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Microscopic Simulation Study on the Coupled Failure of Key Components during Thermal Runaway of Lithium Iron Phosphate Batteries

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Abstract: Understanding the microscopic initiation of thermal runaway (TR) in LiFePO_4 batteries is critical for developing high-safety energy-storage systems. Here, we employ reactive force-field molecular dynamics (ReaxFF MD) and density functional theory (DFT) to elucidate the atomistic coupled-failure mechanisms of the solid electrolyte interphase (SEI), polyolefin separator, and electrolyte under thermal abuse. First, multicomponent SEI models reveal competitive decomposition pathways and identify component abundance as decisive for SEI thermal stability. Second, simulations of an alumina-coated polyethylene separator show that the ceramic coating preserves structural integrity through spatial anchoring, thereby mitigating thermomechanical degradation. Third, combined multi-interface models and DFT calculations reveal the evolution of electrolyte solvation structures and PF_5 -catalyzed degradation pathways. Finally, a coupled SEI-electrolyte-separator model identifies cross-interface mass transport and demonstrates how SEI and separator instabilities synergistically accelerate electrolyte degradation. This work maps the complete microscopic mechanistic chain from single-component failure to multiphase-coupled thermal-runaway evolution. This framework integrates the three principal battery components.

Keywords: lithium iron phosphate battery; thermal runaway initiation; density functional theory (DFT); reactive molecular dynamics (ReaxFF MD); microscopic failure mechanism

1 Introduction

Electrochemical energy storage offers flexible deployment, rapid response, and high energy density, making it an important technology for the large-scale grid integration of renewable energy [1-3]. Lithium iron phosphate (LFP) batteries have become one of the principal electrochemical energy-storage technologies because of their low cost, long service life, and comparatively high safety [4, 5]. As cell capacity and system scale continue to increase, however, the safety risks associated with thermal runaway become more severe. During the initiation stage in particular, the solid electrolyte interphase (SEI), separator, and electrolyte begin to fail and interact. Their coupled degradation promotes heat accumulation and parasitic reactions inside the cell and is therefore central to the transition from a local abnormality to irreversible, self-accelerating failure [6, 7].

The thermal-runaway characteristics of LFP batteries have been investigated extensively through both experiments and simulations. Experimental studies obtain key observables under controlled abuse conditions and establish empirical trends, whereas simulations reconstruct internal state variables and coupled processes that cannot be measured directly, thereby supporting mechanistic interpretation, threshold identification, and risk assessment.

Experimental studies have considered several triggering modes, with particular attention to temperature evolution and material-property changes. Huang et al. [8] triggered thermal runaway in a 38 Ah NCM cell by overheating and measured the temperature evolution, mass loss, and gas composition throughout the event. Jia et al. [9] compared heat generation and venting from LFP cells under overcharge and overheating and found that the vent-flow rate and gas-release rate were substantially higher during overheating. Kang et al. [10] and Mohamad Syazarudin et al. [11] further showed that larger-capacity cells exhibit a greater propensity for thermal runaway, a shorter time to thermally activated exothermic reactions, and more severe heat release. Studies of LFP cells at different states of charge (SOC) [12-15] have confirmed the strong SOC dependence of thermal runaway and have also shown that connection configuration, cell number, and connector thickness [16] affect the outcome.

Numerical studies have used equation-based electrochemical-thermal-mechanical models and multiphysics finite-element platforms to evaluate triggering thresholds, heat-diffusion pathways, and propagation risks, providing quantitative guidance for structural design, thermal management, and mitigation strategies [16-18]. At the microscopic scale, theoretical approaches based on quantum mechanics and molecular dynamics (MD) have become important tools for resolving thermal-runaway mechanisms. Reactive force-field molecular dynamics (ReaxFF MD) can explicitly describe bond breaking and formation and is therefore indispensable for analyzing thermal decomposition. Density functional theory (DFT) is widely used to calculate electronic structures and identify transition states, enabling accurate evaluation of molecular structures and electronic energy levels and providing deeper insight into thermal-runaway reaction mechanisms [19-21]. Wang et al. [22] used ReaxFF MD to examine the evolution of solid-electrolyte interphase components and combined it with DFT calculations of reactive centers. Alzate-Vargas et al. [23] applied accelerated molecular dynamics with bond-order-based reaction-pathway design to overcome the limitations of conventional dynamics and investigate SEI growth in lithium-ion batteries. Multiscale methods further connect DFT-derived electronic-structure information to ReaxFF parameterization and couple reaction kinetics to macroscale heat-transfer models, establishing links from atoms to devices [24, 25].

Despite these advances, most previous studies have focused on macroscopic factors affecting thermal runaway or on the isolated thermal behavior of individual components such as electrodes. Consequently, the microscopic failure laws

and interdependencies associated with nonequilibrium behavior, multiphase transitions, and complex reaction networks remain insufficiently understood, particularly during the triggering stage.

This study therefore focuses on the initiation mechanism of thermal runaway in commercial large-capacity LFP batteries. Multiscale microscopic models of the SEI, polyethylene separator, and electrolyte were constructed, and MD simulations were combined with DFT calculations to investigate the intrinsic evolution and coupled failure of these key components under thermal excitation. Specifically, we:

(1) constructed layered SEI molecular models with different proportions of representative inorganic and organic components and used temperature-ramped ReaxFF MD simulations to determine product-evolution pathways, competitive decomposition between the inorganic and organic phases, and the effect of local component enrichment on overall SEI thermal stability;

(2) constructed polyolefin-separator models containing explicit pores and a surface coating and used temperature-ramped MD simulations to track polymer-chain conformation, fractional free volume, and elastic modulus, thereby quantifying the microscopic constraint imposed by a ceramic coating; and

(3) constructed a multiphase SEI-electrolyte-separator model and used temperature-ramped ReaxFF MD to identify the principal solvent-degradation pathways and products. DFT calculations were then used to clarify PF_5 catalysis and the effect of molecular structure on pathway selectivity, while the coupled model was used to determine how SEI and separator instabilities affect electrolyte degradation.

2 Materials and Methods

2.1 Representative SEI compositions and layered model construction

The initiation of battery thermal runaway (TR) is characterized by the early destabilization of thermally sensitive interfaces and the onset of sustained self-heating side reactions. The SEI can undergo structural degradation, component rearrangement, and even thermal decomposition at moderate temperatures of approximately 80-120 °C [26, 27]. This process directly compromises anode passivation and is accompanied by early heat and gas generation, making it a key trigger for subsequent TR evolution. We therefore constructed multicomponent molecular models based on representative SEI compositions and combined ReaxFF MD with DFT to simulate dynamic decomposition during heating and to quantify the dissociation energies of key chemical bonds. The objective was to resolve the thermal-decomposition kinetics of the SEI at the atomic scale and reveal the intrinsic mechanism of early interfacial destabilization.

The SEI is a composite of inorganic and organic phases. The inorganic phase originates mainly from the deep reduction of lithium salts, solvents, or anions in a strongly reducing environment and from impurity-induced side reactions, and commonly includes LiF, Li_2CO_3 , Li_2O , and $\text{Li}_x\text{PO}_y\text{Fz}$. LiF is a thermally stable and chemically inert ionic crystal that forms a dense framework in the inner SEI and suppresses continued solvent reduction. Li_2CO_3 is a carbonate-rich deposit that can participate in side reactions and promote gas generation at high temperature or under strongly reactive conditions. Li_2O and $\text{Li}_x\text{PO}_y\text{Fz}$ are representative deep-reduction products and decomposition products of the electrolyte salt LiPF_6 , respectively [28, 29]. The organic phase is derived mainly from reductive ring opening, transesterification, and polymerization of carbonate solvents such as ethylene carbonate (EC). It provides flexibility and

hosts reactive intermediates. Its principal constituents include lithium alkyl carbonates (ROCO_2Li), lithium alkoxides (ROLi), and related polymers [30]. ROCO_2Li contains a carbonate functional group whose carbonyl and ether oxygen atoms provide multiple coordination sites, whereas ROLi is based on Li-O-C structural units.

Using a layered-structure/representative-component/controlled-variable strategy, six comparative models were constructed by varying the proportions of the principal SEI components. Li_2CO_3 , LiF , and Li_2O represented the carbonate-deposition, stable-fluoride, and oxide phases, respectively. Their distinct lattice configurations, polarities, and local coordination environments capture representative physicochemical properties of the inorganic SEI. To reflect the EC/DEC/DMC/EMC carbonate electrolyte used in commercial 280 Ah LFP cells, the organic phase included the major reduction products lithium alkyl carbonate ($\text{R}'\text{OCO}_2\text{Li}$) and lithium alkoxide (R^2OLi). R' comprised $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, and $-\text{CH}_2$ fragments, whereas R^2 comprised $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ groups. This multisubstituent design captures realistic variations in carbon-chain length and local configuration while maintaining a controlled parameter space. The molecular counts and compositions of the six models are listed in Table 1. All models were constructed and pre-equilibrated in Materials Studio (Accelrys), as illustrated in Fig. 1.

Table 1 Molecular counts and compositions of the SEI models

Group	Li_2CO_3	LiF	Li_2O	$\text{R}'\text{OCO}_2\text{Li}$			R^2OLi	
				$\text{CH}_3\text{OCO}_2\text{Li}$	$\text{C}_2\text{H}_5\text{OCO}_2\text{Li}$	$(\text{CH}_2\text{OCO}_2\text{Li})_2$	CH_3OLi	$\text{C}_2\text{H}_5\text{OLi}$
1	168	168	168	84	42	42	84	84
2	360	120	120	60	30	30	60	60
3	120	360	120	60	30	30	60	60
4	120	120	360	60	30	30	60	60
5	120	120	120	180	90	90	60	60
6	120	120	120	60	30	30	180	180

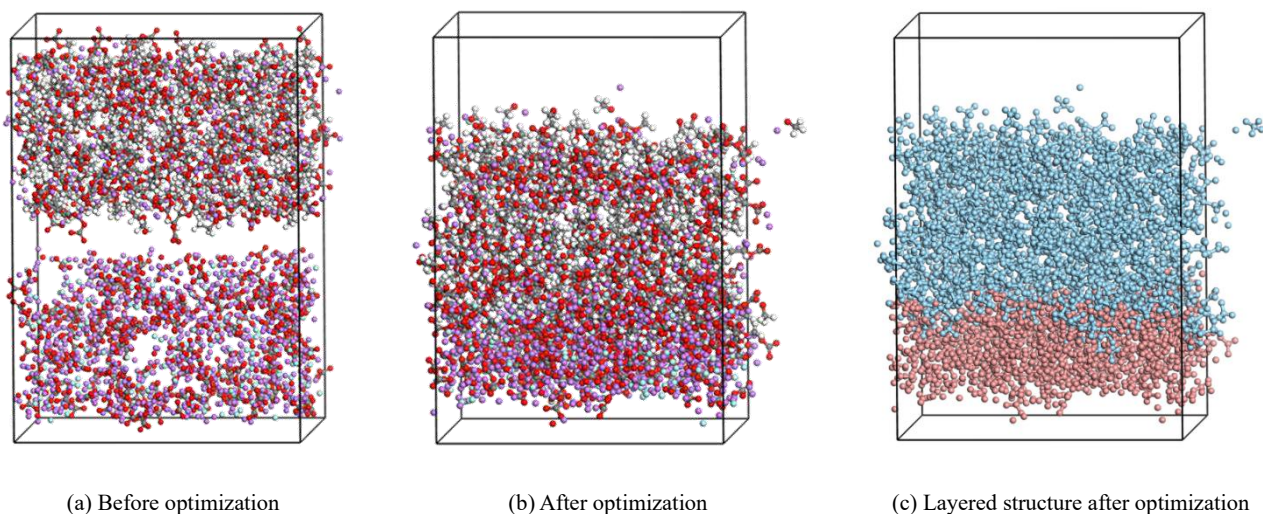


Fig. 1 Construction workflow for the SEI models

2.2 Construction of uncoated and ceramic-coated separator models

The separator is the principal physical barrier between the electrodes, and its thermomechanical stability during TR initiation determines whether the cell enters irreversible self-heating. Thermal shrinkage or rupture can induce extensive internal short circuits (ISCs), and the resulting Joule heating can rapidly accelerate catastrophic thermal runaway. We therefore constructed representative separator models at the molecular scale and performed non-isothermal MD simulations. Polymer-segment dynamics, conformational evolution, interfacial interactions, and macroscopic mechanical responses were analyzed to resolve the microscopic progression of separator thermal failure and to provide a physical basis for subsequent simulations of advanced TR stages.

