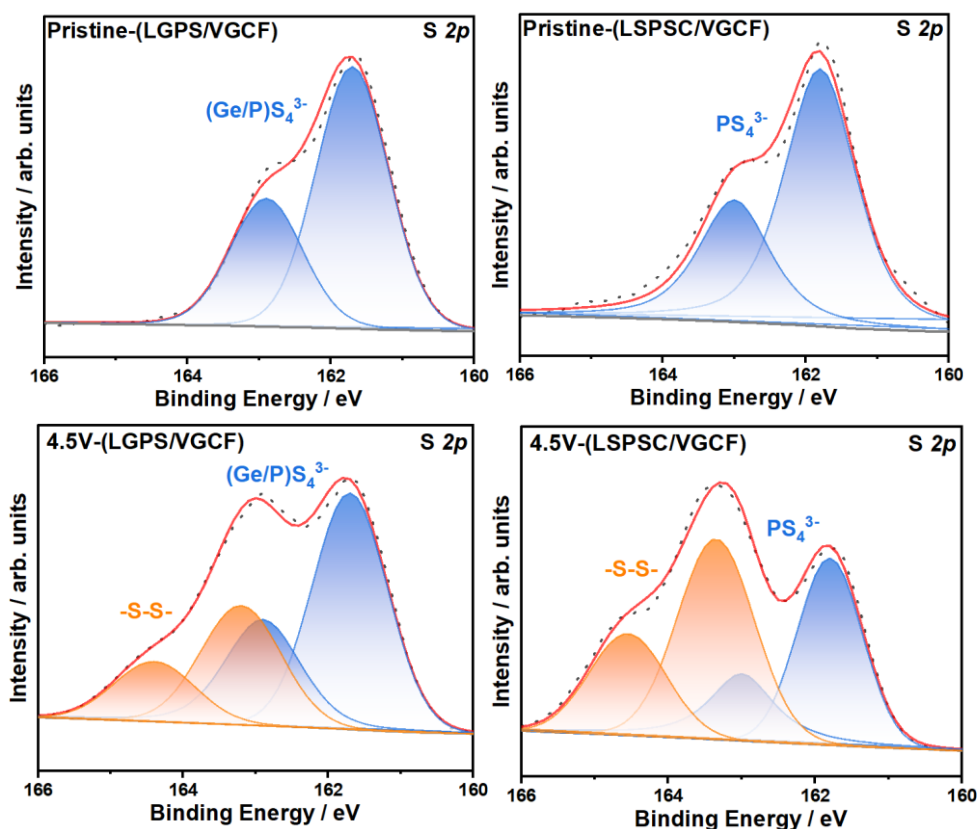
This experiment aims to investigate the thermal runaway behaviors of the 100% SOC LGPS and LSPSC composite positive electrodes under a constant heating rate of 5 °C min⁻¹. 100% SOC LGPS composite positive electrode exhibited severe self-heating, with the sample temperature rapidly increases to 287 °C at 203 °C. And 100% SOC LSPSC composite positive electrode also exhibited severe self-heating, with the sample temperature rapidly increases to 303 °C at 200 °C. These indicate that thermal abuse can trigger thermal runaway in these composite positive electrodes.

Additionally, the 100% SOC LPSC (Supplementary Fig. 4), LGPS, and LSPSC composite positive electrodes all exhibited significant severe self-heating around 200°C, suggesting that this phenomenon may be caused by the same underlying mechanism. We will further investigate this in subsequent studies.



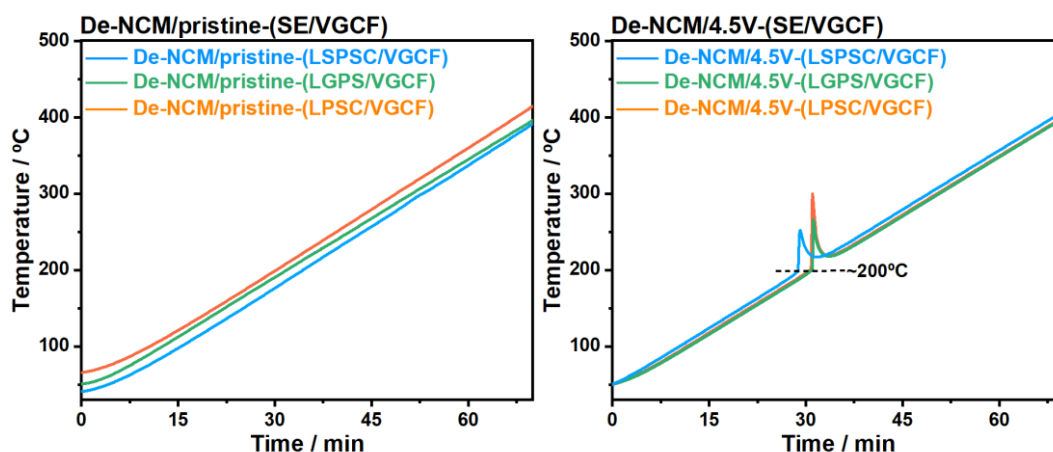
Supplementary Fig. 44 DSC and MS profiles of the 100% SOC LGPS (left) and LSPSC (right) composite positive electrodes (NMC811, SE, and VGCF in a weight ratio of 70:30:3).

The aim of this experiment is to investigate the exothermic and gas-generation behaviors of the 100% SOC LGPS and LSPSC composite positive electrodes. The enthalpy changes of the first exothermic reaction for the 100% SOC LGPS and LSPSC composite positive electrodes were $320.7 \text{ J}\cdot\text{g}^{-1}$ and $346.4 \text{ J}\cdot\text{g}^{-1}$, respectively, accompanied by the generation of SO_2 .



