

Revealing and suppressing hot spot driven interface thermal runaway for all-solid-state lithium metal batteries

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 Cite this article: Nano Research, 2026, 19, 94909025. <https://doi.org/10.26599/NR.2026.94909025>

ABSTRACT: All-solid-state lithium metal batteries based on nonflammable inorganic ceramic electrolytes hold promise for achieving both high energy density and safety. However, inadequate physical contact and chemical incompatibility at the Li/electrolyte interface can provoke interfacial thermal runaway far exceeding that in liquid-electrolyte batteries. Here, we employ *in situ* high-resolution thermal imaging to monitor thermal runaway at the $\text{Li}|\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) interface in real time. Results show that after the initial contact reaction at 320 °C, the interface enters a stochastic stress-release stage, during which LATP cracks nucleate and localized hot spots form at the cracks, with the representative hotspot region showing a temperature-rise rate of $\sim 9.5\text{ }^\circ\text{C}\cdot\text{s}^{-1}$ before violent ignition. Transitioning to violent ignition and combustion, the heating rate surges beyond $1943.8\text{ }^\circ\text{C}\cdot\text{s}^{-1}$ and interfacial temperature exceeds 1500 °C, causing catastrophic thermal breakdown. *In situ* imaging coupled with *ex situ* characterization delineates a safety failure pathway wherein interfacial failure generates hot spots that drive localized thermal runaway. Guided by this, we design a dual-passivation $\text{Li}|\text{amorphous silicon (a-Si)}$ heterogeneous interlayer that substantially suppresses interfacial heat and oxygen-containing species-releasing reactions, eliminating hot spot initiation and thermal runaway at their source. The all-solid-state lithium metal symmetric batteries with this interlayer demonstrate stable cycling at 150 °C. This work paves the way for developing safe and high-energy all-solid-state batteries.

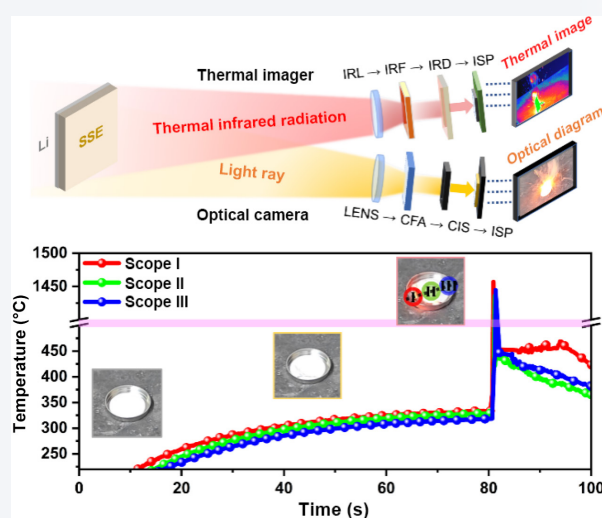
KEYWORDS: all-solid-state batteries, thermal runaway, hot spots, interface design, high safety

1 Introduction

The pursuit of higher energy density and intrinsic safety is driving the evolution of energy storage systems beyond conventional lithium-ion batteries [1, 2]. All-solid-state lithium metal batteries (ASSLMBs), which replace flammable liquid electrolytes with solid-state electrolytes (SSEs) and thereby enable the direct use of a Li

metal anode ($3860\text{ mAh}\cdot\text{g}^{-1}$, -3.04 V vs. standard hydrogen electrode (SHE)), stand at the forefront of next-generation energy storage devices [3–6]. The nonflammable nature of inorganic SSEs has long underpinned the development of ASSLMBs as a next-generation energy storage device combining high safety and high energy density [4, 5, 7, 8]. However, a growing body of research reveals that interfacial contact issues between SSEs and electrodes not only lead to poor cyclability but also pose serious safety hazards for ASSLMBs [8–10].

A central challenge underlying these hazards lies in the complex solid-solid interface between the lithium metal anode and SSEs [9, 10]. Physically, the intrinsic mechanical rigidity of SSEs precludes flawless conformal contact with Li metal, inevitably



Received: June 15, 2026; Revised: July 8, 2026

Accepted: July 13, 2026

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resulting in interfacial voids and asperities [10–12]. These defects constrict ion transport pathways and induce localized current density concentration during lithiation [11–13]. The consequent inhomogeneous electrodeposition drives lithium dendrite nucleation and filamentary propagation into the electrolyte, ultimately causing internal short circuits and subsequent thermal runaway [12–15]. In a direct visualization study, Ning et al. demonstrated that lithium plating can induce mechanical cracking of the SSE, revealing how local mechanical failure facilitates lithium penetration and short-circuit risk [12]. Chemically, the thermodynamic mismatch in chemical potential between the lithium metal anode and SSE triggers spontaneous interfacial reactions that release heat and oxygen-containing combustible species [16–19]. These exothermic processes can lead to interfacial thermal failure and even thermal runaway, posing grave safety risks, including fire and combustion [8, 19]. The chemical potential mismatch between lithium metal and SSE induces violent, self-accelerating interfacial reaction cascades, rendering all-solid-state batteries susceptible to even more pronounced thermal runaway than their liquid electrolyte counterparts [8, 16–21]. This issue is particularly acute at the interface between lithium metal and oxide SSEs, where the chemical potential disparity is substantial [18–21]. For instance, Chen et al. demonstrated that $\text{Li}|\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) and $\text{Li}|\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) undergo severe thermal runaway, with peak temperatures exceeding 900 °C and maximum self-heating rates surpassing 1.0×10^4 °C·min⁻¹ [19]. Yan et al. further revealed that the thermal runaway of $\text{Li}|\text{LATP}$ is accompanied by microcrack formation, molten lithium diffusion, intense localized exothermic reactions, and severe structural degradation [21]. Sulfide SSEs, though often regarded as more processable, also react violently with lithium metal [22]. Riegger et al. showed that halide SSEs, such as Li_3InCl_6 and Li_3YCl_6 , are thermodynamically unstable against lithium metal and form continuously growing interphases [23].