Polyethylene (PE) was selected as the substrate because of its widespread use in commercial LFP-cell separators. Long PE chains formed the polymer framework, and explicit voids were introduced into the simulation cell to represent ion-transport pathways. Three-dimensional periodic boundary conditions (PBCs), consistent with those used for the SEI and electrolyte models, ensured compatibility for subsequent interfacial coupling. The construction workflow for the uncoated PE separator is shown in Fig. 2a. Starting from the equilibrated PE model, an alumina-coated composite separator (CCS) was constructed. Al_2O_3 was selected as the coating because of its high thermomechanical stability, stiffness, and broad commercial relevance. The model was used to clarify how a passive inorganic layer suppresses polymer thermal destabilization and enhances mechanical stability at the atomic scale; the detailed workflow is shown in Fig. 2b.

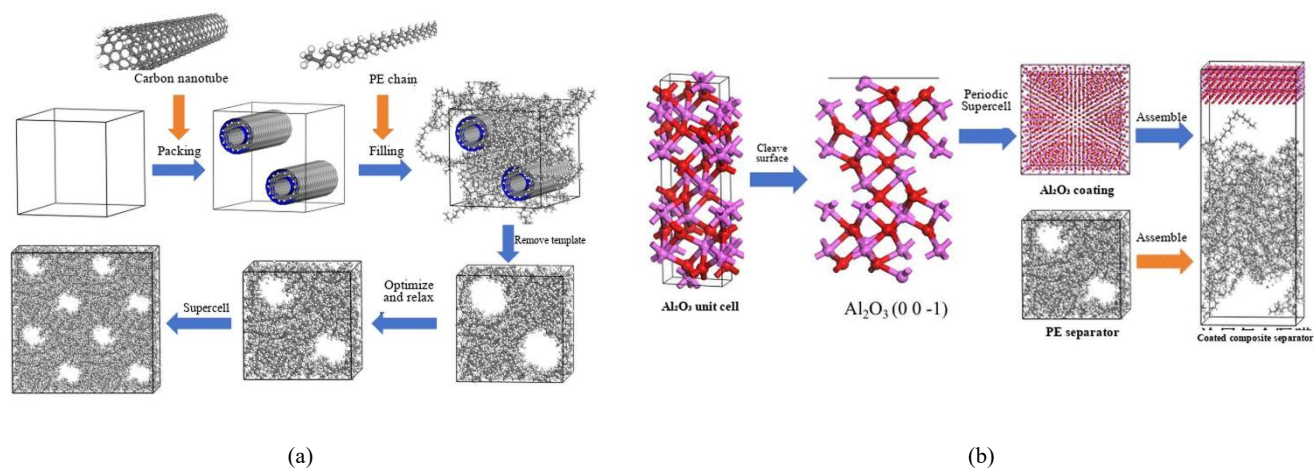


Fig. 2 Construction workflows for (a) the uncoated PE separator and (b) the alumina-coated composite separator

2.3 Electrolyte model construction

The electrolyte is both the principal ion-transport medium and a major combustible component of a battery. During TR initiation, it participates in parasitic reactions and undergoes thermal decomposition; the resulting heat and gases directly influence the severity and hazard of subsequent TR. After SEI decomposition and separator melting, cell stability decreases sharply and physical isolation is lost, making the electrolyte a key medium linking early component failure to advanced thermal runaway. This section therefore analyzes the molecular structure, thermal-decomposition behavior, and reaction mechanisms of the electrolyte and examines its decomposition in the presence of both the SEI and separator.

To investigate the microscopic evolution of the electrolyte during thermal runaway, the formulation used in a commercial 280 Ah LFP cell (1 mol L^{-1} LiPF_6 in EC/DEC/DMC/EMC = 4:4:7:4 by volume) was adopted. The component properties are listed in Table 2. Balancing computational cost and statistical representativeness, an amorphous

periodic cell containing 40 LiPF₆ ion pairs and 452 solvent molecules (126 EC, 70 DEC, 174 DMC, and 82 EMC) was constructed at an initial density of 1.088 g cm⁻³. The structures and properties of the solvent molecules are provided in Table 2. Geometry optimization, annealing, and MD relaxation were then performed sequentially to obtain a stable, representative initial configuration and eliminate high-energy contacts introduced during random packing. The resulting electrolyte structure is shown in Fig. 3.

Table 2 Molecular structures and physical properties of the electrolyte solvents

Solvent	EC	DEC	DMC	EMC
Molecular formula	C ₃ H ₄ O ₃	C ₅ H ₁₀ O ₃	C ₃ H ₆ O ₃	C ₄ H ₈ O ₃
Molar mass (g mol ⁻¹)	88.06	118.13	90.08	104.10
Density (g cm ⁻³)	1.321	0.975	1.064	1.006

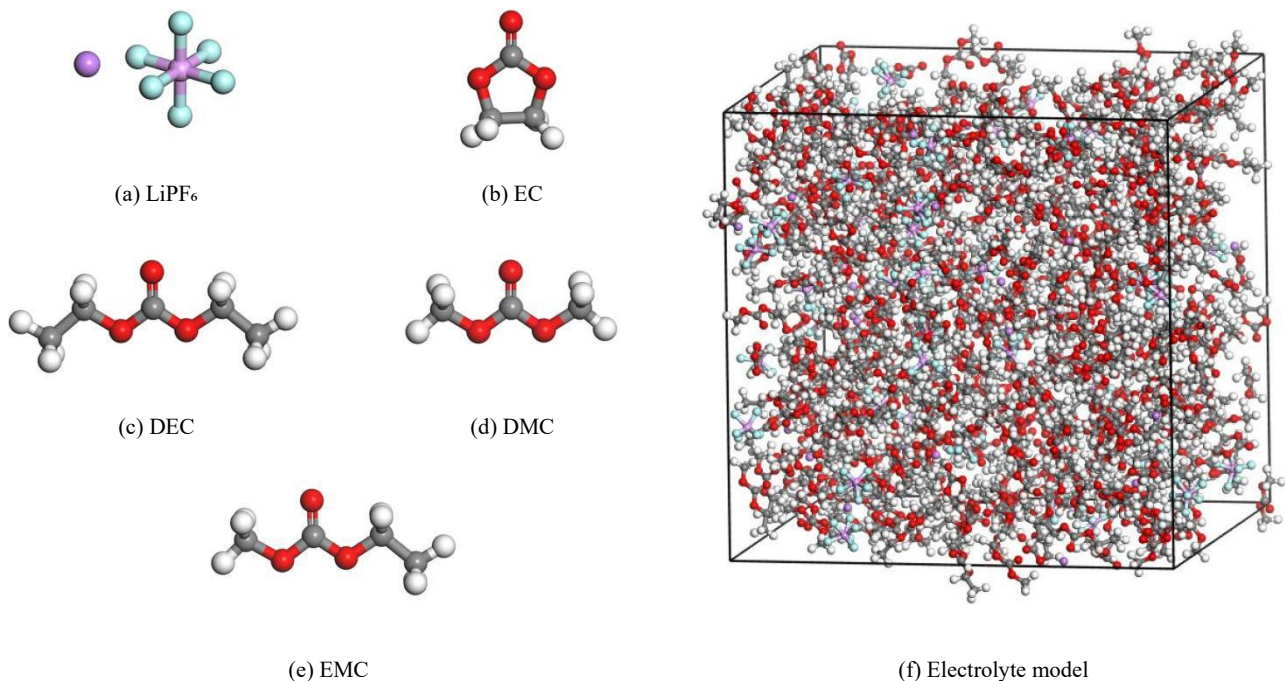


Fig. 3 Solvent molecules and the electrolyte simulation cell

3 Results

3.1 Thermal decomposition behavior and mechanism of the SEI

To capture dynamic chemical evolution under severe thermal conditions, reactive force-field (ReaxFF) molecular dynamics was employed. Unlike conventional fixed-topology force fields, ReaxFF uses a quantum-chemically trained dynamic bond-order formalism to track bond breaking and formation on microscopic time scales [31]. The total ReaxFF energy is decomposed as follows:

$$\begin{aligned}
 E_{\text{sys}} = & E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{triple}} + E_{\text{val}} + E_{\text{pen}} \\
 & + E_{\text{tors}} + E_{\text{conj}} + E_{\text{hb}} + E_{\text{vdW}} + E_{\text{Coulomb}}
 \end{aligned}
 \tag{1}$$

Within this framework, the total energy is a continuous function of atomic coordinates. In addition to conventional bonded terms (bond stretching, angle bending, molecular translation, torsion, and hydrogen bonding) and nonbonded terms (van der Waals and electrostatic interactions), the expression includes reaction-specific contributions such as overcoordination/undercoordination penalties, lone-pair energy, and conjugation energy [32].

A ReaxFF-Li parameter set optimized for electrolytes and SEI systems was used to describe the complex reaction kinetics at lithium-containing interfaces [33, 34]. During heating, all six SEI models followed a common sequence of structural perturbation, local bond scission, fragmentation, and small-molecule release. However, the onset temperature, dominant products, and gas-release intensity depended on composition. Representative structural evolution is shown in Fig. 4.