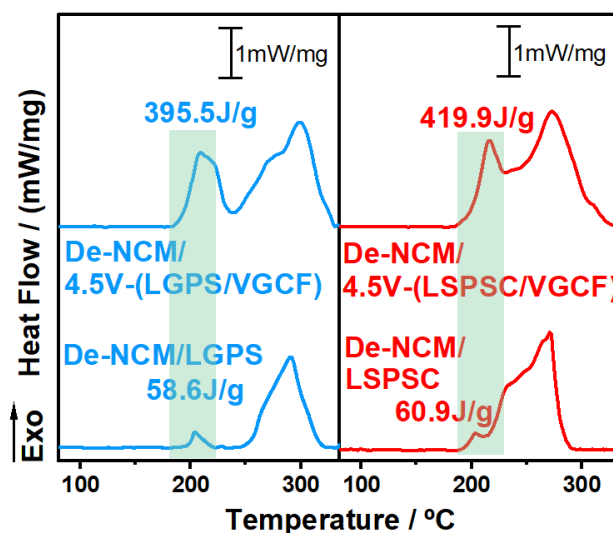
Supplementary Fig. 45 S 2*p* XPS spectra for the LGPS/VGCF (LGPS and VGCF in a weight of 9:1) and LSPSC/VGCF (LSPSC and VGCF in a weight of 9:1) before and after charging to 4.5V (vs. Li⁺/Li).

This experiment aims to obtain the electrochemically decomposed LGPS and LSPSC. Similar to LPSC (Supplementary Fig. 17), both types of SEs also produced decomposition products such as -S-S- and -P-S-P- after electrochemical decomposition.



Supplementary Fig. 46 Adiabatic ramp test thermal profiles of delithiated-NCM (De-NCM)/pristine-(SE/VGCF) and De-NCM/4.5V-(SE/VGCF) at a scanning rate of 5 °C min⁻¹ in ARC.

The objective of this experiment is to demonstrate that the severe self-heating behavior observed in 100% SOC LPSC, LGPS, and LSPSC composite positive electrodes around 200 °C is caused by the electrochemical decomposition of SEs. Severe self-heating behavior were detected near 200 °C in the ramp test of De-NCM/4.5V-(SE/VGCF), which corresponded to the temperature observed in the 100% SOC LPSC (Supplementary Fig. 4), LGPS (Supplementary Fig. 27), and LSPSC (Supplementary Fig. 27) composite positive electrodes, whereas no such phenomenon occurred in De-NCM/pristine-(SE/VGCF). These findings suggest that the electrochemical decomposition of SEs induces severe self-heating in the 100% SOC LPSC, LGPS, and LSPSC composite positive electrodes, which is the primary cause of the earlier and more intense exothermic behavior of the sample.



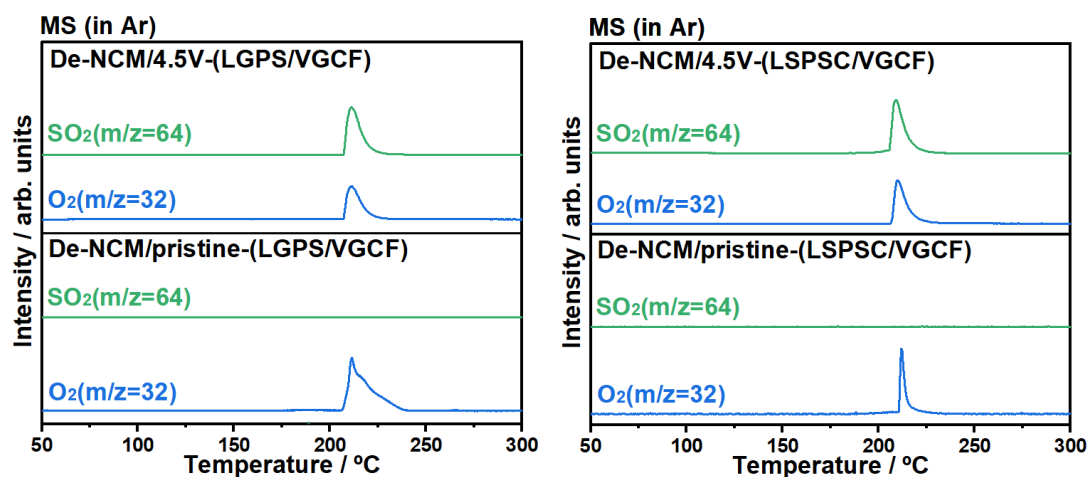
Supplementary Fig. 47 DSC profiles of the delithiated NCM811(De-NCM)/LGPS (De-NCM and LGPS in a weight ratio of 7:3), De-NCM/LSPSC (De-NCM and LSPSC in a weight ratio of 7:3), De-NCM/4.5V-(LGPS/VGCF) (De-NCM, LGPS, and VGCF in a weight ratio of 70:30:3), and De-NCM/4.5V-(LSPSC/VGCF) (De-NCM, LSPSC, and VGCF in a weight ratio of 70:30:3).

The purpose of this experiment is to investigate whether a reaction occurs between De-NCM and SEs (LGPS and LSPSC) during the first exothermic process, as well as to explore the influence of the electrochemical decomposition of SEs (LGPS and LSPSC) on the heat release.

For De-NCM/LGPS and De-NCM/LSPSC, the enthalpy changes of the first exothermic process were $58.6 \text{ J} \cdot \text{g}^{-1}$ and $60.9 \text{ J} \cdot \text{g}^{-1}$, respectively. In previous studies, we have demonstrated that the heat released by the phase transition of De-NCM in De-NCM/SE (De-NCM and SE in a weight ratio of 7:3) is approximately $60.1 \text{ J} \cdot \text{g}^{-1}$ (Supplementary Fig. 23). This value closely matches the enthalpy changes observed for De-NCM/LGPS and De-NCM/LPSC during the first exothermic process. These results indicate that SEs (LGPS and LPSC) and delithiated NCM do not react during the first exothermic process.

