

Review Article

Targeted Advances in Lithium-ion Batteries: A Critical Review of Synergetic Improvements in Energy Density, Life Cycle, and Safety

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Abstract

Dependable and efficient energy storage systems are indispensable for modern sustainable energy applications. Lithium-ion batteries (LIBs), with their proven reliability and high energy density, have become the foundation of contemporary energy storage, powering applications ranging from portable electronics to electric vehicles (EVs) and grid-scale renewable energy systems. Critically, LIBs are increasingly vital for integrating variable renewable resources, such as solar and wind, into large-scale electrical grids. By enabling the efficient capture and on-demand discharge of electricity, they provide essential electricity and flexibility to modern sustainable power systems. Despite their dominance, challenges persist in terms of energy density, life cycle, and safety, which limit their full potential. Consequently, LIB technology remains paramount for realizing a cleaner, electrified future across several diverse sectors. This review systematically examines recent advancements in LIB technology, focusing on three critical performance metrics: (1) energy density, where innovations in high-capacity silicon anodes, nickel-rich cathodes, and solid-state electrolytes have pushed boundaries; (2) life cycle, addressing degradation mechanisms such as solid electrolyte interphase (SEI) growth and lithium-plating through advanced electrolytes and manufacturing techniques; and (3) safety, mitigating thermal runaway risks via ceramic-coated separators, flame-retardant additives, and robust battery management systems (BMS). Furthermore, the review highlights emerging technologies such as lithium-sulfur and solid-state batteries, which promise transformative gains. This review identifies significant gaps by synthesizing material innovations, failure mechanisms, and industry trends. It provides a road map for future research, emphasizing the need for sustainable materials, scalable manufacturing, and stringent safety protocols to meet the growing demands of next-generation energy storage.

Keywords

Lithium-ion Batteries, Energy Density, Life Cycle, Thermal Runaway, Solid-state Electrolytes, Sustainable Energy Storage

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1. Introduction

Rechargeable batteries trace their origins to the 19th-century inventions of lead-acid and nickel-cadmium batteries [1]. Commercialization accelerated in the 20th century with LIBs and nickel-metal hydride (NiMH) batteries, revolutionizing portable electronics (e.g., smartphones, laptops) and emerging as pivotal for EVs and renewable energy storage [2]. Batteries convert chemical energy to electrical energy reversibly. Battery Energy Storage Systems (BESS) bolster grid stability across the generation, transmission, and distribution sectors [3]. Among battery technologies, LIBs dominate due to their high energy density, long life cycle, and low self-discharge [4]. Alternatives, like lead-acid, sodium-ion, and solid-state batteries, serve niche applications, but LIBs remain unmatched for mainstream use [5]. The three critical performance pillars for LIBs are: energy density (crucial for EV range and device miniaturization [6]), life cycle (reduces replacement costs and enhances sustainability [7]), and safety (prevents catastrophic failures in high-risk applications like EVs [8]). This review examines advancements in these areas, highlighting material innovations, degradation mechanisms, safety protocols, and future challenges.

LIBs' superior energy density (~250–300 Wh/kg), long life cycle (>1000 cycles), and better costs (\$132/kWh as of 2021) make them indispensable for the global transition to clean energy. The escalating demand for higher performance-driven by EVs requiring >500 km ranges and renewables needing efficient storage-exposes critical limitations in current LIB technology [9]. While LIBs outperform lead-acid and NiMH batteries, their gravimetric energy density remains insufficient for next-gen applications. For instance, aviation and long-haul EVs demand >400 Wh/kg, which traditional graphite anodes and layered oxide cathodes cannot achieve without compromising stability [5]. Capacity fade due to solid electrolyte interface (SEI) growth, lithium plating, and mechanical stress limits LIBs to ~2000 cycles, far below the 5000+ cycles needed for grid storage [6]. Thermal runaway-triggered by dendrite penetration, overcharging, or mechanical abuse-has caused high-profile failures in EVs (e.g., Tesla fires) and energy storage systems [10] (e.g., Arizona grid battery explosion [7]). These challenges are interconnected. For example, high-energy-density nickel-rich cathodes (e.g., NMC811) exacerbate thermal instability [8], while silicon anodes suffer from volume expansion that degrades the life cycle [11]. Thus, synergetic improvements are essential to break the existing trade-offs.

Prior reviews have often treated energy density, life cycle, and safety as isolated domains [1, 4, 9, 10, 12–28]. For instance, material-centric reviews focus on singular advancements (e.g., silicon anodes [29]) without addressing their impact on safety or longevity. Safety studies overemphasize thermal runaway mechanisms [30], but neglect how novel electrolytes (e.g., ionic liquids) can simultaneously enhance

energy density and life cycle [31]. Life cycle analyses rarely integrate manufacturing innovations -such as dry electrode coating [32] with cycling strategies to close the material loop.