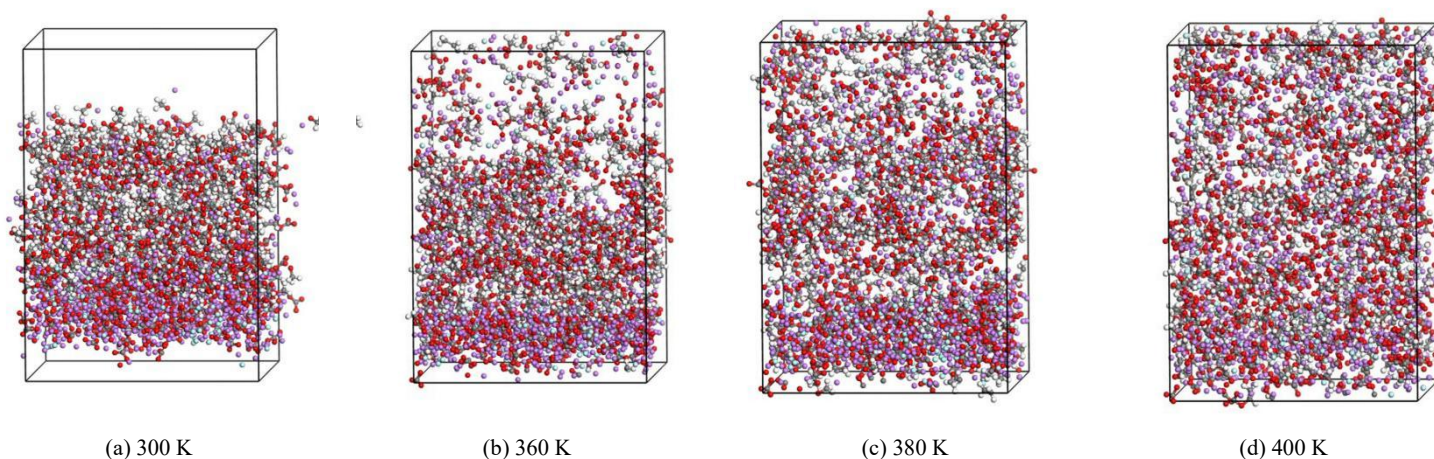


Fig. 4 Structural evolution of the SEI model with temperature

At the beginning of heating, electrostatic and van der Waals interactions maintained the layered configuration of the SEI. As thermal perturbations intensified, the relatively weak C-O framework and Li-O coordination network in the flexible organic phase destabilized first, producing conformational relaxation and structural preactivation. Near the critical threshold of approximately 360 K, extensive pyrolysis began: organic components underwent irreversible bond scission, evolved through intermediates such as carbonate (CO_3) fragments, and released CO_2 and CO. Subsequent large-scale depolymerization caused local collapse of the continuous film, while the newly generated micropore network opened pathways for the bulk diffusion and escape of small molecules.

To quantify the thermodynamic vulnerability of the key components, molecular degradation trajectories were tracked for five representative organic lithium salts: CH_3OLi , $\text{C}_2\text{H}_5\text{OLi}$, $\text{CH}_3\text{OCO}_2\text{Li}$, $\text{C}_2\text{H}_5\text{OCO}_2\text{Li}$, and $(\text{CH}_2\text{OCO}_2\text{Li})_2$. The corresponding degradation curves are shown in Fig. 5.

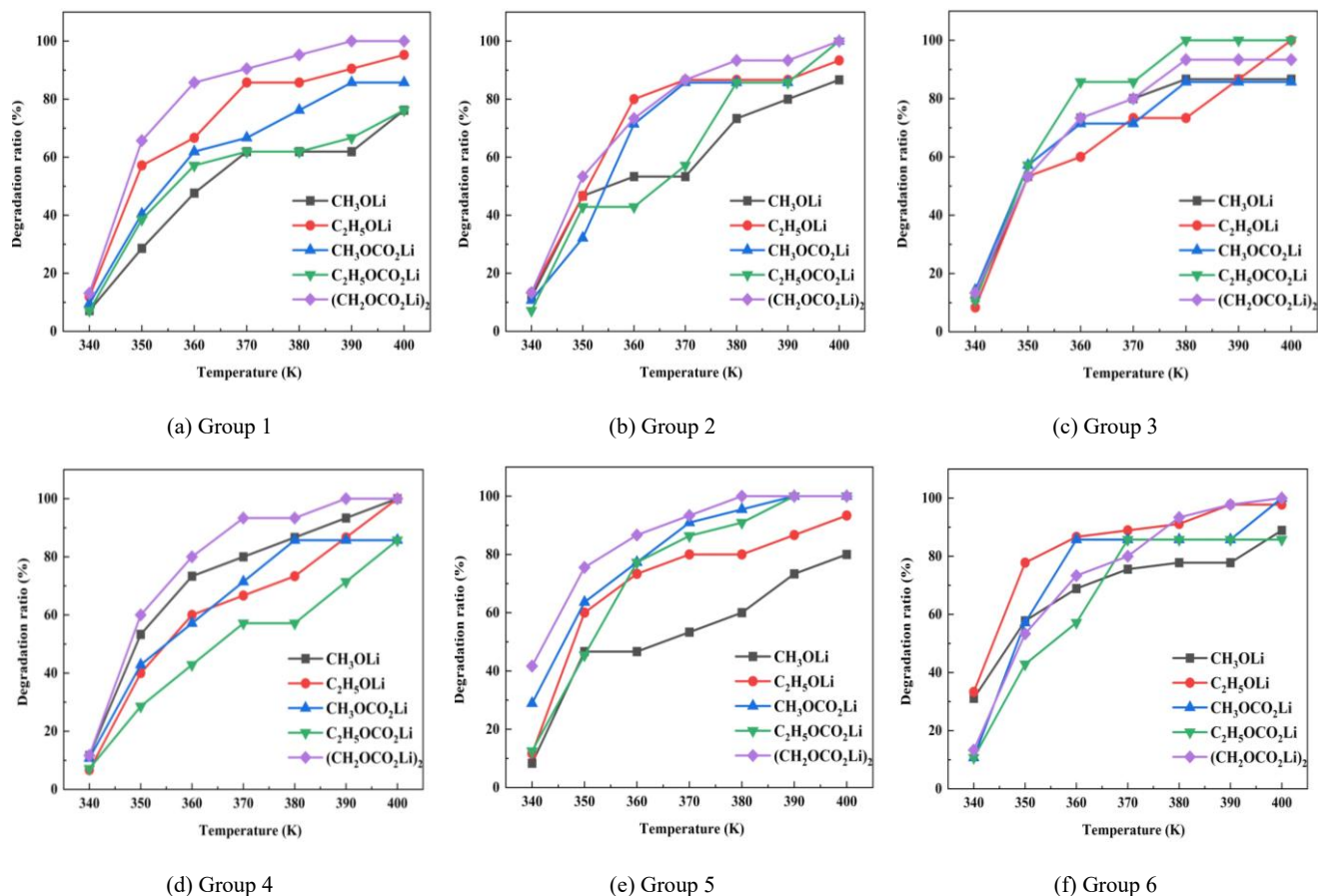


Fig. 5 Molecular degradation curves for the SEI systems

All organic phases exhibited a pronounced nonlinear change near 370 K. Local enrichment of an organic component lowered its own decomposition threshold: when the relative fraction of either carbonate or lithium alkoxide was increased (Groups 5 and 6), the degradation ratio exceeded 30% at only 340 K. By contrast, large changes in the inorganic fraction (Group 4) had little effect on cleavage of the organic framework. Thus, the pyrolysis kinetics of the organic SEI depend strongly on the local concentration of the organic phase but are relatively insensitive to the overall fraction of the inorganic framework.

At the intrinsic thermodynamic level, the organic salts exhibited a clear structure-stability relationship. The frameworks of lithium alkyl carbonates (R^1OCO_2Li) were generally more vulnerable than those of lithium alkoxides (R^2OLi), making the carbonates the leading initiators of thermally induced cleavage. Comparison of homologues further revealed that steric effects and chain length reduce thermal stability. The dinuclear dimer $(CH_2OCO_2Li)_2$ was markedly more susceptible to cleavage than the monomeric carbonates, and the ethyl-containing C_2H_5OLi collapsed and cleaved more readily than the shorter-chain CH_3OLi .

To resolve the microscopic origin of SEI destabilization, the complex decomposition networks of the five principal organic components were mapped. Figure 6 summarizes the degradation pathways of the organic lithium salts. The preferred pathways were highly component-specific and were governed by framework structure and the local coordination environment.

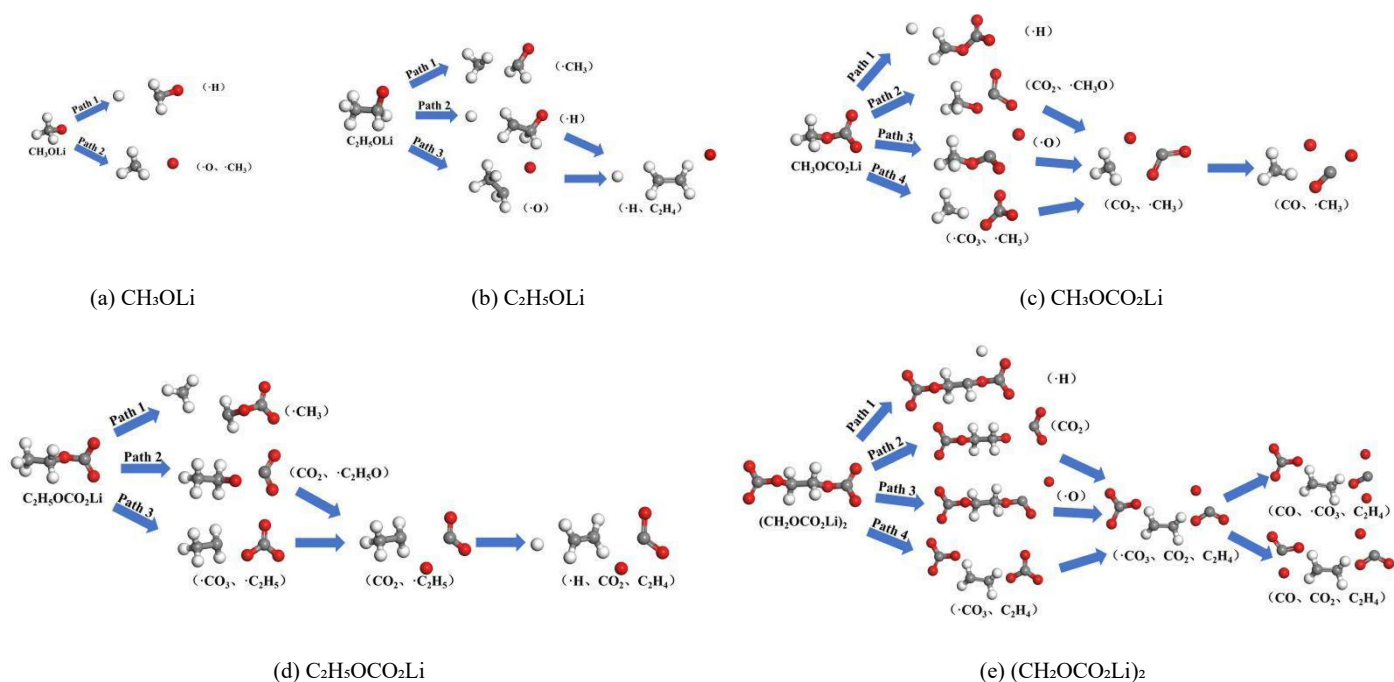


Fig. 6 Degradation pathways of organic lithium salts in the SEI

Because lithium alkyl carbonates ($\text{R}'\text{OCO}_2\text{Li}$) contain both a carbonate framework and ether-oxygen sites, their gas-forming degradation pathways are strongly branched. Upon thermal activation, carbonyl polarization renders the adjacent C-O bond the most vulnerable initiation site. Its cleavage produces two principal CO_2 -release cascades: one forms an alkoxide intermediate that further decomposes into alkyl and oxygen radicals (CH_3 radical and C_2H_5 radical), whereas the other directly generates a CO_3 fragment followed by CO_2 release. During secondary evolution, long-chain $\text{C}_2\text{H}_5\text{OCO}_2\text{Li}$ tends to undergo C-C skeleton cleavage because of its greater conformational freedom, whereas shorter-chain species such as $\text{CH}_3\text{OCO}_2\text{Li}$ and the dimer favor local dehydrogenation or deoxygenation. In contrast, lithium alkoxides (R^2OLi) follow non- CO_2 -producing pathways. Relaxation and dissociation of the Li-O-C network expose highly reactive alkoxy fragments (CH_3O radical and $\text{C}_2\text{H}_5\text{O}$ radical), which then undergo dehydrogenation and recombination to form small aldehydes (CH_2O and $\text{C}_2\text{H}_4\text{O}$) or release oxygen to form alkenes such as C_2H_4 .