For De-NCM/4.5V-(LGPS/VGCF) and De-NCM/(LSPSC/VGCF), the enthalpy changes of the first exothermic process were $395.5 \text{ J} \cdot \text{g}^{-1}$ and $419.9 \text{ J} \cdot \text{g}^{-1}$, respectively. In previous studies, we have demonstrated that in the De-NCM/(SE/VGCF), the heat

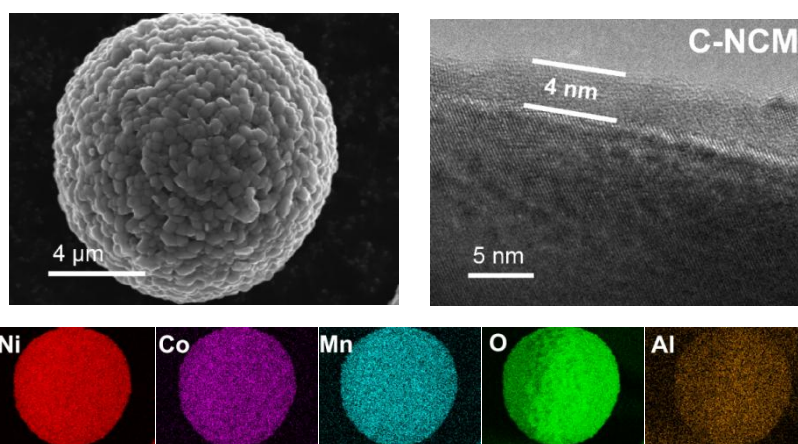
released by the phase transition of De-NCM is approximately $58.4 \text{ J}\cdot\text{g}^{-1}$, and the heat released by the reaction between VGCF and delithiated NCM is $90.8 \text{ J}\cdot\text{g}^{-1}$ (Supplementary Fig. 23). Similarly, in the De-NCM/4.5V-(SE/VGCF) system, these two contributions remain unchanged. Therefore, in De-NCM/4.5V-(LGPS/VGCF), the additional $246.3 \text{ J}\cdot\text{g}^{-1}$ ($395.5 - 60.1 - 90.8 \text{ J}\cdot\text{g}^{-1}$) of heat release is attributed to the exothermic reaction between the electrochemical decomposition products of LGPS and De-NCM. In De-NCM/4.5V-(LSPSC/VGCF), the additional $270.7 \text{ J}\cdot\text{g}^{-1}$ ($419.9 - 58.4 - 90.8 \text{ J}\cdot\text{g}^{-1}$) of heat release is attributed to the exothermic reaction between the electrochemical decomposition products of LSPSC and De-NCM. These results indicate that in both De-NCM/4.5V-(LGPS/VGCF) and De-NCM/(LPSC/VGCF), the first exothermic process is dominated by the reaction between the electrochemical decomposition products of the sulfide SEs and NCM811. These findings highlight the significant influence of electrochemical processes on thermal runaway.



Supplementary Fig. 48 MS profiles of delithiated-NCM(De-NCM)/pristine-(SE/VGCF) and De-NCM/4.5V-(SE/VGCF) for LGPS (left) and LSPSC (right).

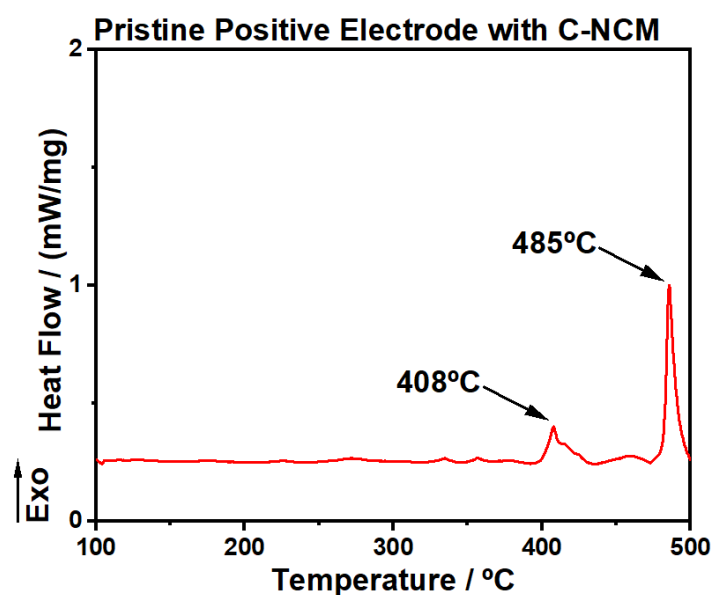
The objective of this experiment is to demonstrate that the generation of SO₂ during the heating process of the 100% SOC LGPS and LSPSC composite positive electrodes is caused by the electrochemical decomposition of LGPS and LSPSC.

No SO₂ generation was detected in De-NCM/pristine-(LGPS/VGCF) and De-NCM/pristine-(LSPSC/VGCF), whereas SO₂ was detected in De-NCM/4.5V-(LGPS/VGCF) and De-NCM/4.5V-(LSPSC/VGCF), indicating that the introduction of the electrochemical decomposition of LGPS and LSPSC led to the generation of SO₂.



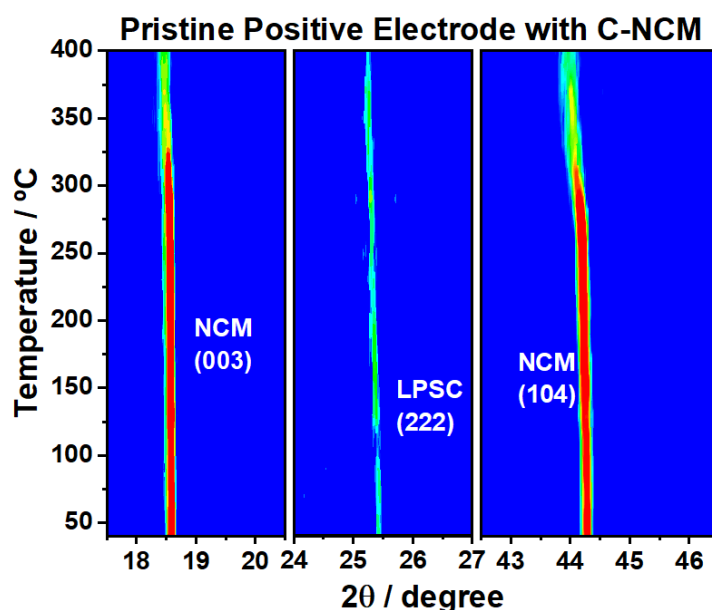
Supplementary Fig. 49 Typical surface SEM-EDS and TEM images of Al₂O₃ coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (named as C-NCM) samples.

It was observed by TEM imaging that the thickness of Al₂O₃ coating was 4 nm and coating homogeneous.