Recent investigations have revealed that thermal runaway in ASSLMBs is not initiated by a uniform interfacial thermal event, but originates from localized regions at the $\text{Li}|\text{SSE}$ interface [21, 24, 25]. For instance, using *in situ* high-resolution thermal imaging, Lin et al. captured a complete localized thermal runaway process driven by local thermal anomalies at the $\text{Li}|\text{LAGP}$ interface prior to fire and combustion [24]. Yan et al. observed that the thermal runaway and combustion of $\text{Li}|\text{LATP}$ exhibit pronounced spatial heterogeneity, with some LATP regions remaining largely intact in morphology and structure [21]. Zhu et al. further demonstrated that localized temperature elevation can accelerate lithium penetration along defect structures and increase short-circuit risk, indicating that non-uniform temperature fields amplify lithium-related interfacial instability [25]. These findings collectively establish that thermal runaway at the $\text{Li}|\text{SSE}$ interface is a process triggered by localized thermal failure sites, and that this localized thermal runaway behavior is directly correlated with the microstructural characteristics of the $\text{Li}|\text{SSE}$ interface [21, 24–31].

To address this, researchers have constructed artificial interlayers on electrolytes that are chemically stable against the lithium metal anode to suppress interfacial side reactions and heat release, thereby elevating the thermal runaway triggering temperature of the interface to 300 °C [26]. However, owing to the lack of high-resolution *in situ* monitoring techniques for thermal runaway at the $\text{Li}|\text{SSE}$ interface, the characteristics of the evolution and propagation of such hot spots initiated localized thermal runaway

remain poorly understood [32–34]. This knowledge gap, in turn, limits our ability to effectively regulate thermal failure and thermal runaway in $\text{Li}|\text{SSE}$ systems [32–34].

In this work, we select the highly reactive Li metal|oxide SSE (LATP) system as a model platform to investigate the characteristic behavior of localized thermal runaway in ASSLMBs, given that oxide SSEs exhibit violent thermal runaway reactions with lithium metal, with extremely rapid kinetics and exceptionally high peak temperatures. We develop an *in situ* monitoring method that integrates high-resolution thermal imaging with an optical camera to capture the entire process of localized thermal runaway at the Li metal and oxide SSEs interface, spanning from hot spot initiation and propagation to eventual fire and combustion. Meanwhile, combined with correlated *ex situ* characterization, this technique enables us to elucidate the spatiotemporal temperature evolution and coupled structural-chemical failure behavior throughout the thermal runaway process, specifically resolving the sequence of hot spots generation, propagation, and ultimate combustion. Furthermore, we propose a dual-passivation strategy for the lithium metal anode and SSE, constructing a $\text{Li}|\text{amorphous silicon (a-Si)}$ heterogeneous interfacial layer (HIL) at the $\text{Li}|\text{LATP}$ interface. This HIL effectively suppresses interfacial reactions, homogenizes the interfacial thermal distribution, and inhibits hot spot initiation arising from interfacial failure. Through this approach, we elevate the thermal runaway triggering temperature of the $\text{Li}|\text{LATP}$ interface in ASSLMBs to 330 °C. Our work provides a comprehensive framework combining advanced *in situ* diagnostics with targeted interface engineering to address the thermal safety challenge of high-energy-density ASSLMBs.

2 Results and discussion

Figure 1(a) presents a schematic illustration, as reported in the literature, of all-solid-state lithium metal batteries undergoing interfacial failure induced by lithium dendrite penetration, thermal abuse, and mechanical abuse, which subsequently leads to severe thermal runaway and ultimately ignition and combustion [35]. This failure process indicates that the thermal safety of all-solid-state lithium metal batteries is not solely determined by the non-flammability of the solid-state electrolyte itself, but is primarily governed by physical and chemical contact failure at the $\text{Li}|\text{SSE}$ interface. To investigate the local evolution of the temperature field during thermal runaway at the lithium-metal|solid-state electrolyte interface, an ultrahigh-resolution *in situ* infrared thermal imaging technique was developed (Fig. 1(b)). This technique was used to record the spatiotemporal evolution of the temperature field during thermal runaway. Optical images were also captured at critical stages to track the morphological changes on the electrolyte surface. By combining thermal and optical information, the correlation between structural failure and temperature evolution was established. The high spatial and temporal resolution of this system enables the detection of subtle localized hot spots before violent ignition, which is critical for identifying the local origin of interfacial thermal runaway. The real-time optical and infrared thermal images in Fig. 1(c) fully capture the complete thermal runaway process of the $\text{Li}|\text{LATP}$ system. Upon initial contact, the LATP pellet maintains an intact surface structure with a relatively uniform temperature distribution (~ 300 °C), indicating that no severe interfacial reaction occurs during this initial contact stage (Stage I). As the temperature further increases to 320 °C, local hot spots