These trajectories identify a key substituent effect governing the thermal stability of the organic SEI. Ethyl-containing species, with longer carbon chains and greater conformational freedom, readily undergo C-C cleavage and structural rearrangement and are therefore highly thermally vulnerable. Compact methyl derivatives, in contrast, retard pyrolysis.

The predicted products separate into highly volatile gases (CO_2 , CO , and C_2H_4) and complex condensed fragments, including oxygen-containing organic species and Li-coordinated residues. The early increase in CO_2 directly reflects the preferential decarboxylation of lithium alkyl carbonates, whereas the delayed evolution of CO and C_2H_4 indicates that the film has entered a later stage of deep carbon-skeleton dissociation.

To determine the thermodynamic origin of this sequential cleavage, DFT was used to calculate the bond dissociation energies (BDEs) of representative bonds in the core reaction network. Quantifying the energy required for initial bond cleavage provides a fundamental basis for comparing component vulnerability and identifying the dominant pathways [35, 36]. The results are listed in Table 3.

Table 3 Bond dissociation energies of key bonds in the organic SEI components

Bond dissociation energy (kJ mol ⁻¹)	Path 1	Path 2	Path 3	Path 4
CH ₃ OLi	412.62	448.86	-	-
C ₂ H ₅ OLi	402.76	456.00	448.45	-
CH ₃ OCO ₂ Li	458.57	416.79	975.06	389.50
C ₂ H ₅ OCO ₂ Li	423.82	418.11	391.23	-
(CH ₂ OCO ₂ Li) ₂	754.73	376.56	974.89	394.10

The initial bond-cleavage barriers of lithium alkyl carbonates (R¹OCO₂Li) were generally lower than those of lithium alkoxides (R²OLi). In particular, the dimer (CH₂OCO₂Li)₂ had a low intrinsic cleavage threshold of 376.56 kJ mol⁻¹, consistent with its high susceptibility as a thermally induced failure initiator. CH₃OCO₂Li (389.50 kJ mol⁻¹) and C₂H₅OCO₂Li (391.23 kJ mol⁻¹) exhibited very similar barriers. This result distinguishes the roles of the framework and substituent: the carbonate framework is the intrinsically active center that controls initial dissociation, whereas the alkyl substituent mainly regulates subsequent cascade pathways. The lithium alkoxides showed higher cleavage barriers (CH₃OLi, 412.62 kJ mol⁻¹; C₂H₅OLi, 402.76 kJ mol⁻¹), delaying their structural degradation during the early stage. This BDE-based thermodynamic ordering agrees with the degradation kinetics described above.

3.2 Microscopic structural evolution and mechanism of separator melting

To reveal the thermally induced failure of the porous PE separator, stepwise-heating MD simulations were performed from 340 to 500 K using a nonreactive force field. Because the analysis focuses on physical melting, the structural evolution of both the uncoated and coated separator models during heating is shown in Fig. 7.

The trajectories show that the uncoated PE substrate undergoes pronounced chain-conformation rearrangement and pore contraction near 400 K. Above this threshold, the system enters a molten state, and the porous framework has largely disappeared by 500 K. The ceramic coating markedly delays these structural changes. Between 340 and 400 K, rigid support and interfacial anchoring by the coating strongly suppress relaxation of adjacent PE segments and preserve the pore geometry. Pore-closure kinetics remain substantially slower even at 400-440 K, and the topological outline is still discernible. Above 440 K, however, the composite inevitably enters accelerated pore closure, and the PE substrate softens extensively under the extreme thermal load at 500 K. Thus, interfacial confinement by the inorganic coating broadens the safe temperature window against thermal shrinkage and delays framework collapse, but it cannot overcome the intrinsic melting limit of PE.

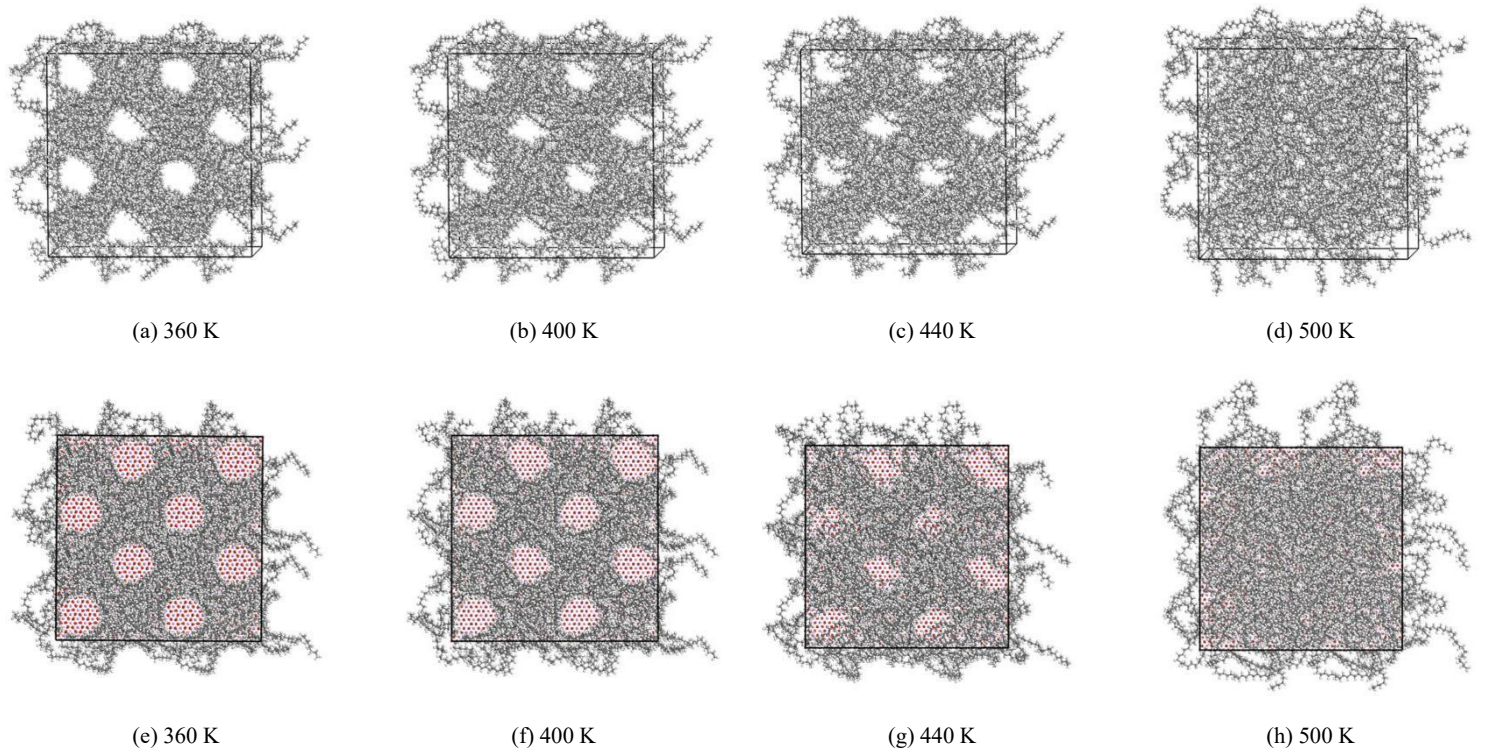
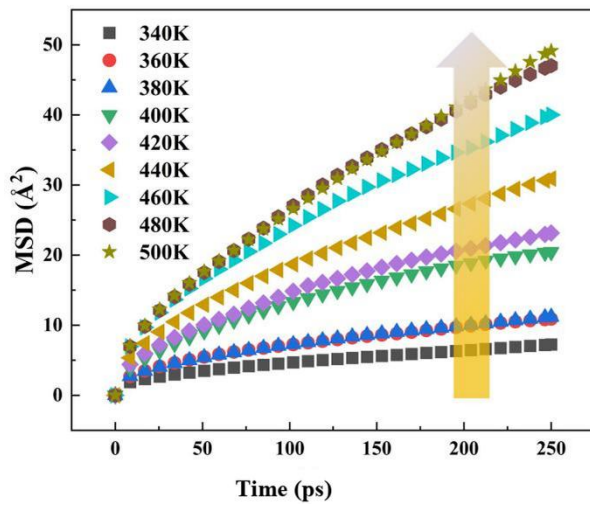


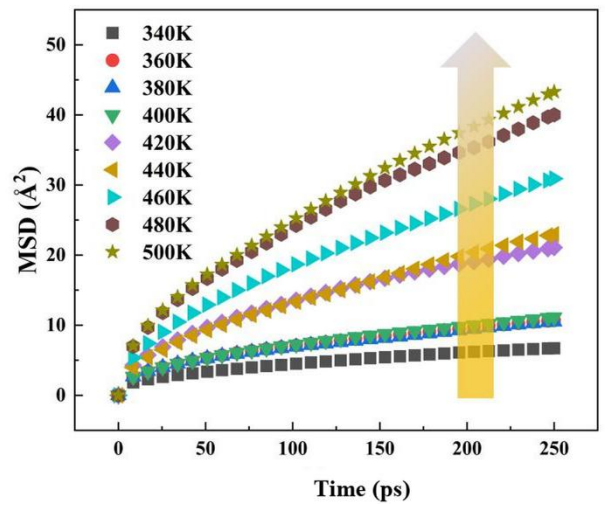
Fig. 7 Structural evolution during heating of (a-d) the uncoated separator and (e-h) the coated composite separator

To quantify the progressive physical failure associated with separator melting, the mean square displacement (MSD), radius of gyration (R_g), fractional free volume (FFV), interfacial binding energy, and elastic modulus were selected as key descriptors. The MSD and R_g of the PE segments at different temperatures are shown in Fig. 8.