Supplementary Fig. 50 DSC profiles of the pristine composite positive electrode (Al_2O_3 coated NCM811 (named as C-NCM), LPSC, and VGCF in a weight ratio of 70:30:3).

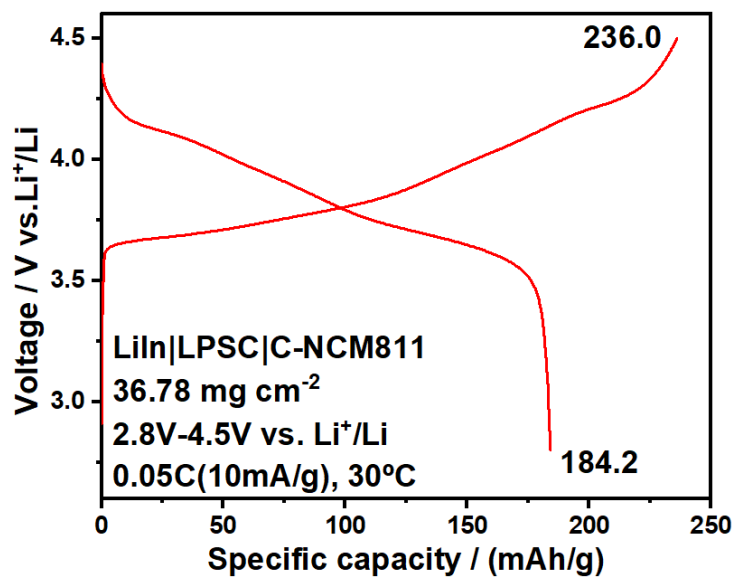
The objective of this experiment is to demonstrate, from a thermochemical stability perspective, that the interfacial compatibility between C-NCM and LPSC is superior to that between NCM (bare NCM811) and LPSC. The two exothermic peaks of the pristine composite positive electrode composed of C-NCM (C-NCM, LPSC, and VGCF in a weight ratio of 70:30:3) (408 °C and 485 °C) were delayed compared to that of NCM (bare NCM811) (373 °C and 465 °C). The higher reaction temperature indicates that the Al_2O_3 coating enhances the interfacial compatibility between layered oxide positive electrode and LPSC.



Supplementary Fig. 51 In situ heating XRD characterization of the pristine composite positive electrode (Al_2O_3 coated NCM811 (named as C-NCM), LPSC, and VGCF in a weight ratio of 70:30:3).

The objective of this experiment is to demonstrate, from a thermochemical stability perspective, that the interfacial compatibility between C-NCM and LPSC is superior to that between NCM (bare NCM811) and LPSC.

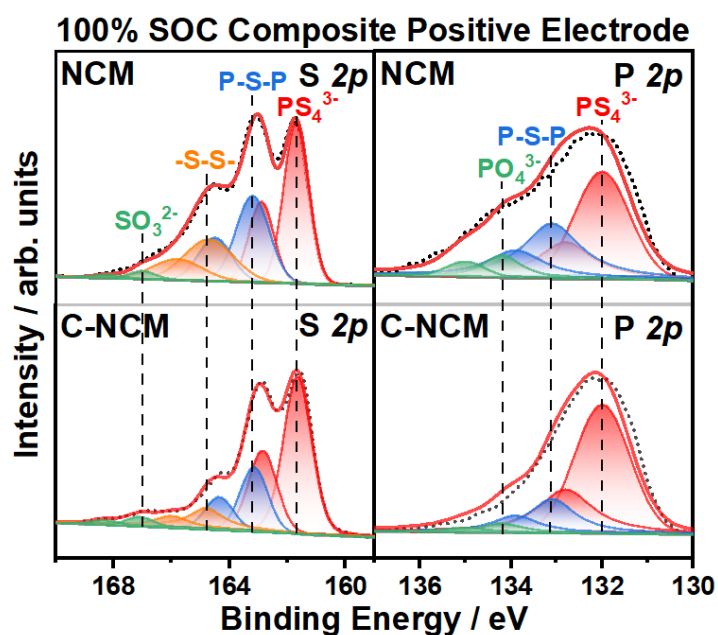
In the pristine composite positive electrode system composed of C-NCM, no distinct NiO characteristic signals were observed when heated to 400 °C. In contrast, the pristine composite positive electrode system composed of bare NCM exhibits strong NiO characteristic signals when heated to around 373 °C. The higher reaction temperature indicates that the Al_2O_3 coating enhances the interfacial compatibility between layered oxide positive electrode and LPSC.



Supplementary Fig. 52 Typical charge-discharge curves of the cell of Al₂O₃ coated NCM811 (named as C-NCM)/LPSC/Li-In in the voltage range of 2.8-4.5 V (vs. Li⁺/Li) at 0.05C (10mA/g) and 30 °C.

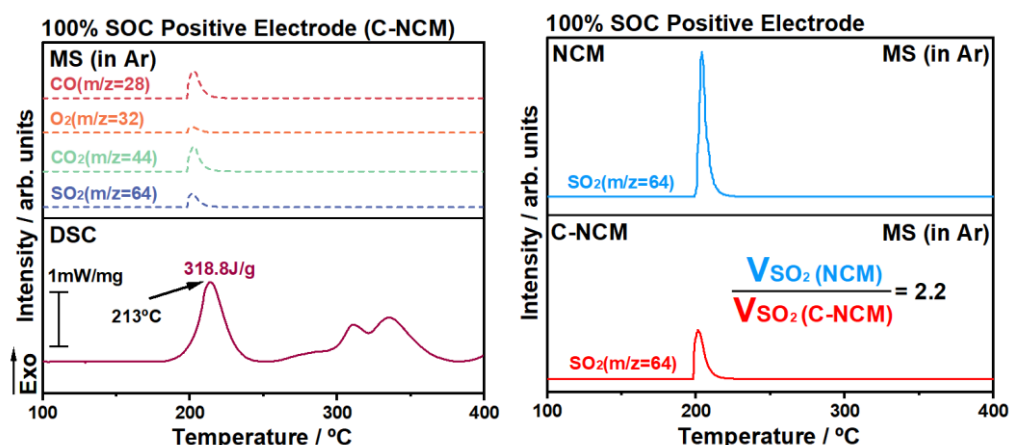
The ASSBs obtained from this experiment are used for thermal runaway testing.