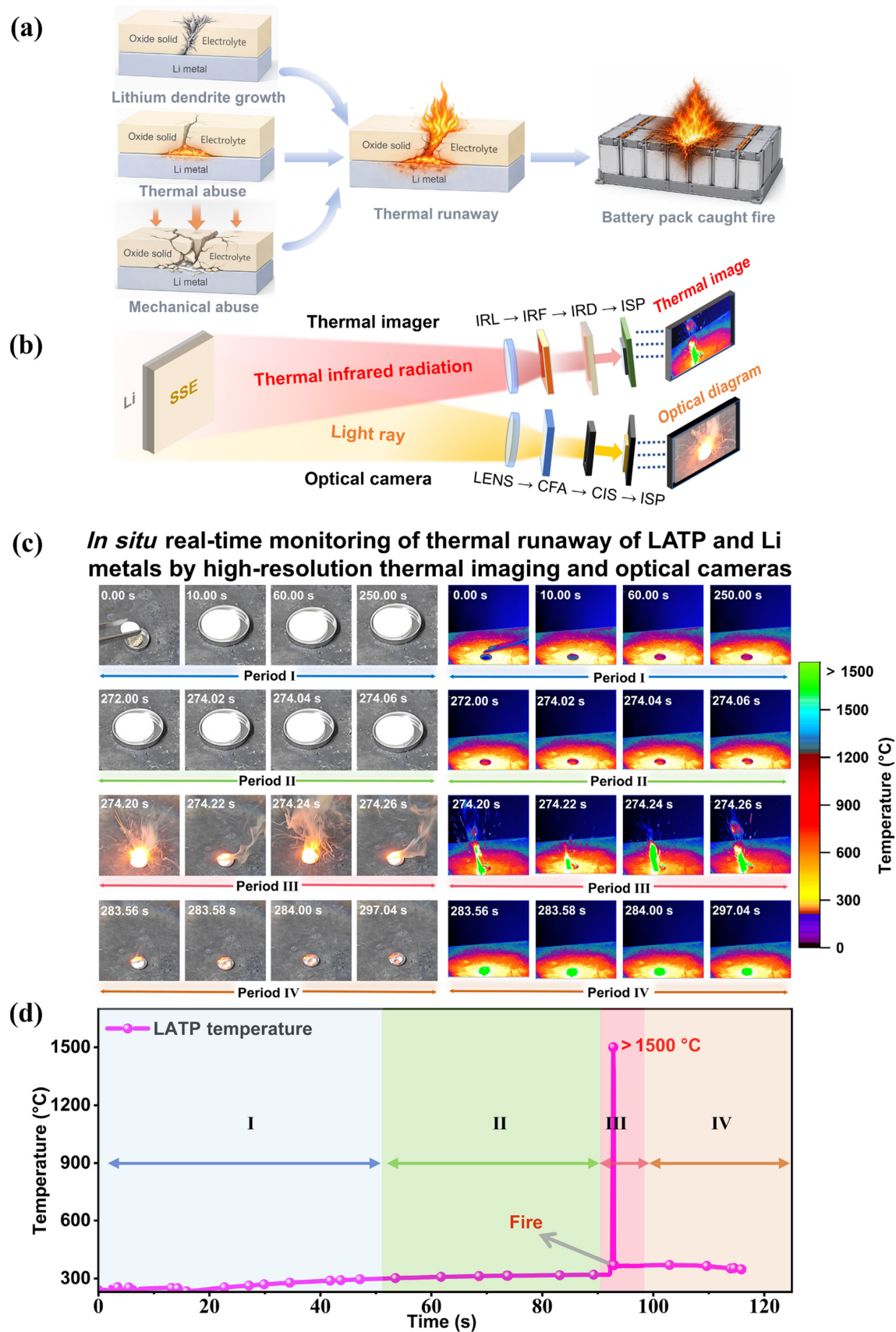


Figure 1 Thermal runaway behavior of the Li|LATP interface. (a) Schematic illustration of typical triggering pathways for interfacial thermal runaway. (b) Schematic illustration of the *in situ* optical and high-resolution thermal imaging system. (c) Optical and thermal images showing the high-temperature thermal-runaway process at the Li|LATP interface. (d) Average surface-temperature evolution of LATP during thermal runaway.

emerge on the LATP surface in contact with lithium metal (Stage II). Subsequently, these local hot spots intensify rapidly and evolve into visible flames and combustion within an extremely short period (Stage III); after the violent energy release, the flames gradually decay, yet the residual high-temperature region remains confined to the electrolyte surface (Stage IV). The temperature–time curve in Fig. 1(d) further corroborates this staged evolution: During Stage I and Stage II, the LATP surface temperature rises slowly (corresponding to a heating rate reaching $3.5\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$); upon entering Stage III, the local temperature signal undergoes an abrupt jump and rapidly reaches the upper calibrated limit of the infrared thermal imaging system, namely $1500\text{ }^{\circ}\text{C}$, indicating extremely intense localized combustion at the Li|LATP interface. The corresponding apparent temperature-rise rate exceeds $1940\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$. These results demonstrate that the thermal runaway of lithium metal/solid-state electrolyte follows a safety failure pathway wherein interfacial failure triggers the formation of local hot spots that ultimately lead to ignition and combustion. The identification of hot spots as a critical indicator is essential for early warning of thermal runaway in all-solid-state batteries and for enhancing safety through the mitigation of interfacial failure.

To suppress the vigorous interfacial reaction between lithium metal and LATP, we further evaluated the possible reaction pathways and associated reaction energies of different interfacial contact configurations using pymatgen. As shown in Fig. 2(a), the direct-contact Li|LAGP and Li|LATP interfaces exhibit strongly negative reaction energies of -0.722 and $-0.630\text{ eV}\cdot\text{atom}^{-1}$, respectively, indicating the intrinsic thermodynamic instability between NASICON-type oxide solid-state electrolytes and lithium metal. For the Li|LATP interface, the computationally predicted reaction products include Li_4TiO_6 , Li_5AlO_6 , Li_2O , Li_3P , and Li_3PO_4 -related phases, revealing that LATP is susceptible to reductive decomposition upon contact with lithium metal at elevated temperatures (Table S1 and Fig. S1 in the Electronic Supplementary Material (ESM)). After replacing the direct Li|LATP contact with an a-Si-modified LATP surface, the reaction energy of the a-Si|LATP interface increases to approximately $-0.42\text{ eV}\cdot\text{atom}^{-1}$, which is substantially weaker than the driving force of the direct Li|LATP interface (Table S2 in the ESM). Meanwhile, the Li|a-Si reaction energy is $-0.244\text{ eV}\cdot\text{atom}^{-1}$, and the Li_xSi interphase formed during lithium plating/stripping can passivate further decomposition reactions (Table S3 in the ESM) [36]. The reaction energies of the Li|a-Si and Li|LiI interfaces approach thermodynamic neutrality, indicating a markedly reduced spontaneous reaction tendency among Li, LiI, and a-Si compared with the direct Li|LATP interface. Therefore, the Li|a-Si heterogeneous interface layer (HIL) design essentially converts the highly reactive Li|LATP direct-contact interface into a multi-layer interface consisting of Li|LiI, Li|a-Si, and a-Si|LATP, thereby reducing the overall interfacial reaction driving force (Fig. S2 in the ESM).