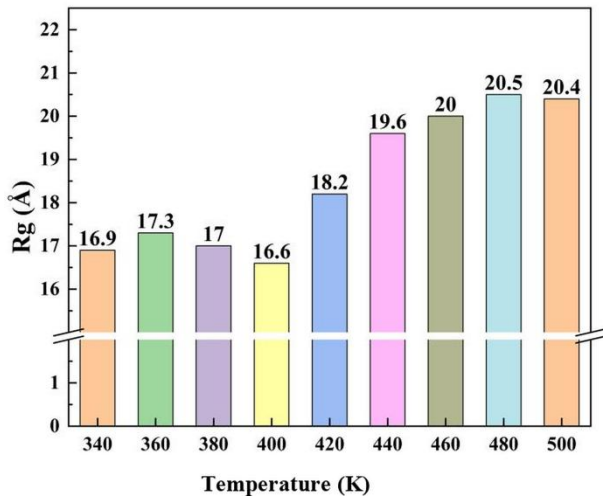
Thermal activation of the PE segments exhibited a distinct threshold response. In the uncoated PE substrate, the MSD increased sharply at approximately 380 K, indicating a transition from localized vibrational motion to unstable long-range diffusion. The nonmonotonic R_g response delineated three stages of conformational collapse: (1) below 360 K, local extension during conformational pre-relaxation produced a slight increase in R_g ; (2) from 360 to 400 K, thermally activated curling and inward contraction minimized surface energy, and the decrease in R_g reflected macroscopic pore-wall contraction; and (3) above 400 K, the loss of interchain van der Waals constraints produced a sharp increase in R_g , large-scale chain uncoiling and rearrangement, and eventual collapse of the porous topology. The coated separator maintained a substantially lower MSD baseline throughout the temperature range, and the transitions associated with inward contraction and large-scale uncoiling were delayed to 420–440 K. These results confirm that interfacial anchoring and spatial confinement by Al_2O_3 suppress polymer relaxation at low and intermediate temperatures and substantially delay large-scale segment rearrangement, although they cannot reverse intrinsic melting at high temperature.



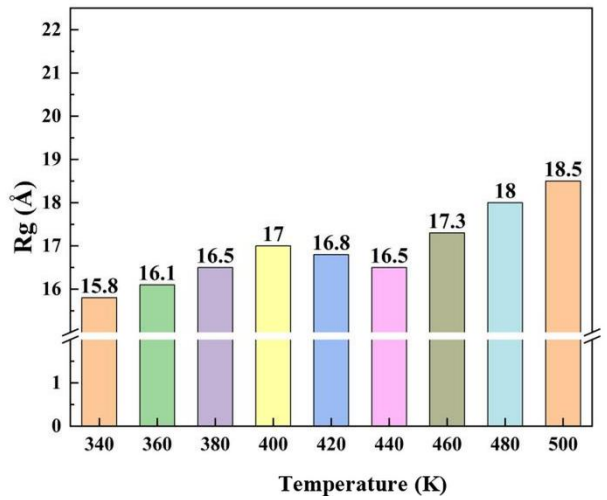
(a)



(b)



(c)



(d)

Fig. 8 (a, b) Mean square displacement and (c, d) radius of gyration of PE segments at different temperatures

The fractional free volume (FFV), which provides the microscopic geometric space for ion transport and segment relaxation, directly reflects the topological evolution of the porous PE network (Fig. 9). With increasing thermal perturbation, the FFV decreased from 29.67% at 340 K to 16.04% at 500 K and showed a staged collapse. Below 380 K, the FFV decreased slowly to 26.86%, indicating that the porous framework retained good connectivity under mild thermal stress. Between 380 and 400 K, accelerated pore-wall contraction caused extensive closure of connected pores and a sharp FFV decrease. A transient increase near 400 K resulted from local micropore distortion and spatial redistribution during large-scale chain uncoiling. Above 400 K, global melting eliminated most of the effective internal free volume. The dynamic loss of free volume therefore provides a geometric explanation for the failure of the separator as an ion-transport medium during thermal deformation.

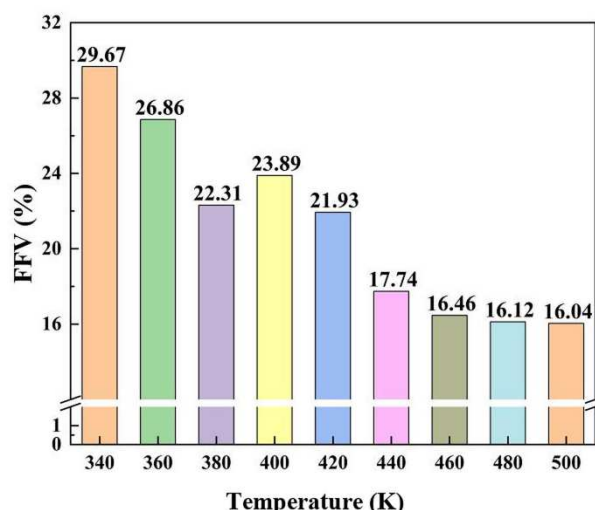
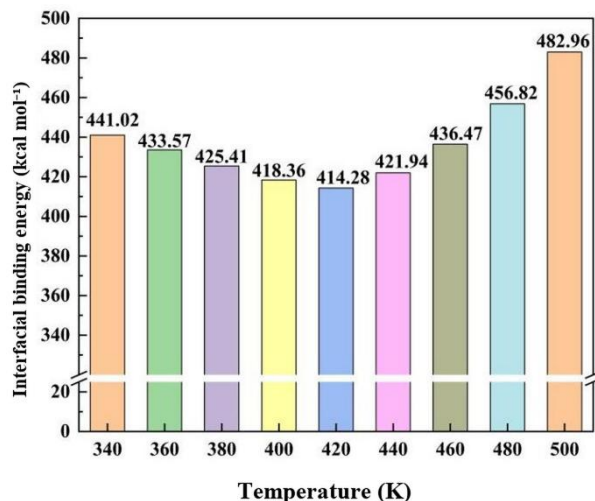


Fig. 9 Fractional free volume of the uncoated separator at different temperatures

For the coated separator, the temperature-dependent interfacial binding energy reveals competition between thermal desorption and melt wetting during deformation; its absolute value is plotted in Fig. 10a. The binding energy followed a V-shaped trend. Below the melting regime (<440 K), thermal perturbations promoted PE-chain detachment and inward conformational contraction (Fig. 10b,c), reducing the effective contact area and lowering the binding energy to $414.28 \text{ kcal mol}^{-1}$ at 420 K. Above 440 K, the PE substrate softened deeply and became rheological (Fig. 10d,e). The highly activated segments then underwent pronounced melt wetting and rearrangement on the Al_2O_3 surface. This conformational collapse produced dense conformal contact between the polymer and inorganic phase, rebuilding the interfacial interaction and increasing the binding energy to $482.96 \text{ kcal mol}^{-1}$ at 500 K. Thus, severe pore collapse at very high temperature passively densifies the polymer-coating interface.



(a)

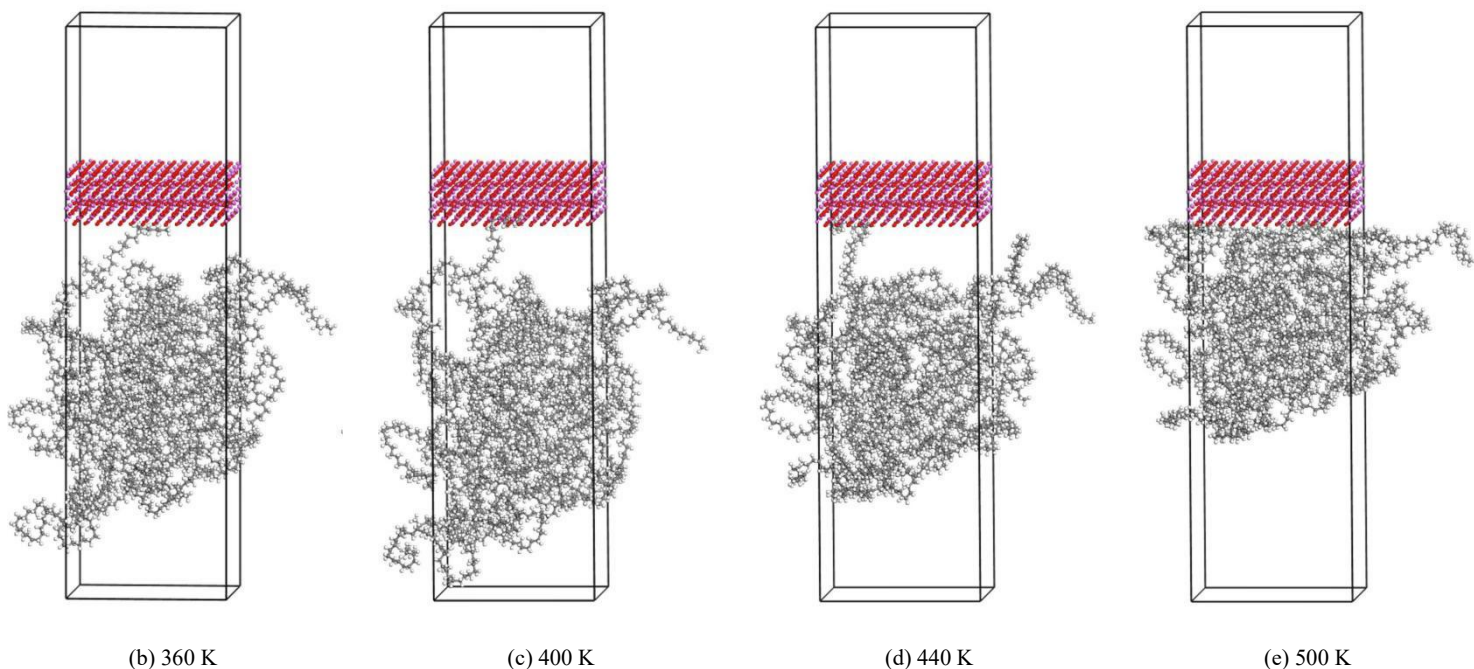


Fig. 10 (a) Interfacial binding energy of the coated separator and (b-e) interfacial structures at different temperatures

The temperature-dependent bulk, shear, and Young's moduli are shown in Fig. 11 and directly reflect the loss of load-bearing capacity during thermal deformation. Increasing temperature activates chain motion and decouples intermolecular interactions, deeply softening the physical network that supports the porous framework. Consequently, both separators showed continuously decreasing resistance to compression, shear, and tensile deformation.