The as-obtained cells delivered an initial charge specific capacity of 236.0 mAh·g⁻¹ and an initial discharge specific capacity of 184.2 mAh·g⁻¹.



Supplementary Fig. 53 S 2p and P 2p XPS spectra of the 100% SOC composite positive electrode (layered oxide positive electrode, LPSC, and VGCF in a weight ratio of 70:30:3) with Al_2O_3 coated NCM811 (named as C-NCM) and NCM (bare NCM811).

The aim of this experiment is to demonstrate that the Al_2O_3 coating layer can effectively alleviate the electrochemical decomposition of LPSC. The 100% SOC composite positive electrode with C-NCM presented weaker signals of -S-S- , -P-S-P- , and PO_4^{3-} compared to those detected from NCM, further confirming Al_2O_3 -coated NCM811 effectively alleviated the electrochemical degradation of LPSC.

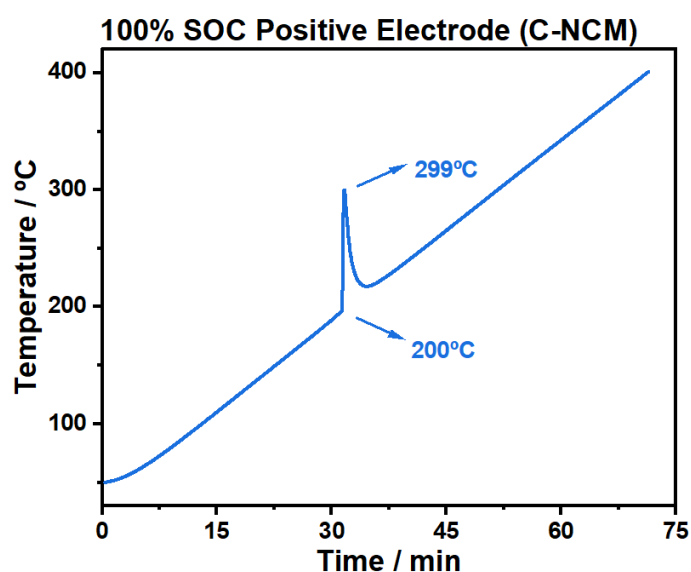


Supplementary Fig. 54 DSC (left) and MS (right) profiles of the 100% SOC composite positive electrode (Al₂O₃ coated NCM811 (named as C-NCM), LPSC, and VGCF in a weight ratio of 70:30:3), and SO₂ evolution of the 100% SOC composite positive electrode with C-NCM and NCM (bare NCM811).

The aim of this experiment is to investigate whether the Al₂O₃ coating can enhance the thermal safety of the composite positive electrode system.

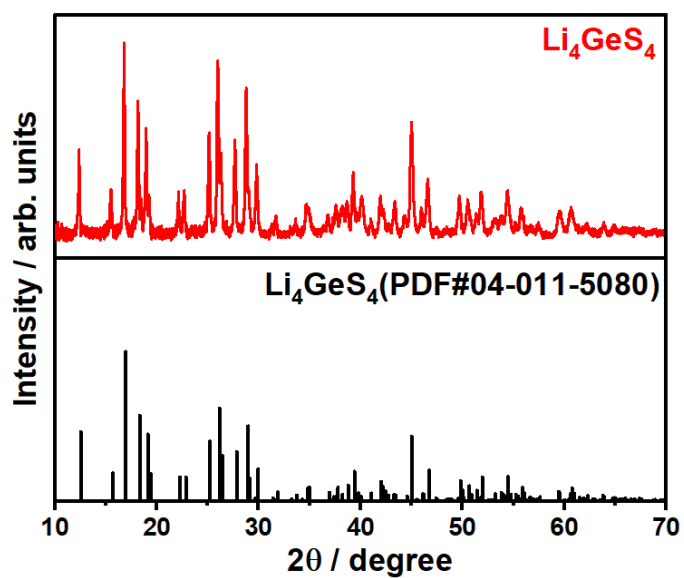
For the 100% SOC C-NCM composite positive electrode, DSC result exhibited that the first exothermic peak appears at 213 °C, with an enthalpy change of 318.8 J·g⁻¹, lower than the 209 °C and 399.6 J·g⁻¹ from B-NCM composite positive electrode, respectively.

We maintained identical mass for both composite positive electrodes and the same flow rate of the purge gas throughout the testing process. By integrating the gas signal intensity over time, we compared the amount of SO₂ gas released. The SO₂ release from the 100% SOC composite positive electrode composed of NCM (bare NCM) was 2.2 times that of the 100% SOC composite positive electrode composed of C-NCM. The Al₂O₃ coating reduced heat release and SO₂ gas generation to some extent.



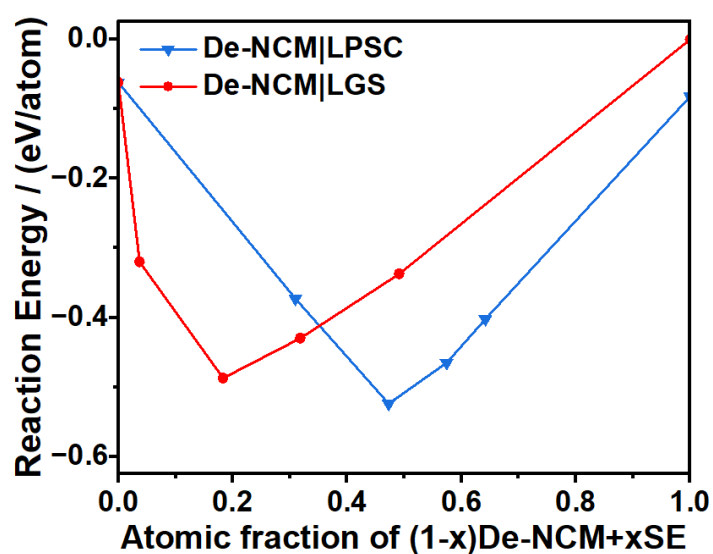
Supplementary Fig. 55 Adiabatic ramp test thermal profiles of the 100% SOC composite positive electrode (Al_2O_3 coated NCM811 (named as C-NCM), LPSC, and VGCF in a weight ratio of 70:30:3) under a constant heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in ARC.