Figure 2(b) illustrates the fabrication process and morphological evolution of the Li|a-Si HIL between the Li anode and the LATP electrolyte. The pristine LATP surface displays distinct grain boundaries and surface defects. After the deposition of a 60–70 nm a-Si layer via plasma-enhanced chemical vapor deposition (PECVD), the surface pores and defects are effectively filled, resulting in a more continuous and heterogeneous interface on the electrolyte side. Subsequently, a LiI layer is formed *in situ* on the lithium metal surface through a 30 min spontaneous reaction between lithium metal and iodine vapor. Serving as a protective

layer on the lithium side, the LiI layer reduces direct contact between active lithium and LATP, further suppresses interfacial side reactions, stabilizes the lithium metal interface, and regulates lithium-ion transport by improved contact [37].

Figure 2(c) shows the spatiotemporal evolution of the temperature field on the LATP electrolyte surface after introducing a Li|a-Si HIL between lithium metal and the solid-state electrolyte. Compared with the LATP in direct contact with lithium metal shown in Fig. 1, the HIL-modified LATP surface exhibits a markedly more uniform temperature distribution. During Stages I and II, the temperature field remains relatively uniform, and no distinct local high-temperature hot spots appear on the LATP surface. Even upon entering Stage III and throughout the prolonged high-temperature holding period up to Stage IV, no ignition or combustion occurs at the interface. Over the entire observation period, no cracks are observed on the surface of the LATP solid-state electrolyte. The temperature–time curves in Fig. 2(d) further quantify the enhancement of interfacial thermal stability conferred by the introduction of the heterointerface. For the unmodified Li|LATP interface, upon contact at $330\text{ }^{\circ}\text{C}$, the temperature jumps sharply to above $1500\text{ }^{\circ}\text{C}$ after approximately 80 s, accompanied by violent ignition and combustion. In stark contrast, the lithium metal/solid-state electrolyte with the HIL exhibits a considerably milder and more controllable temperature rise, with the surface temperature remaining at approximately $305\text{ }^{\circ}\text{C}$ after prolonged heating and showing no abrupt temperature spikes. The magnified temperature curve further confirms that the Li|a-Si HIL effectively suppresses the exothermic interfacial reaction. These results demonstrate that the Li|a-Si heterointerface not only reduces the thermodynamic driving force for the interfacial reaction but also significantly mitigates heat generation from the Li|LATP interfacial reaction. Consequently, introducing the HIL improves the Li|LATP interfacial contact, effectively suppresses the exothermic reaction at this interface, achieves a uniform temperature distribution, and raises the thermal runaway trigger temperature to $330\text{ }^{\circ}\text{C}$, compared with the value of $280\text{ }^{\circ}\text{C}$ previously reported in Ref. [21].

To further elucidate the localized triggering characteristics of thermal runaway at the Li|LATP interface, we performed local temperature and heating rate analyses at three representative regions. As shown in Fig. 3(a), S_I is located at the region where thermal runaway initiates preferentially, S_{II} at the center of the electrolyte, and S_{III} at the region opposite to S_I . Under identical external heating conditions, a higher dT_i/dt (where T_i is temperature and t is time) generally indicates a stronger local net heat accumulation capability (see Eq. (S1) in the ESM). For the LATP electrolyte in direct contact with lithium metal, the temperature profiles of S_I , S_{II} , and S_{III} diverge at the early stage of heating. The dT/dt values during the contact reaction stage are 9.5, 9.2, and $8.8\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$, respectively, following the order $S_I > S_{II} > S_{III}$. This indicates that the S_I region accumulates heat more rapidly under the same external heating. Combined with the appearance of cracks in the optical images, we infer that the interface enters the stress release stage (Stage II) at 30 s, at which point the maximum temperature difference among the three regions reaches $23.5\text{ }^{\circ}\text{C}$, revealing a spatially localized non-uniform temperature distribution. As heating continues, S_I consistently maintains the highest temperature. At approximately 80 s, the temperatures of S_I , S_{II} , and S_{III} reach 333.7, 329.1, and $318.6\text{ }^{\circ}\text{C}$, respectively, with a regional temperature difference still maintained at about $15.8\text{ }^{\circ}\text{C}$. A