The Al₂O₃-coated separator exhibited a pronounced mechanical delay. In addition to providing rigid surface support, interfacial confinement redistributed stress and dissipated stress concentrations in weak pore-wall regions, thereby delaying local pore failure. Once the temperature exceeded 440 K, however, the extreme rheological softening caused by deep melting of the PE substrate overcame the rigid constraint of the coating, and the mechanical properties declined rapidly.

The combined evolution of topology, segment dynamics, free volume, and macroscopic mechanical properties

defines distinct thermal-failure thresholds. The uncoated PE substrate underwent marked multiphysics degradation at 400 K, identifying the onset of substantial melting failure. For the coated separator, multidimensional confinement by the inorganic interface delayed accelerated softening and topological collapse to 440 K. These quantified thresholds provide a physical basis for predictive models linking thermal-runaway initiation to failure of internal electrical isolation.

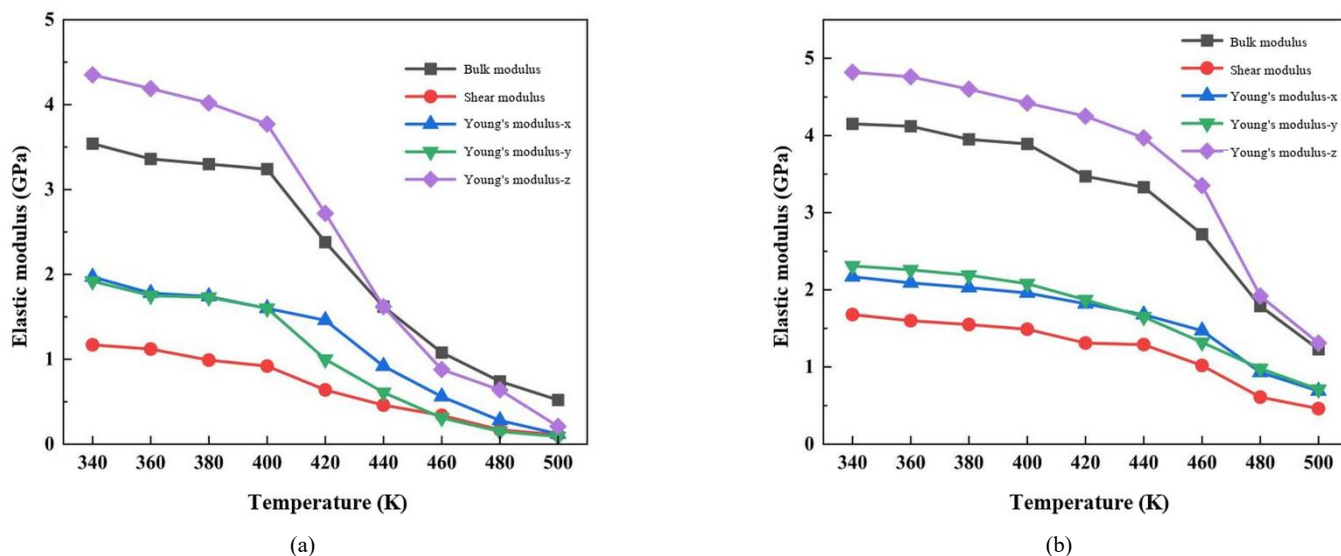


Fig. 11 Elastic moduli of the separators at different temperatures

3.3 Electrolyte decomposition in the coupled multiphase system

Thermal runaway in a real cell is not an isolated single-phase process. Electrolyte pyrolysis generally follows SEI decomposition and separator melting and is strongly constrained by the spatiotemporal coupling of multiphase interfaces. To move beyond a homogeneous electrolyte model, a spatially resolved SEI-electrolyte-separator model was constructed. Representative SEI components and the uncoated PE substrate were assembled and relaxed by energy minimization with the COMPASS III force field to remove steric hindrance and abnormal interpenetration introduced during assembly. The resulting thermodynamically stable layered multiphase configuration is shown in Fig. 12.

To represent multiphase cross-talk over the physical temperature range of 340-620 K, accelerated NVT reactive MD simulations were performed using a corresponding simulation range of 680-1240 K in increments of 80 K. Periodic boundaries were applied in the x and y directions, whereas nonperiodic reflecting walls were imposed along z. This treatment prevented the nonphysical escape of polar molecules through the thickness direction and reproduced the confined, pressurized environment of a closed cell. The resulting three-phase framework provides a computational basis for resolving electrolyte-derived gas-generation mechanisms at complex solid-liquid interfaces.



Fig. 12 Layered composite model (a) before and (b) after optimization

The structural evolution in Fig. 13 reveals progressive breakdown of the internal interfacial barriers. At the

beginning of heating, the SEI, electrolyte, and separator retained distinct physical boundaries. Above 380 K, fragments released by SEI depolymerization cross-diffused into the liquid phase while surface segments of the separator relaxed. At the highest temperatures, physical interfacial confinement was lost completely, and the system developed pronounced cross-phase penetration and mass-transfer coupling.

The kinetic analysis in Fig. 14 shows that the complex multiphase environment eliminates the stepwise degradation observed in the pure liquid phase and produces a nonlinear, continuous increase in solvent decomposition. The coupled system was comparatively inert during the initial thermal response, but the reaction rate increased sharply above 460 K, identifying this temperature as a critical threshold for rapid electrolyte decomposition in the multiphase environment.

The absolute amount of solvent degradation in the SEI-electrolyte-separator system was nevertheless substantially lower than in the pure-liquid reference. This kinetic retardation can be attributed to competition for enthalpy dissipation: endothermic SEI depolymerization and phase-change melting of the PE separator form microscopic heat sinks that reduce the effective energy available for electrolyte bond cleavage. Multiphase components therefore alter both the local reaction topology and the distribution of heat flux, strongly modulating chain degradation in the electrolyte.

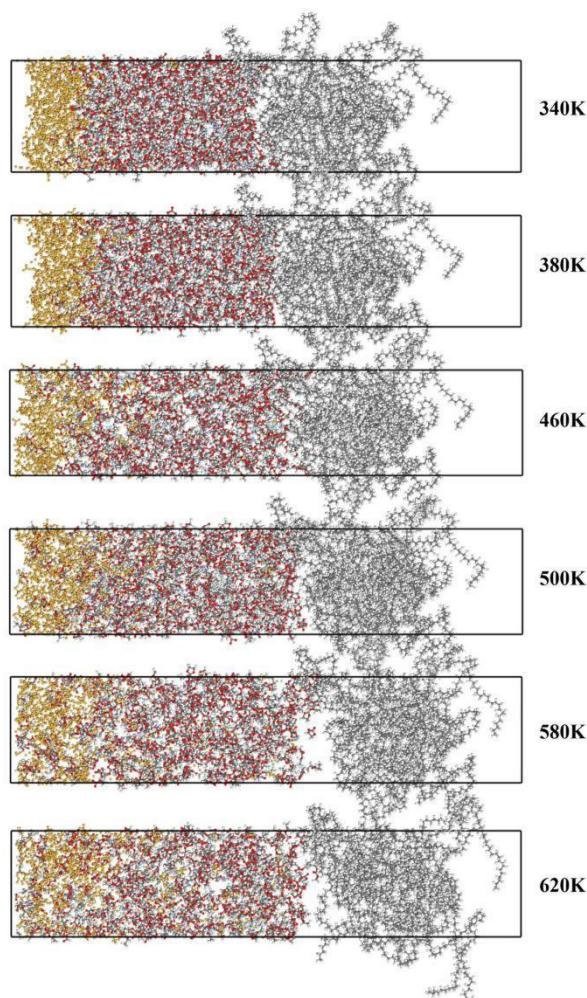


Fig. 13 Structural evolution of the coupled SEI-electrolyte-separator system

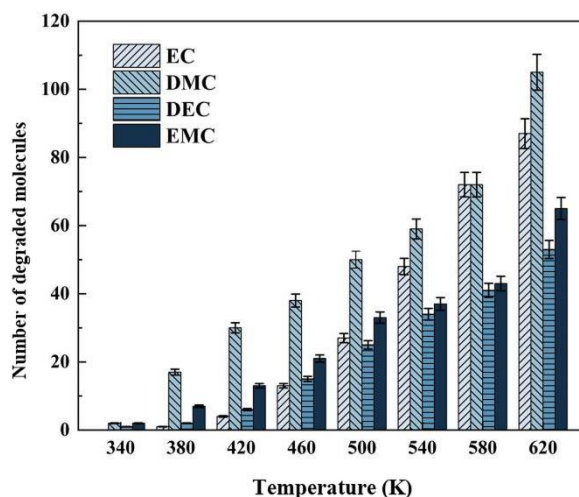
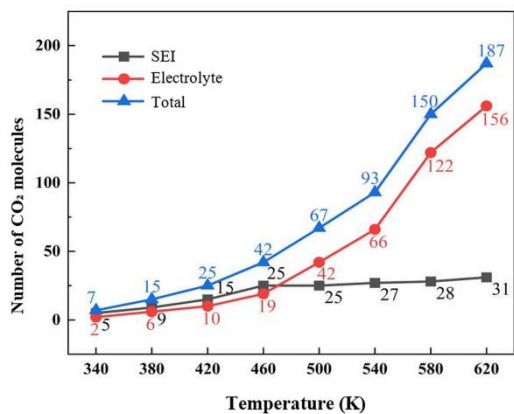


Fig. 14 Number of degraded solvent molecules in the coupled multiphase system

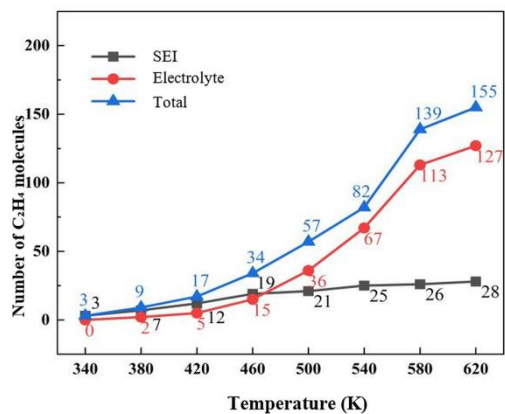
Gas evolution during thermal runaway directly drives internal pressurization and physical collapse. Figure 15 shows the numbers of gaseous products generated in the coupled system as a function of temperature. Source attribution for CO_2 , C_2H_4 , and CO reveals their onset temperatures, growth inflection points, and origins within the confined multiphase environment.

CO_2 , a marker of decarboxylation, and combustible C_2H_4 , a marker of carbon-skeleton cleavage, were the dominant products and evolved synergistically. Below 420 K, the initial gas source was the preferential decomposition of carbonate and ether-oxygen sites in the organic SEI. Above 500 K, after the readily decomposed SEI components were depleted, deep side-chain cleavage of electrolyte solvents became dominant. In the closed, oxygen-deficient environment, CO was only a minor product of deeper cleavage of oxygen-containing fragments, with comparable contributions from the SEI and electrolyte.