This experiment aims to investigate whether the Al_2O_3 coating can address the thermal safety issue of severe self-heating around $200\text{ }^\circ\text{C}$ in the 100% SOC composite positive electrode. Unfortunately, the 100% SOC composite positive electrode composed of C-NCM still exhibited severe self-heating characteristics during the ramp test, with the sample temperature rapidly increases to $200\text{ }^\circ\text{C}$ at $299\text{ }^\circ\text{C}$. Even with the Al_2O_3 coating, it is not possible to completely suppress the severe thermal runaway induced by the electrochemical decomposition of LPSC.



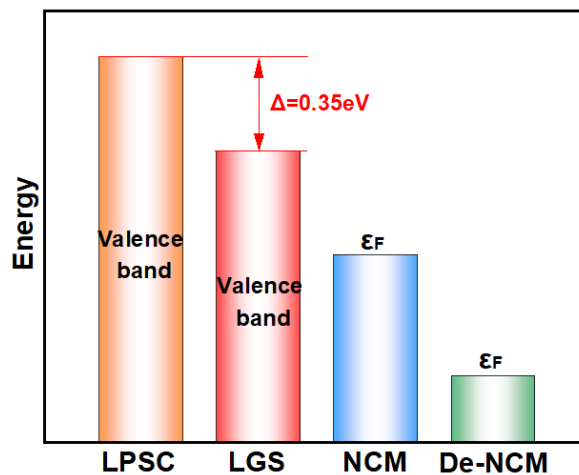
Supplementary Fig. 56 XRD patterns of the as-synthesized Li_4GeS_4 samples.

The as-synthesized LGS samples are used as the conductive additive in the composite positive electrode (NMC811, LGS, and VGCF in a weight ratio of 70:30:3).



Supplementary Fig. 57 Reaction energies of De-NCM811/LPSC and De-NCM811/LGS by first-principles calculations.

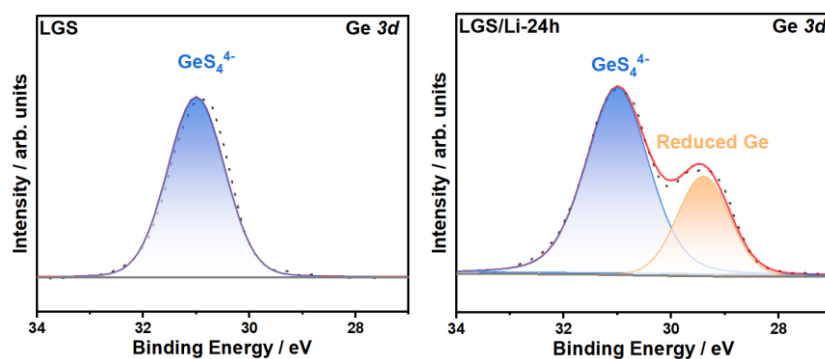
The results confirmed that the reaction energy between delithiated NCM and LGS is significantly less exothermic (i.e., the reaction energy is less negative) than that between delithiated NCM and LPSC. This clearly indicates enhanced interfacial compatibility when LPSC is replaced by LGS, even under delithiated conditions.



Supplementary Fig. 58 Schematic of oxidative degradation mechanism of sulfide SEs (LPSC and LGS) in contact with positive electrode active material (NCM811 and De-NCM811) based on band theory of solids.

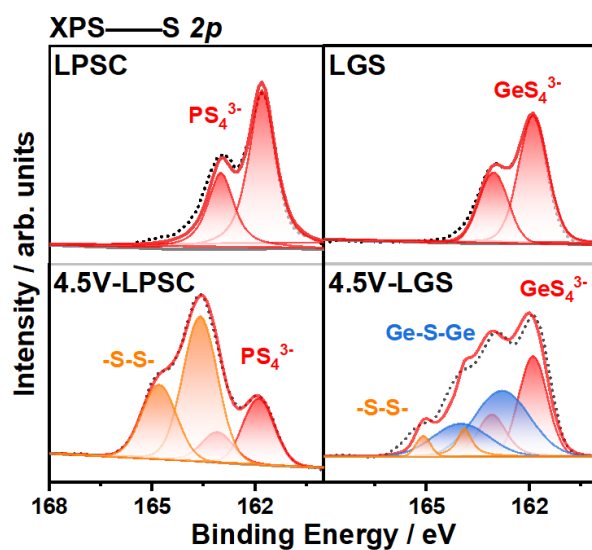
The purpose of this experiment is to demonstrate that the compatibility of LGS/NCM is superior to that of LPSC/NCM.

LGS successfully reduced the gap between the VBM of the sulfide solid electrolyte and the Fermi level of NCM811 and De-NCM811, validating the Ge-substitution strategy for interface optimization.



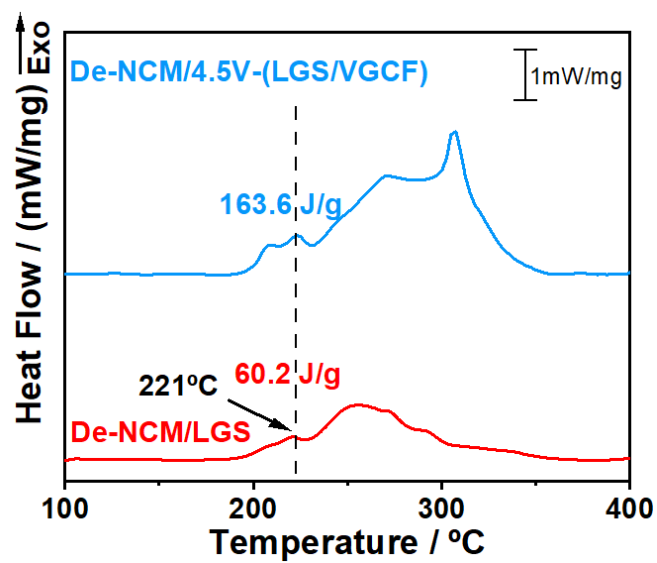
Supplementary Fig. 59 Ge 3d XPS spectra of LGS (left) and LGS/Li (right) pressed into tablets after 24 hours.