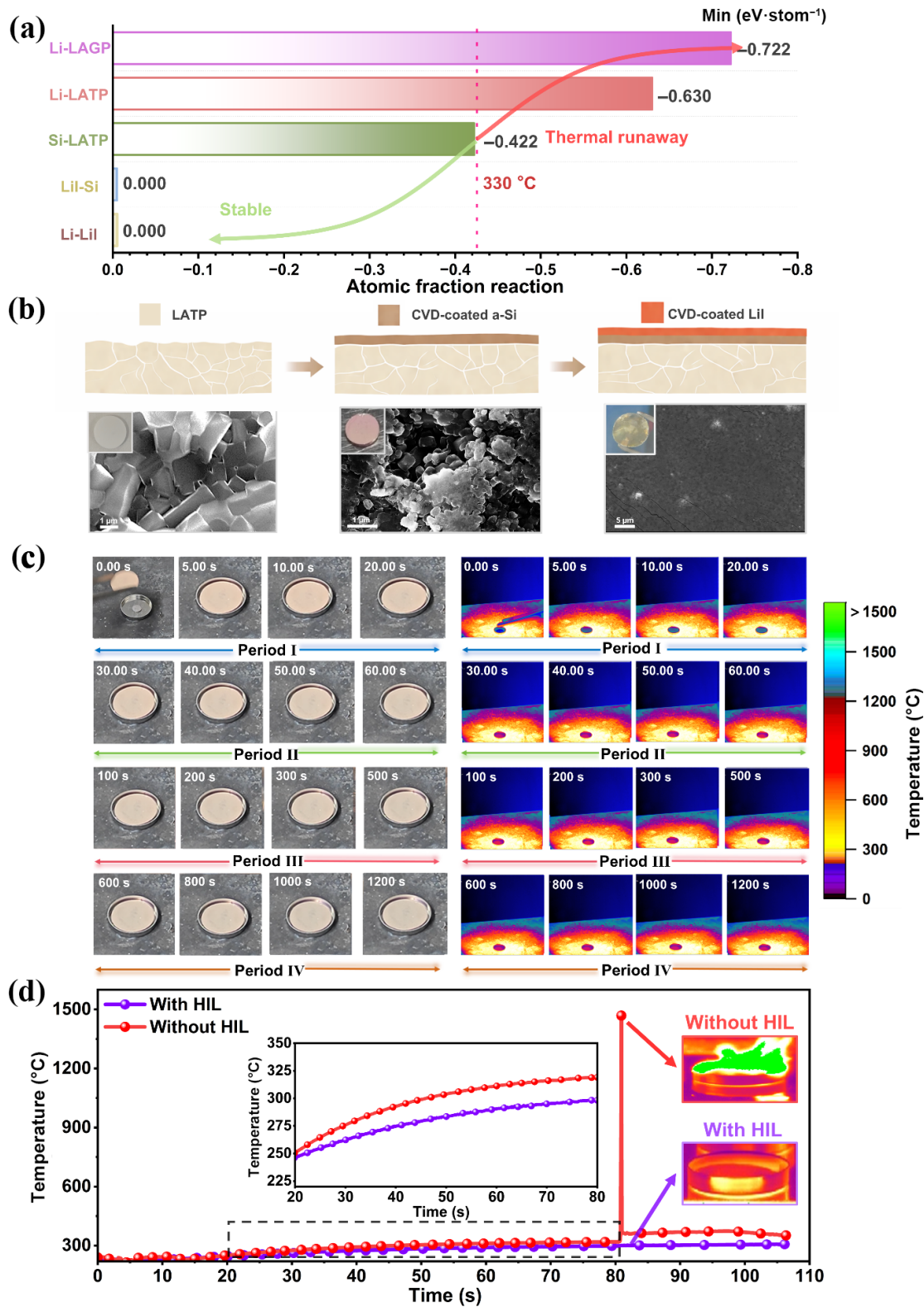


Figure 2 Design and thermal-stabilization effect of the Li|a-Si HIL. (a) Calculated reaction energies of different interfacial contact systems. (b) Schematic illustration of the Li|a-Si HIL construction process. (c) Optical and high-resolution thermal images of the Li|a-Si HIL-modified Li|LATP interface under high-temperature conditions. (d) Average surface-temperature evolution of LATP with and without the Li|a-Si HIL.

hot spot first emerges at S_I and triggers violent thermal runaway, preceding S_{II} and S_{III} by 0.36 s, with a maximum heating rate exceeding $1943.78\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$ at the onset of thermal runaway. The optical and infrared thermal images further reveal how thermal

runaway evolves from a local event into global thermal runaway (Fig. 3(b)). For the unmodified Li|LATP, the sample remains macroscopically stable during the early stage of heating. As the contact time increases, cracks appear on the solid-state electrolyte