This fragmented approach overlooks interdependencies among these metrics. For example, silicon-graphite composite anodes improve energy density, but require tailored electrolytes to mitigate SEI growth [33]. Similarly, solid-state batteries promise higher energy density and safety, but face challenges in interfacial stability that affect the life cycle [34]. This review bridges these gaps by interdisciplinary synthesis-correlating advancements across materials, life cycle engineering, and safety design to identify synergies, as the existing works underprovide this issue [18]. Critical analysis highlighting understudied trade-offs, such as how high-nickel cathodes (NMC811) demand advanced cooling systems to offset thermal risks [35]. Furthermore, the review provides a future roadmap that proposes integrated solutions and policy frameworks to accelerate commercialization. It explains the rationale for the choices, the current possibilities, and the potentials of the technologies, as well as the assumptions contained in these opportunities, together with the problems and concerns linked with them. It aims to support further exploration and develop improvements in lithium-ion battery technology by providing straightforward instructions toward these significant outlooks.

2. Energy Density Improvements

2.1. Introduction to Energy Density in LIBs

Energy density-measured in watt-hours per kilogram (Wh/kg) or watt-hours per liter (Wh/L)-is the most critical performance metric for LIBs. It determines how much energy a battery can store relative to its weight or volume, directly impacting applications such as EVs (driving range of electric vehicles), the run time of portable electronics, and the efficiency of renewable energy storage systems [2, 3]. Despite significant advancements [36], current LIB technologies face fundamental limitations-such as material-level constraints by which the conventional graphite anodes (372mAh/g) [12] and layered oxide cathodes are approaching their theoretical capacity limits, high-capacity materials, like silicon anodes [20] and nickel-rich cathodes often exhibit rapid capacity fade or thermal instability. Moreover, the system challenges-increasing energy density without compromising life cycle or safety require a holistic cell design. The data in Table 1 indicate that there is still a lot of opportunity for development in Li-ion cells' capacity to store energy. "Where has all the energy gone?" is the issue raised by these findings.

Table 1. Energy density of LIBs [4].

Chemistry	Size	WhL ⁻¹ theoretical	WhL ⁻¹ actual	%	Wh kg ⁻¹ theoretical	Wh kg ⁻¹ actual	%
LiFePO ₄	54208	1980	293	14.8	587	156	26.6
LiMn ₂ O ₄	26700	2060	296	14.4	500	109	21.8
LiCoO ₂	18650	2950	570	19.3	1000	250	25.0
Si-LiMO ₂ Panasonic	18650	2950	919	31.2	1000	252	25.2

2.2. Cathode Materials: Pushing the Boundaries of Capacity and Stability

2.2.1. Nickel-Rich Layered Oxides (NMC/NCA)

Table 2. Degradation Mechanisms and Mitigation Strategies.

Degradation Mechanism	Impact on performance	Mitigation strategy	Key references
Cation mixing	Blocks Li ⁺ diffusion, increases impedance	Al/Ti doping (e.g., NCMA)	[32, 33]
Oxygen release at high voltage	Triggers exothermic reactions, thermal runaway	Gradient core-shell designs (Ni-rich core, Mn-rich shell)	[34, 35]
Micro-crack formation	Particle fracture, electrolyte decomposition	Single-crystal synthesis	[3, 37]
Transition metal dissolution (Mn, Co)	Accelerates SEI growth, capacity fade	Surface coatings,	[38]

These cathodes have emerged as leading candidates for high-energy density LIBs, offering capacities of 200–220 mAh/g compared to 160–180 mAh/g for conventional NMC111 [30, 31]. However, their commercialization is hindered by severe degradation mechanisms as shown in Table 2.

While NMC811 increases energy density by ~25% versus NMC111, enabling EVs with 500+ km ranges (e.g., Tesla’s 4680 cells achieve ~300 Wh/kg) [39], and aluminum doping (NCMA) improves thermal stability while maintaining high capacity [40]. Challenges such as-limited life cycle (~800–1,000 before 20% capacity loss) due to structural degradation, and requirements for advanced battery management systems

(BMS) to prevent overcharging and overheating seek urgent solutions. As a result, upcoming studies should employ multi-element doping to stabilize crystal structures [41] and will benefit from artificial intelligence-assisted optimization of doping concentrations and synthesis parameters [42].