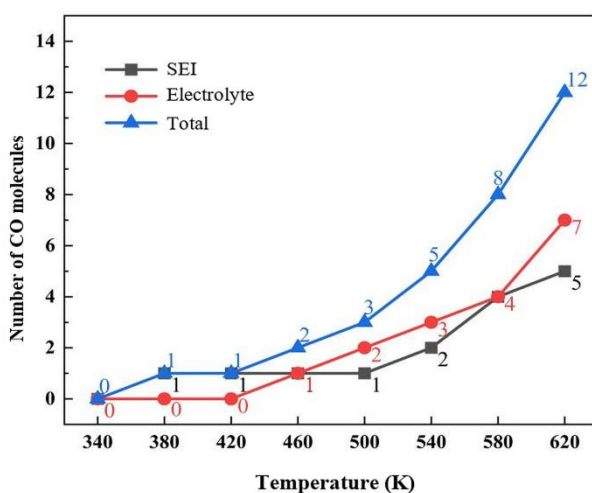
Gas evolution in the coupled system can therefore be divided into three stages. Stage I (<420 K) is interfacial pyrolysis, during which preferential oxygen-containing bond cleavage in the SEI produces a small initial gas accumulation. Stage II (420-460 K) is multiphase co-generation, in which residual SEI decomposition proceeds alongside initial electrolyte activation; the system crosses a kinetic inflection point and the gas-generation rate increases rapidly. Stage III (>460 K) is liquid-phase decomposition, in which electrolyte degradation dominates and CO_2 and combustible C_2H_4 increase exponentially, marking entry into advanced, irreversible thermal runaway.



(a) Number of CO₂ molecules



(b) Number of C₂H₄ molecules



(c) Number of CO molecules

Fig. 15 Numbers of gaseous products generated in the coupled multiphase system as a function of temperature

4 Discussion

The SEI results demonstrate a cascade of conformational relaxation, local bond cleavage, extensive depolymerization, and gas release. Its thermal stability is governed primarily by the local concentration of the organic phase and is relatively insensitive to the overall inorganic fraction. The low-dissociation-energy carbonate framework controls initial cleavage and early CO₂ release, whereas ethyl-containing species and dimers, owing to their greater conformational freedom, regulate the subsequent formation of C₂H₄ and CO.

The separator results reveal progressive thermal failure through pre-relaxation, pore-wall contraction, and topological collapse. Interfacial confinement by the Al₂O₃ coating cannot overcome the intrinsic melting limit of PE, but it delays the threshold for extensive destabilization from 400 K to 440 K. Above this threshold, increased long-range segment diffusion, nonmonotonic conformational rearrangement, loss of free volume, and collapse of the elastic moduli jointly drive the loss of mechanical support and ion-transport pathways.

The electrolyte is a central medium in thermal-runaway evolution, and its pyrolysis is constrained by both the multiphase

microenvironment and molecular electronic structure. SEI depolymerization and separator melting form microscopic heat sinks whose competition for enthalpy dissipation significantly retards electrolyte degradation. Gas evolution progresses from initial SEI-derived products to electrolyte-dominated generation at high temperature; above 460 K, liquid-phase cleavage causes an exponential increase in combustible gases and marks entry into irreversible advanced thermal runaway.

5 Conclusions

A multiscale approach combining molecular dynamics and density functional theory was used to investigate the microscopic failure of the SEI, separator, and electrolyte during thermal-runaway initiation in representative large-capacity LFP cells. The principal conclusions are as follows.

(1) The SEI follows a cascade of conformational relaxation, local bond cleavage, extensive depolymerization, and gas release. Its overall thermal stability is governed primarily by the local concentration of the organic phase and is relatively insensitive to the inorganic fraction. Near the nonlinear transition at approximately 370 K, the low-dissociation-energy carbonate framework initiates cleavage and early CO₂ release. Long-chain ethyl groups and dimers are especially vulnerable because of their high conformational freedom and drive the delayed evolution of C₂H₄ and CO. The calculations thus connect framework-controlled initial cleavage with substituent-controlled cascade branching across scales.

(2) The separator exhibits a progressive sequence of pre-relaxation, pore-wall contraction, and topological collapse. Although interfacial confinement by the inorganic coating cannot exceed the intrinsic melting limit of PE, it shifts the threshold for extensive destabilization from 400 K for the uncoated substrate to 440 K for the coated separator. Above the threshold, rapid long-range segment diffusion (MSD) and nonmonotonic conformational rearrangement (Rg) drive severe softening. The accompanying loss of effective free volume, collapse of elastic moduli, and dynamic transition from thermal desorption to melt wetting explain the loss of mechanical support and ion-transport pathways.

(3) The electrolyte is a central medium in thermal-runaway evolution, and its pyrolysis is regulated by both the multiphase microenvironment and molecular electronic structure. Introducing SEI and separator boundaries creates microscopic heat sinks through interfacial depolymerization and melting, and the resulting competition for enthalpy dissipation retards electrolyte degradation. Gas evolution follows three stages, shifting from initial SEI-derived products to electrolyte-dominated generation at high temperature. Above the critical threshold of 460 K, liquid-phase cleavage produces an exponential increase in combustible gases and marks the onset of irreversible advanced thermal runaway.

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Declaration of interests

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

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Appendix: Model Validation

A.1 Validation of the SEI model

Fig. 16 shows the time-dependent density and energy during MD relaxation. Both quantities converged gradually, indicating that the SEI model reached equilibrium.

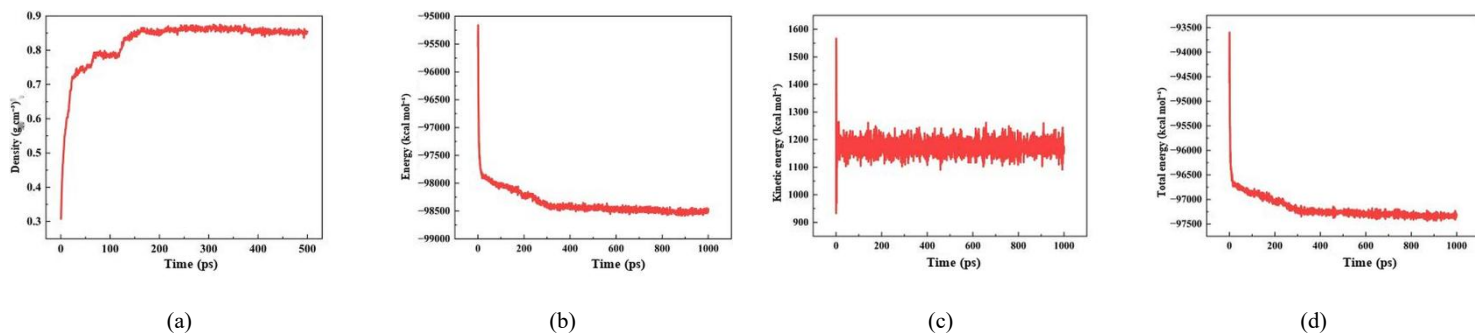


Fig. 16 Density and energy profiles during equilibration of the SEI model

A.2 Validation of the separator models

Polymer-chain characteristics

Fig. 17a shows the room-temperature dynamics of the PE-backbone carbon atoms. Both the MSD and its slope were lower for the coated separator than for the uncoated substrate.

Fig. 17b shows the Rg profiles over the complete equilibration trajectory. Both systems were fully relaxed, and the mean Rg values converged to approximately 15.5 and 15.3 Å for the uncoated and coated separators, respectively.

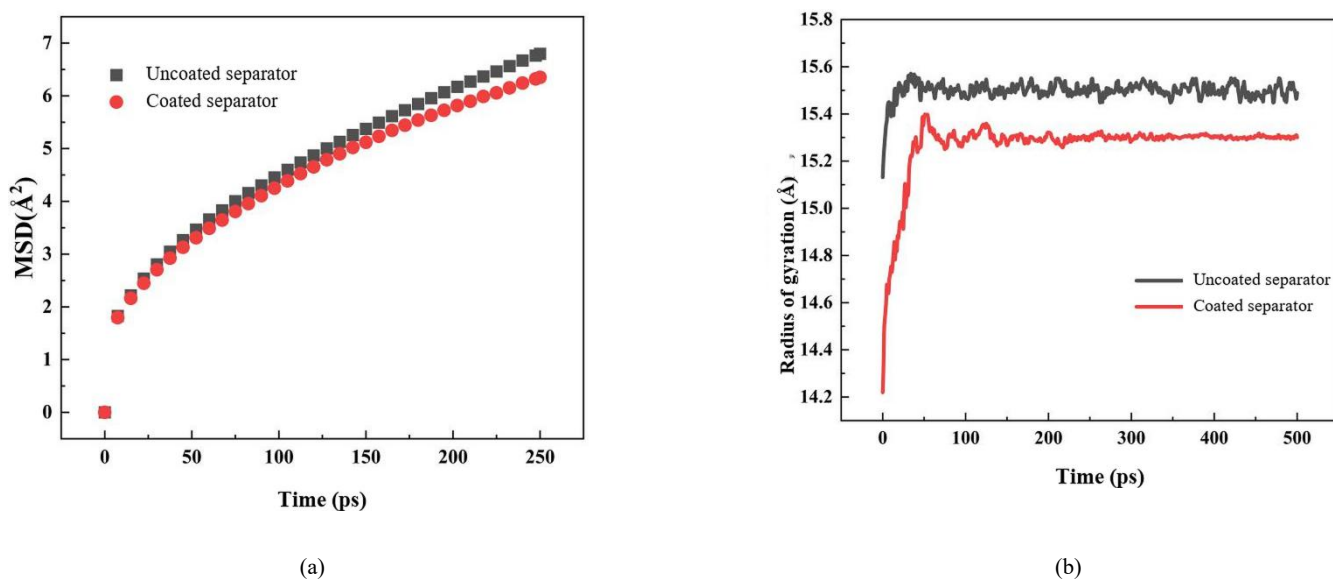


Fig. 17 (a) Mean-square displacement and (b) radius of gyration of PE chains during equilibration

Fractional free volume

Fig. 18 shows the free-volume distribution in the relaxed uncoated separator. The free space was spatially

heterogeneous. The absolute free volume was 19,643.12 Å³, corresponding to an FFV of 30.69%.

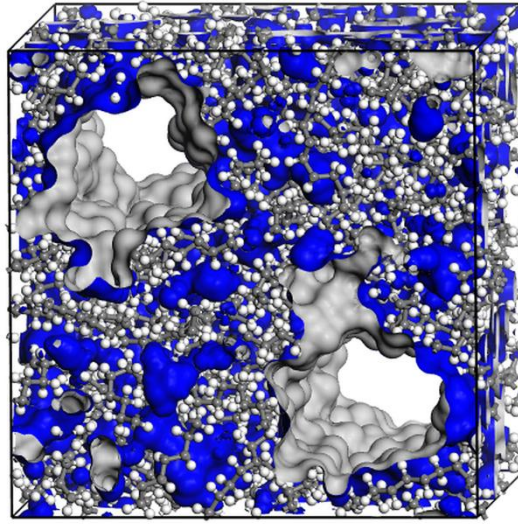


Fig. 18 Free-volume distribution in the uncoated PE separator

Interfacial binding energy

The coating-substrate interaction is central to the thermomechanical stability of the composite separator. To quantify the compatibility between the Al₂O₃ coating and PE substrate, the interfacial binding energy was calculated using Eq. (A1):

$$E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{polymer}}) \quad (\text{A1})$$

where $E_{\text{interaction}}$ is the interfacial binding energy, E_{total} is the total energy of the composite separator, E_{surface} is the energy of the isolated Al₂O₃ coating, and E_{polymer} is the energy of the isolated PE substrate.