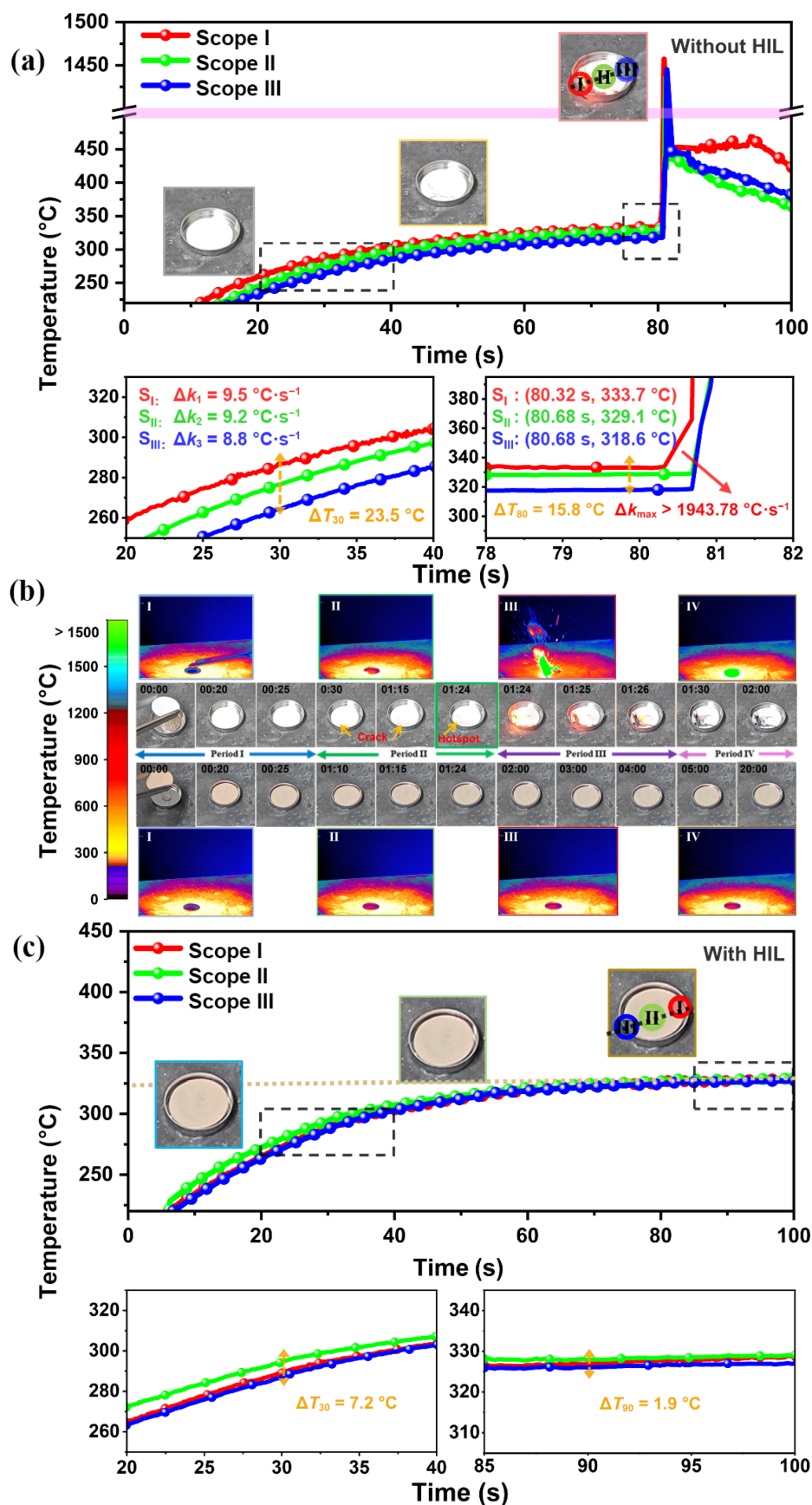


Figure 3 Regional temperature analysis of localized hot spot formation and spatial propagation during thermal runaway at the Li|LATP interface. (a) Temperature evolution of three representative regions in the unmodified Li|LATP sample. (b) Optical images and infrared thermal images of Li|LATP interfaces with and without the HIL under high-temperature conditions. (c) Temperature evolution of the corresponding three regions after HIL introduction.

accompanied by the emergence of hot spots, indicating that interfacial failure induced by physical and chemical contact preferentially triggers hot spots and ultimately leads to thermal runaway and ignition. These observations highlight the inherently localized nature of thermal runaway at the lithium metal/solid-state electrolyte interface. The hot spots originate preferentially at regions where local failure occurs, and exothermic reactions are most pronounced.

After introducing the Li|a-Si HIL, this localized thermal runaway behavior is significantly suppressed (Fig. 3(c)). The temperature profiles of S_p , S_{IB} , and S_{III} remain closely matched throughout the heating process. At 30 s, the maximum temperature difference is reduced from 23.5 to 7.2 °C; upon further heating to 90 s, the difference decreases to 1.9 °C, indicating that the temperature gradually stabilizes and becomes spatially uniform. Optical and infrared images also confirm that the HIL-modified LATP electrolyte exhibits no crack propagation, hot spot formation, or thermal runaway, but instead maintains a stable and uniform temperature field that remains close to the applied heating temperature. Therefore, the Li|a-Si HIL suppresses hot spot generation and the associated localized thermal runaway by homogenizing the interfacial thermal response. This thermal homogenization originates primarily from the synergistic regulation of interfacial physical contact and chemical reactions by the Li|a-Si HIL. On the one hand, the PECVD-deposited a-Si layer effectively fills the pores and defects on the LATP surface, creating a more continuous and smooth interface on the electrolyte side, thereby mitigating localized stress concentration and heat accumulation caused by contact inhomogeneity. On the other hand, the Li| layer stabilizes the lithium-side interface, buffers the direct contact between lithium metal and LATP, and suppresses sustained interfacial side reactions.

Figure 4 further verifies the structural, chemical, and electrochemical stabilization effects of the Li|a-Si HIL at the Li|LATP interface. As shown in the scanning electron microscopy (SEM) images in Fig. 4(a), the deposited a-Si layer covers the LATP surface and fills the surface pores and defects, forming a more continuous and compact electrolyte-side interface. After high-temperature contact with lithium metal, the a-Si-modified LATP still maintains a relatively intact particle morphology, without obvious melting collapse, penetrating cracks, or severe ablation (Fig. S3 in the ESM). This result indicates that the a-Si layer can mitigate the structural damage caused by direct contact between LATP and active lithium. The X-ray diffraction (XRD) patterns in Fig. 4(b) further confirm the phase stability of the protected LATP surface. After high-temperature contact with molten lithium, the main diffraction peaks of LATP are retained. This suggests that the LATP framework is largely preserved and that the a-Si layer is not completely consumed during thermal exposure. In addition, no obvious new crystalline peaks corresponding to Li_2O , Li_3P , Li_3PO_4 , or $Li_{0.5}TiO_2$ are detected in the protected sample. These phases are typical decomposition products of the unmodified Li|LATP interface after thermal runaway (Figs. S4 and S5 in the ESM). Therefore, the XRD results demonstrate that the a-Si layer suppresses electrolyte-side decomposition and reduces thermally induced reaction products.

The X-ray photoelectron spectroscopy (XPS) spectra in Fig. 4(c) further reveal the chemical stability of the Li|a-Si HIL. In the Si 2p region, the pristine sample shows two peaks at approximately 99.0 and 99.6 eV, corresponding to Si 2p_{3/2} and Si 2p_{1/2}, respectively,

confirming the presence of elemental Si on the LATP surface. A weak peak at 102.8–103.2 eV is assigned to Si⁴⁺, indicating slight surface oxidation of the Si layer. After high-temperature treatment, the Si 2p_{3/2} and Si 2p_{1/2} signals remain visible, showing that the a-Si layer is not fully consumed and can still serve as an interfacial transition/protection layer on LATP. In the I 3d region, the I 3d_{5/2} and I 3d_{3/2} peaks appear at approximately 619.0 and 630.5 eV, respectively, and remain clear after heating. This result confirms that the Li| layer maintains good chemical stability during high-temperature contact with lithium metal.

The electrochemical effect of the stabilized interface was evaluated using Li|Li|a-Si|LATP|a-Si|Li|Li symmetric cells at a current density of 0.1 mA·cm⁻² (Fig. 4(d)). At room temperature, the unmodified Li|LATP symmetric cell shows gradually increasing polarization during cycling. The voltage fluctuation becomes obvious after approximately 40 h, followed by rapid failure before 80 h (Fig. 4(e)), indicating continuous interfacial degradation. In contrast, the Li|a-Si HIL-modified cell cycles stably for approximately 120 h with a more regular voltage response. This improvement is consistent with the structural and chemical results above, confirming that the HIL reduces direct Li|LATP contact, suppresses interfacial side reactions, and maintains a more stable interface during lithium plating/stripping.