Although LGS shows improved stability against oxide positive electrodes, it exhibits high impedance and poor compatibility when in direct contact with lithium metal negative electrodes, as confirmed by our XPS analysis. 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 positive electrode side, preventing direct contact with the negative electrode, while leveraging its ability to suppress positive electrode-side parasitic reactions.



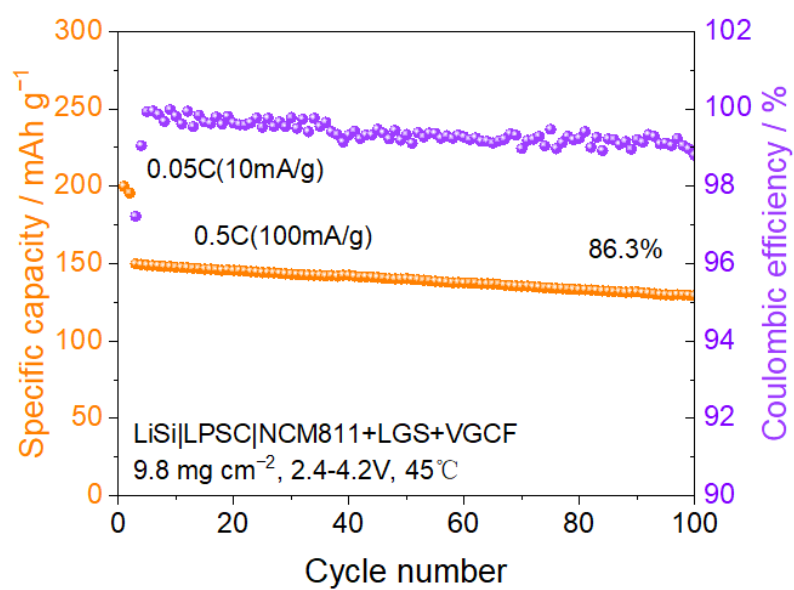
Supplementary Fig. 60 S 2p and P 2p XPS spectra for the LPSC/VGCF and LGS/VGCF before and after being charged to 4.5 V (vs. Li^+/Li).

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 revealed that LGS undergoes notably less electrochemical decomposition than LPSC. Importantly, the formation of highly reactive species such as $-\text{S}-\text{S}-$ and $-\text{Ge}-\text{S}-\text{Ge}-$ was significantly suppressed.

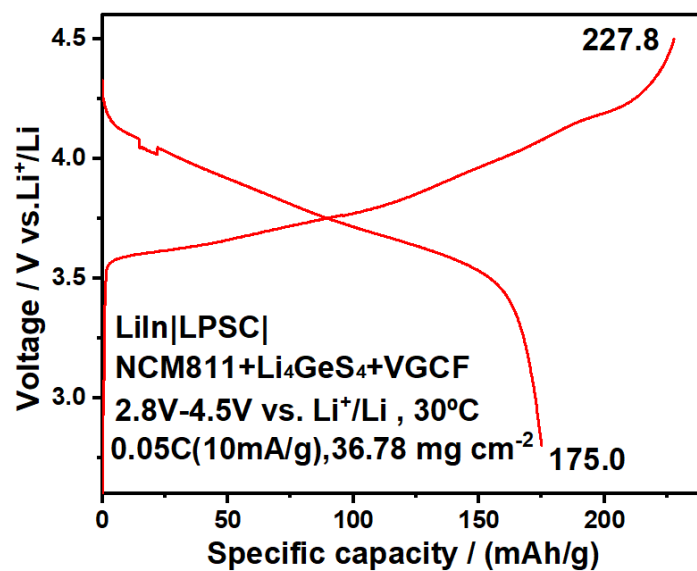


Supplementary Fig. 61 DSC curves of De-NCM/LGS and De-NCM/4.5V-(LGS/VGCF).

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



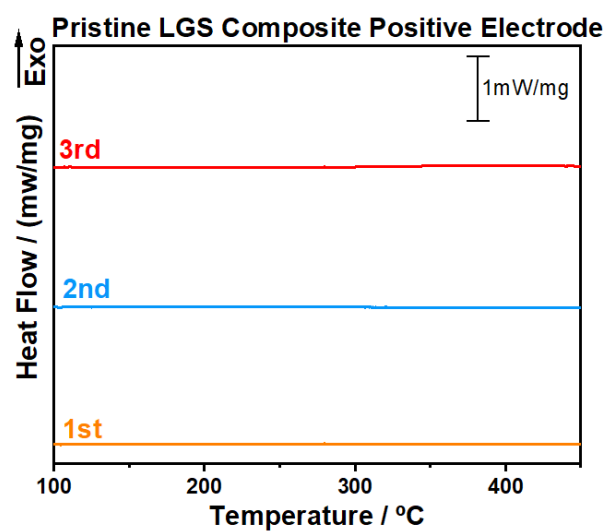
Supplementary Fig. 62 Cycle performance and coulombic efficiency of LiSi|LPSC|NCM811-LGS ASSBs.



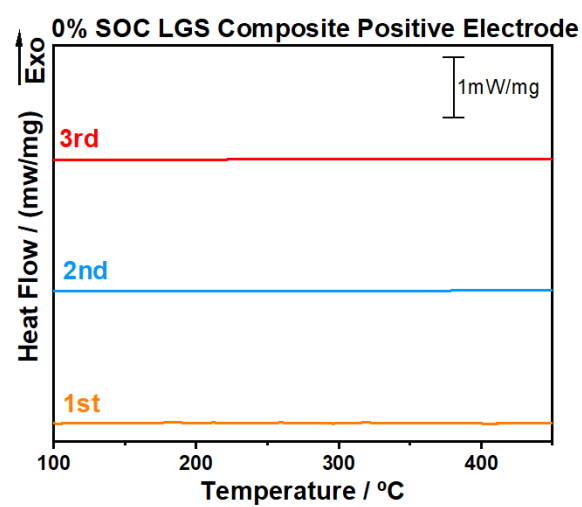
Supplementary Fig. 63 Typical charge-discharge profiles of Li|LPSC|LGS-NCM811 cells in the voltage range of 2.8–4.5 V (vs. Li^+/Li) at 0.05C (10mA/g) and 30 °C.