After relaxation, the interfacial binding energy was -447.89 kcal mol⁻¹. The negative value indicates a stable coating-substrate interaction within the model.

Elastic moduli

The calculated bulk, shear, and directional Young's moduli of the separator models are summarized in Table 4.

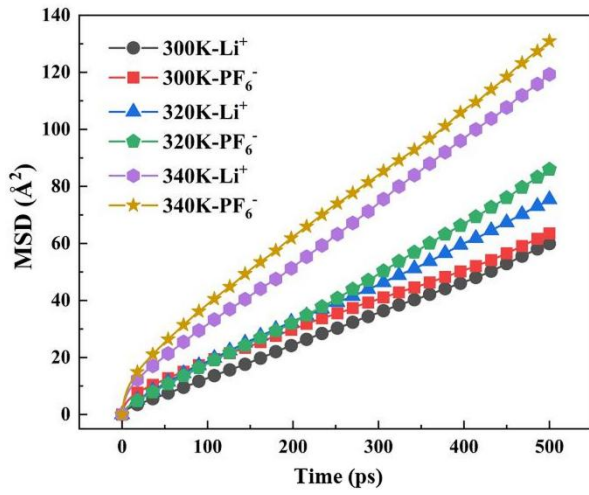
Table 4 Bulk, shear, and Young's moduli of the separator models

	Bulk modulus, K	Shear modulus, G	Young's modulus
Uncoated PE separator	3.19 GPa	1.02 GPa	Ex = 1.62 GPa; Ey = 1.80 GPa; Ez = 4.26 GPa
Al ₂ O ₃ -coated separator	4.05 GPa	1.62 GPa	Ex = 2.06 GPa; Ey = 2.27 GPa; Ez = 4.72 GPa

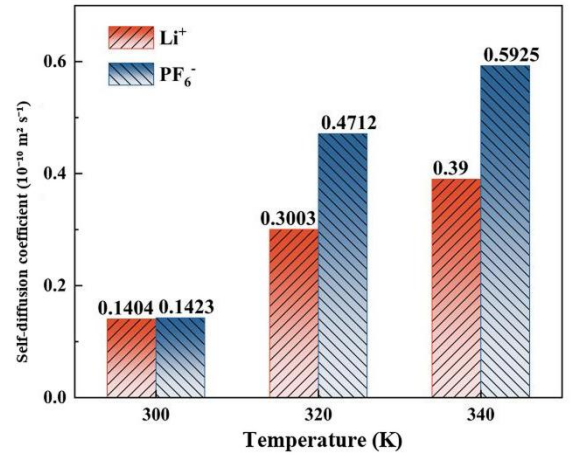
A.3 Validation of the electrolyte model

Diffusion characteristics

Electrolyte transport was evaluated from 300 to 340 K. Fig. 19a shows the mean-square displacements of Li⁺ and PF₆⁻ calculated from the Einstein relation, and Fig. 19b shows the corresponding self-diffusion coefficients.



(a)

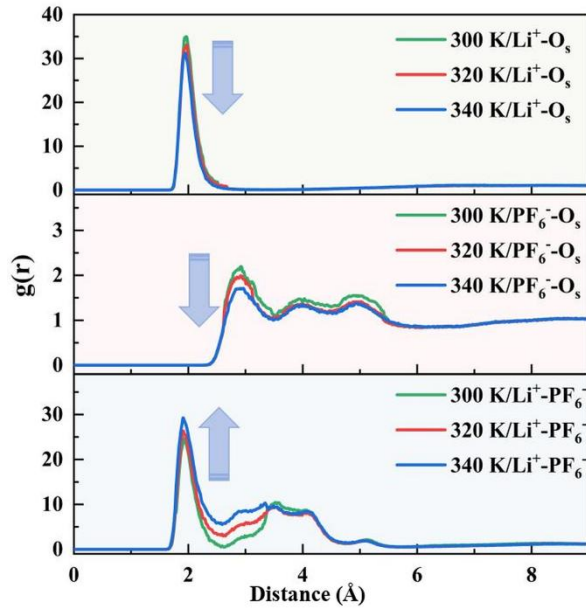


(b)

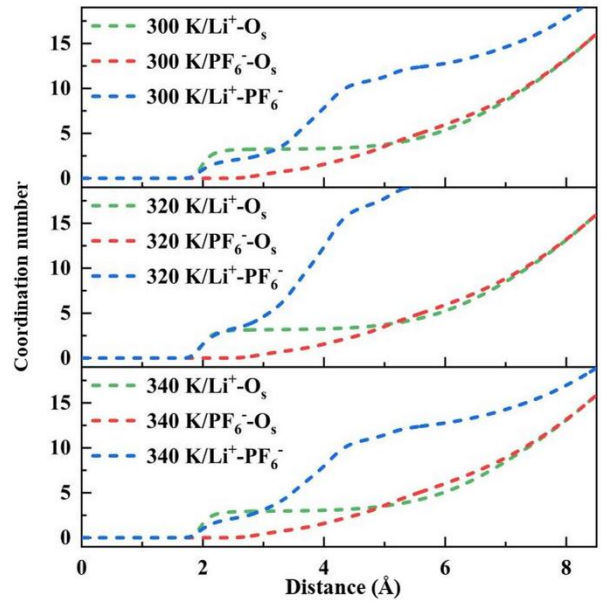
Fig. 19 (a) Mean-square displacements and (b) self-diffusion coefficients of Li^+ and PF_6^-

Solvation characteristics

Fig. 20 shows the local coordination structures. The corresponding thermodynamic energy profiles are presented in Fig. 21 and Table 5.



(a) $g(r)$



(b) CN

Fig. 20 Radial distribution functions and coordination numbers of Li^+ and PF_6^-

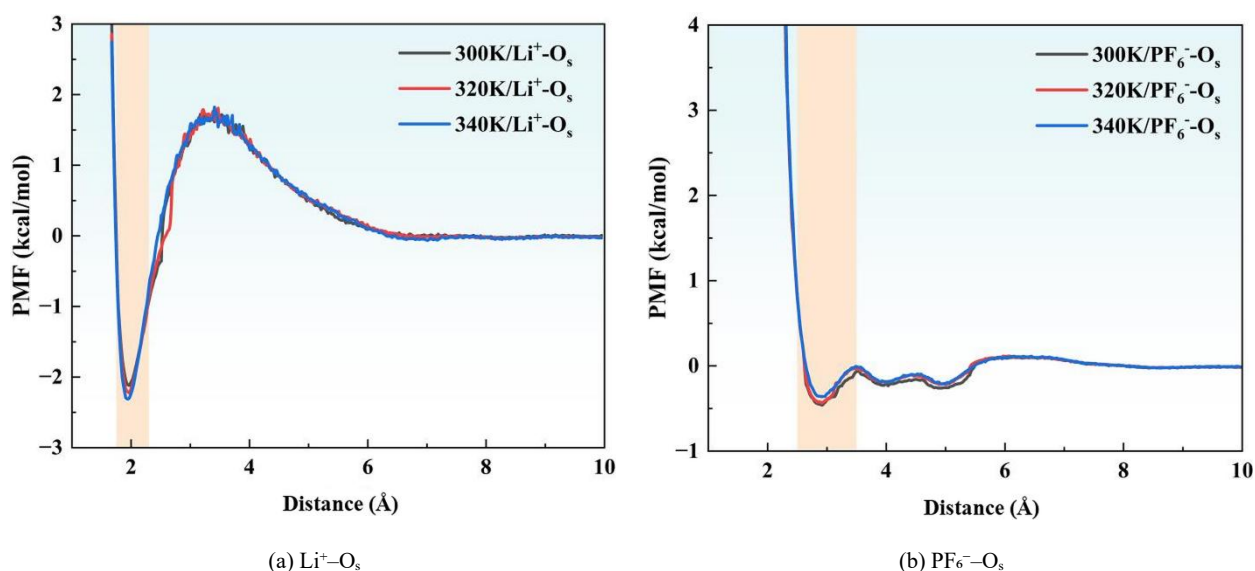


Fig. 21 Potentials of mean force for ion-solvent coordination

Table 5 Binding free energies for ion-solvent coordination

Binding free energy (kcal mol ⁻¹)	300 K	320 K	340 K
Li ⁺ -O _s	-1.48915	-1.48253	-1.44313
PF ₆ ⁻ -O _s	-0.69994	-0.71550	-0.73947

Ion-pairing characteristics

The temperature-dependent Li⁺-PF₆⁻ configurations were classified as solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and ionic aggregates (AGGs). Fig. 22 shows representative structures. Table 6 summarizes their temperature-dependent fractions.

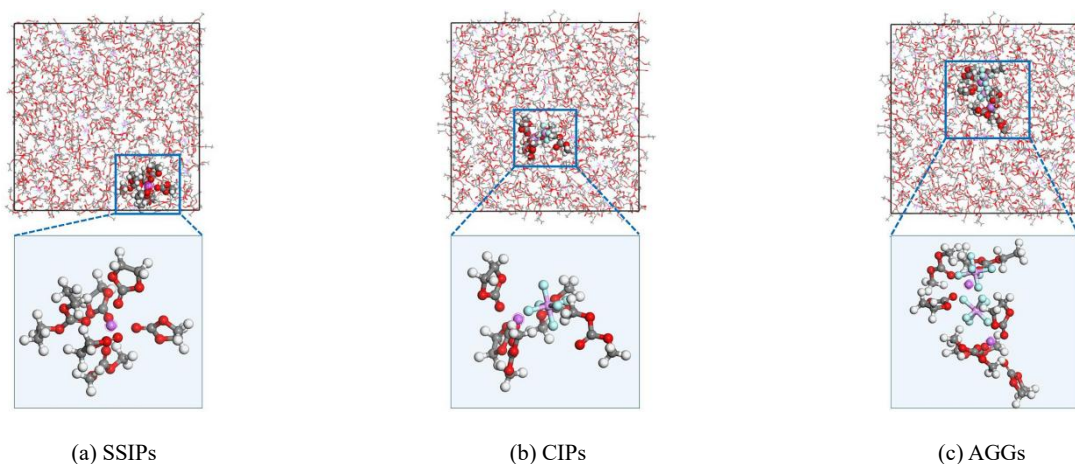


Fig. 22 Representative structures of the three Li⁺-PF₆⁻ ion-pairing configurations

Table 6 Percentages of Li⁺-PF₆⁻ ion-pairing configurations

	SSIPs	CIPs	AGGs
300 K	5.95%	32.74%	61.31%
320 K	3.45%	39.88%	56.67%
340 K	0.95%	44.64%	54.40%