At 150 °C, the stabilizing effect of the Li|a-Si HIL becomes more pronounced (Fig. 4(f)). The unmodified cell fails rapidly within approximately 20 h, with the voltage approaching the testing limit, indicating that elevated temperature accelerates interfacial reactions and contact degradation at the Li|LATP interface. By contrast, the Li|a-Si HIL-modified cell remains cyclable for approximately 90 h at 150 °C. These results demonstrate that the Li|a-Si HIL not only lowers interfacial polarization at room temperature, but also mitigates high-temperature interfacial reactions, stabilizes lithium plating/stripping, and significantly extends the cycling lifetime of the symmetric cell.

The suppression mechanism is summarized in Fig. 4(g). For the unmodified Li|LATP interface, surface defects, pores, and non-uniform contact promote local lithium enrichment, stress concentration, and heat accumulation. As the temperature increases, the reaction between LATP and active lithium is further accelerated, accompanied by Ti⁴⁺ reduction, heat release, and the formation of oxygen-containing species. These localized reaction regions gradually develop into high-temperature hotspots and finally trigger violent thermal runaway. In contrast, after constructing the Li|a-Si HIL, the a-Si layer fills surface defects on LATP and improves interfacial contact, while the Li| layer stabilizes the lithium-side interface and buffers direct Li|LATP reaction. The two components synergistically reduce interfacial reactivity, suppress Ti⁴⁺ reduction and oxygen-containing species generation, and block the failure pathway of “localized hotspot formation-spatial propagation-global thermal runaway” (Fig. S6 in the ESM). Overall, the Li|a-Si HIL improves both thermochemical stability and electrochemical cycling stability of the Li|LATP interface, providing an effective interfacial regulation strategy for high-safety oxide Li metal systems.

3 Conclusions

In summary, by employing *in situ* high-resolution infrared thermography in conjunction with optical imaging, we have directly captured the localized thermal runaway process at the

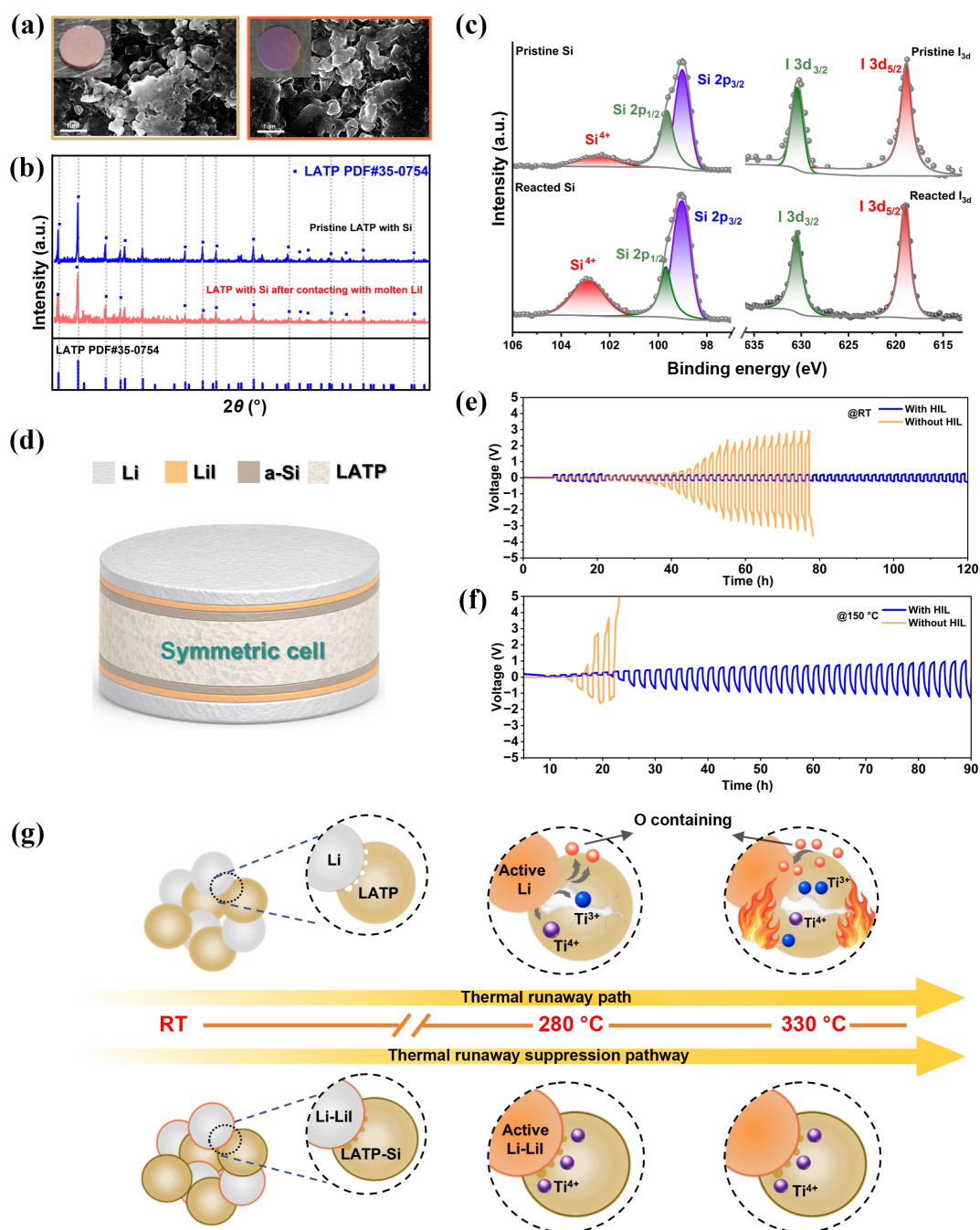


Figure 4 Structural and electrochemical stabilization of the Li|LATP interface by the Li|a-Si HIL. (a) SEM images of Si-modified LATP before and after high-temperature treatment. (b) XRD patterns of a-Si|LATP before and after high-temperature treatment. (c) Si 2p and I 3d XPS spectra of the Li|a-Si-modified interface before and after high-temperature treatment. (d) Schematic illustration of the Li|Li|a-Si|LATP|a-Si|Li|Li symmetric cell. (e) Constant-current cycling profiles of Li|LATP symmetric cells with and without the Li|a-Si HIL at a current density of 0.1 mA·cm⁻² at room temperature. (f) Constant-current cycling profiles of Li|LATP symmetric cells with and without the Li|a-Si HIL at a current density of 0.1 mA·cm⁻² at 150 °C. (g) Schematic illustration of the thermal-runaway suppression mechanism.