2.2.2. Lithium-Rich Manganese-Based (LMR) Cathodes

LMR cathodes utilize cationic and anionic redox, achieving exceptional capacities of 250–300 mAh/g [43]. However, they suffer from voltage decay and poor rate capability:

Table 3. Performance Comparison: LMR vs. NMC811 [14].

Parameter	LMR cathode	NMC811	Implications
Capacity (mAh/g)	250–300	200–220	LMR offers 30–40% higher capacity
Voltage decay	~0.5V after 100 cycles	Minimal	Reduces energy efficiency
Thermal stability	Poor (Oxygen release at 150 °C)	Moderate (180 °C)	Safety concerns for EVs

Parameter	LMR cathode	NMC811	Implications
Commercial adoption	Limited (prototype stages)	Mass produced (Tesla, LG)	LMR requires further R&D

The ultra-high capacity (>300 mAh/g demonstrated in labs) and low cobalt content reduce cost and ethical concerns [44, 45]; however, irreversible oxygen loss leads to rapid voltage decay, and poor thermal ability increases thermal runaway risks [46, 47]. Hence, the promising strategies include: surface modifications to suppress oxygen release, and electrolyte additives (e.g., LiDFOB) to stabilize the cathode electrolyte interface [48, 49].

2.3. Anode Materials: Beyond Conventional Graphite

2.3.1. Silicon (Si) Anodes

Silicon's ultra-high theoretical capacity (3,579 mAh/g vs.

graphite's 372 mAh/g) makes it an attractive anode material, but its 300% volume expansion during lithiation causes severe mechanical degradation [50-53]. The silicon-graphite composites (5–10% of Si) improve energy density by 15–20% in commercial cells, and pre-lithiation mitigates irreversible Li-loss during initial cycles [54]. However, the consumption of electrolyte by thick-SEI formation, increasing the impedance, and electrode swelling (~15–20% volume change), complicating cell assembly, will remain the critical challenges [54, 55]. Therefore, silicon-carbon carbides (e.g., Si@C yolk-shell structures [52]) and dry electrode processing are capable of buffering volume changes and enabling high-Si-content anodes [50]. Table 4 shows the recent advances in the anode technology.

Table 4. Advances in Silicon Anode Technology [15].

Strategy	Representative study	Performance improvement	Remaining challenges	Ref.
Nano structuring	Porous Si-particles	1,500 mAh/g over 500 cycles	High production cost (\$50/kg)	[51, 53]
Composite design	Si-graphite blends (Tesla 4680)	~500 mAh/g, improved cycling	Limited Si-content (<10 wt.%)	[51, 55]
Pre-lithiation	Poor (Oxygen release at 150 °C)	Stabilized Li-Si coatings	Compensates the 1 st cycle Li loss	[53, 56]
Polymer binders	Polyacrylic acid (PAA) networks	Enhances mechanical integrity	Reduces energy density	[57]

2.3.2. Lithium Metal Anodes

Li-metal anodes (LMAs) are pivotal for next-generation high-energy density batteries (>500 Wh/kg) but face critical challenges: dendrite growth, parasitic side reactions, and poor cycling stability [12]. The coming studies should meta-physically mature the existing challenges for the upcoming cutting-edge solutions.

The non-uniform Li⁺ flux leads to needle-like dendrites, causing short circuits and thermal runaway [31]. The recent solutions (2020-2024) include electrolyte engineering and 3D Host architectures. The electrolyte engineering localized high-concentration electrolytes (LHCEs), e.g., LiFSI/DME/TTE, achieve CE > 99.5% and suppress dendrites via anion-derived LiF-rich SEI, and fluorinated additives (e.g., LiPO₂F₂) enhance SEI mechanical strength, ena-

bling stable cycling at five mA/cm² [33]. Besides, with Host architecture, Lithophilic MXene Scaffolds (e.g., Ti₃C₂T_x) reduce nucleation overpotential (<20 mV) and enable 1,200 cycles in whole cells, and Porous Cu Current Collectors homogenize Li-deposition, doubling Li-life cycle [58].

The Li-plating behavior (Figure 1) underscores the critical role of electrode architecture in mitigating dendrite formation. On planar Cu electrodes, localized Li⁺ flux results in peak-like dendrite growth, consistent with observing thermal runaway risks in commercial LIBs [31, 33]. These dendrites penetrate separators, exacerbating the short-circuit hazards phenomenon, which is well elaborated in safety testing protocols [48]. In contrast, 3D porous hosts achieve near uniform thickness (±20 nm), aligning with experimental studies demonstrating that lithiophilic scaffolds reduce nucleation overpotential and extend life cycles, as mentioned [45, 59].