The ASSBs obtained from this experiment are used for thermal runaway testing.

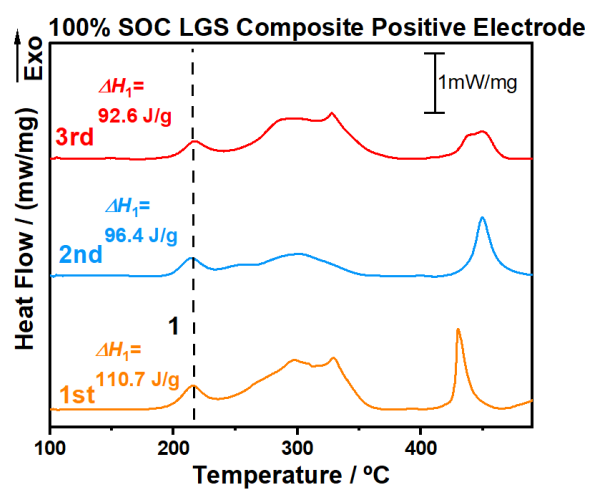
The as obtained cells delivered an initial charge specific capacity of 227.8 $\text{mAh}\cdot\text{g}^{-1}$ and an initial discharge specific capacity of 175.0 $\text{mAh}\cdot\text{g}^{-1}$.



Supplementary Fig. 64 DSC of the pristine LGS composite positive electrode (repeated three times under identical conditions).

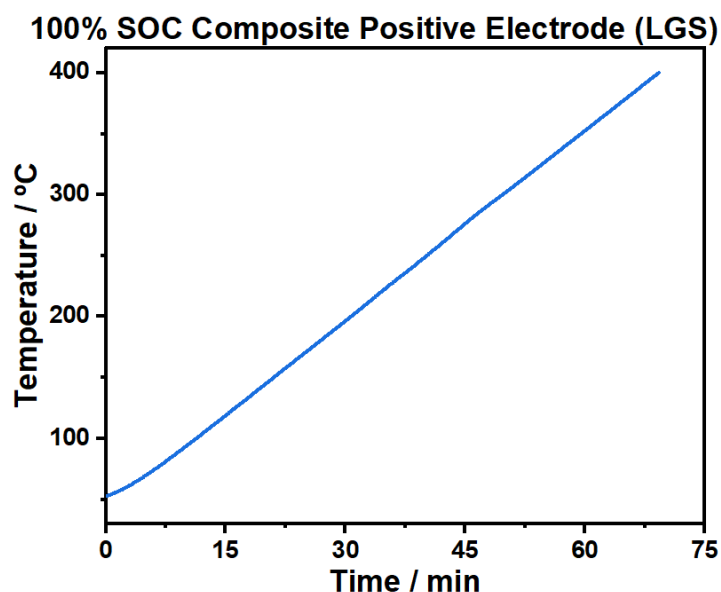


Supplementary Fig. 65 DSC of the 0% SOC LGS composite positive electrode (repeated three times under identical conditions).



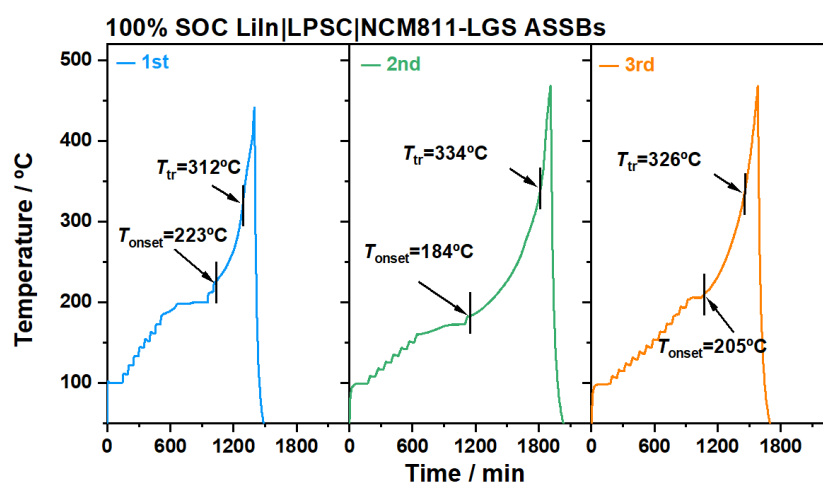
Supplementary Fig. 66 DSC of the 100% SOC composite positive electrode (repeated three times under identical conditions).

$$\Delta H_1 = 99.9 \pm 9.3 \text{ J} \cdot \text{g}^{-1}.$$



Supplementary Fig. 67 Adiabatic ramp test thermal profiles of the 100% SOC LGS composite positive electrode (NMC811, LGS, and VGCF in a weight ratio of 70:30:3) under a constant heating rate of 5 °C min⁻¹ in ARC.

This experiment aims to investigate whether the LGS can address the thermal safety issue of severe self-heating around 200 °C in the 100% SOC composite positive electrode. Clearly, no severe self-heating was observed in the 100% SOC LGS composite positive electrode, indicating that LGS completely suppressed the severe thermal runaway induced by the electrochemical decomposition of sulfide SE, validating the Ge-substitution strategy for interface optimization.



Supplementary Fig. 68 HWS curves of the 100% SOC LiIn|LPSC|NCM811-LGS ASSBs (repeated three times under identical conditions).

$$T_{\text{onset}} = 204.0 \pm 15.9 \text{ } ^\circ\text{C}; T_{\text{tr}} = 324.0 \pm 9.1 \text{ } ^\circ\text{C}.$$

Supplementary Tab. 1 DSC Parameters of the pristine, 0% SOC, and 100% SOC LPSC composite positive electrodes.

Composite sample	1 st peak	ΔH of 1 st peak (ΔH_1)	2 nd peak	ΔH of 2 nd peak (ΔH_2)
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.

Supplementary Tab. 2 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 positive electrode (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.

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