Li|LATP interface and identified hot spots as early-warning signatures that precede catastrophic thermal runaway. Our results demonstrate that thermal runaway does not proceed as a uniform, synchronous event, but rather as a dynamic process driven by interfacial failure, in which hot spots propagate spatially and ultimately trigger localized ignition and combustion. To disrupt this failure pathway, we introduced a Li|a-Si HIL at the Li|LATP interface by chemically modifying the lithium metal and the LATP electrolyte surface via chemical vapor deposition. This HIL improves the physical contact at the interface and substantially

suppresses the vigorous exothermic interfacial reaction, thereby effectively mitigating local heat accumulation and hot spot propagation. Consequently, the HIL-modified Li|LATP interface remains structurally stable under prolonged high-temperature continuous heating, with no evidence of thermal runaway. Electrochemical testing further demonstrates that the interface-engineered all-solid-state lithium metal battery delivers stable cycling for approximately 90 h at 0.1 mA·cm⁻² and 150 °C, significantly outperforming the battery without the interfacial layer. Overall, the Li|a-Si HIL simultaneously enhances the

thermochemical stability and electrochemical cyclability of the Li|LATP interface, providing an effective interfacial design strategy for building high-safety oxide-based all-solid-state lithium metal batteries.

4 Experimental section

4.1 *In situ* observation system

A high-resolution infrared thermal-imaging system, Telops SPARK M60hd infrared camera (Telops, Canada; model: M60HDTL-9596), was used to monitor the local temperature evolution during thermal runaway. The detector resolution was 1280×1024 pixels, with a detector pitch of $8 \mu\text{m}$. The full-frame acquisition rate was 59 Hz, the typical noise-equivalent temperature difference (NETD) was 20 mK, and the calibrated temperature range used in this work was 210–1500 °C. A compact infrared thermal camera (FLUKE Ti480 Pro) was used for auxiliary overall thermal monitoring, while an optical camera (SA-Z) was used simultaneously to record the corresponding visual evolution.

4.2 Solid electrolyte selection

Commercial LATP solid-state electrolyte powder was purchased from Kejing Technology Co., Ltd. The powder exhibited a main phase consistent with PDF#35-0754, an ionic conductivity higher than $10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C, and a water content below 500 ppm. LATP pellets were prepared by pressing the powder into circular pellets with a diameter of 10 mm under a pressure of 5 MPa. The green pellets were then sintered at 850 °C for 6 h in air and naturally cooled to room temperature. After sintering, the pellets were polished with SiC papers to obtain flat surfaces and a final thickness of approximately 2 mm. The prepared LATP pellets were used as oxide solid-state electrolytes in this work.

4.3 Fabrication of the heterogeneous interfacial layer

The LiI layer was formed in an inert-gas glovebox by heating elemental iodine at 120 °C to generate iodine vapor, which spontaneously reacted with Li metal to form LiI on the Li surface. The a-Si layer was deposited on the LATP surface by PECVD using a silane-based precursor gas. Before deposition, the chamber was evacuated to a base pressure of 3.6×10^{-4} Pa. The deposition was performed at 250 °C for 8 min, with a SiH_4/Ar flow ratio of 10:0, yielding an a-Si layer with a thickness of 60–70 nm.

4.4 Materials characterization

Energy dispersive spectroscopy, scanning electron microscope (EDS, SEM, Hitachi SU8010), and XRD (Bruker D8 ADVANCE) were used to characterize the morphology of the material, and XPS (Thermo SCIENTIFIC ESCALAB Xi+) was used to analyze the material.

4.5 Cell assembly and electrochemical measurements

All cells were assembled in an Ar-filled glovebox (MIKROUNA, UNIVERSAL, 1800/750/900). As illustrated in Fig. 4(d), the symmetric cells consisted of Li metal electrodes and LATP solid electrolyte separated by LiI|a-Si heterogeneous interfacial layers under an external force of 490 N. The assembly sequence was as follows: LiI-coated Li metal was placed at the bottom as one electrode, LATP with a-Si layers on both sides was positioned in the middle, and LiI-coated Li metal was placed on top as the counter

electrode, ensuring that the LiI layers directly contacted the Si-modified LATP surfaces. Electrochemical cycling tests were conducted using a battery-testing system (LAND) at both room temperature and 150 °C (Han Yu 101-OOBS) to evaluate cycling stability.

Electronic Supplementary Material: Supplementary material (reaction energy calculation, EDS, XRD, and XPS characterization analysis after thermal runaway) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909025>.

Data availability

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

Acknowledgements

This research is partially supported financially by the National Natural Science Foundation of China (No. 61921005), Open Research Projects at the State Key Laboratory of Solid State Microstructure Physics of Nanjing University (Nos. M38066 and M38085), and the Postgraduate Research and Practice Innovation Program Projects of Nanjing University of Aeronautics and Astronautics (No. xcjh20252114).

Declaration of competing interest

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

Author contribution statement

H. C. S.: Writing – review & editing, supervision, resources, project administration, funding acquisition. Z. X. W.: Experiment, data processing, writing – editing, writing – original draft, visualization, investigation, conceptualization. Q. Y. H.: Experiment, data processing, formal analysis. Z. H. Z.: Experiment, writing – review & editing, formal analysis. S. J. Y.: Software, characterization. Z. H. L.: Characterization. M. W.: Characterization, experiment. X. L. D.: Formal analysis, conceptualization. J. H. W.: Characterization. D. E. L.: Materials. G. B. Z.: Resources, methodology. C. S. W.: Project administration. J. W.: Formal analysis. W. L.: Materials. J. X.: Supervision, resources, project administration, funding acquisition, conceptualization. All the authors have approved the final manuscript.

Use of AI statement

During the preparation of this work, the authors used ChatGPT (Open AI) in order to generate partial schematic illustrations (Figs. 1(a) and 4(d)). After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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