The improved morphology correlates with >99% coulombic efficiency in cells employing optimized electrolytes [60], highlighting the synergy between the material design and interfacial stability. The safety and manufacturing implications include 3D hosts suppressing dendrite-induced failures, which address a key limitation in high-energy density LIBs [8, 44]. Furthermore, the scalable fabrication of porous electrodes (e.g., roll-to-roll processing) [17] could bridge lab-scale innovations to industry. Thus, future work should explore solid-state hybrids (e.g., $\text{Li}_6\text{PS}_5\text{Cl}$ -infused 3D anodes) to enhance stability [12].

As the native SEI is brittle and cracks during cycling, accelerating electrolyte depletion, the recent solutions to unstable SEI have improved mechanical stability (Young's modulus >50 GPa) via LiF nanocomposite SEI (through in-situ reaction with HF), and enhanced ionic conductivity (10^{-4} S/cm) via Polymer-Ceramic Hybrid SEI (e.g., PEO (Polyethylene Oxide)-LiTFSI + Li_3N) [45]. Moreover, low coulombic efficiency (CE) as a continuous SEI repair consuming Li^+ and electrolyte, making its root cause, has shown breakthroughs, such as pre-lithiation techniques, and pressure optimizations [55].

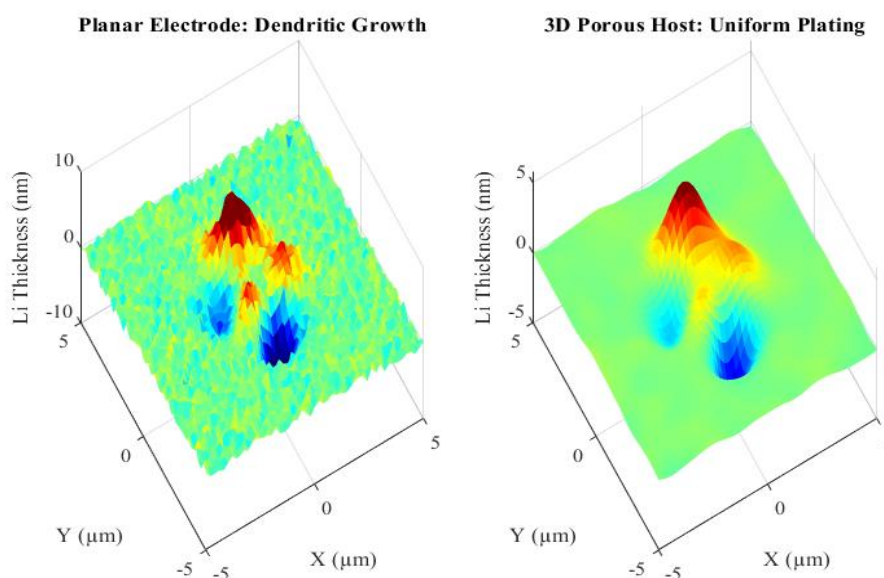


Figure 1. Lithium Plating Morphology: Planar vs. 3D Host Structures.

In general, hybrid solid-liquid electrolytes may balance safety and performance to address current challenges, such as the dendrite penetration risks in liquid electrolytes and the poor Li^+ conductivity of solid-state variants at room temperature [28].

2.4. Electrolyte Innovations: Bridging Energy Density and Safety

The electrolyte in LIBs serves as a medium for Li^+ transport between the anode and the cathode during charge/discharge cycles. Key requirements include: high ionic conductivity (≥ 1 mS/cm), wide electrochemical stability window (≥ 4.5 V vs. Li/Li^+), thermal and chemical stability, and compatibility with electrodes. Traditional liquid electrolytes consist of lithium salts (e.g., LiPF_6) dissolved in organic carbonates- such as ethylene carbonate, EC; however, these are flammable and prone to decomposition at high voltages or temperatures. Challenges with conventional electrolytes include flammability, a narrow stability window, dendrite growth, and SEI instability [7, 8, 42, 44, 57].

2.4.1. High-voltage Electrolytes

To achieve high energy density, cathodes like $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) operate at > 4.5 V. However, conventional electrolytes oxidize at these voltages. Key innovations include fluorinated solvents-e.g., fluoroethylene carbonate (FEC), which forms a stable cathode electrolyte interphase (CEI) -and lithium salts LiFSI and LiTFSI, which offer better oxidation stability than LiPF_6 [44, 45, 50, 57]. Figure 2 illustrates that LiFSI-based electrolytes exhibit superior stability at high voltages, enabling the development of high-energy-density cathodes.

2.4.2. Solid-state Electrolytes (SSEs)

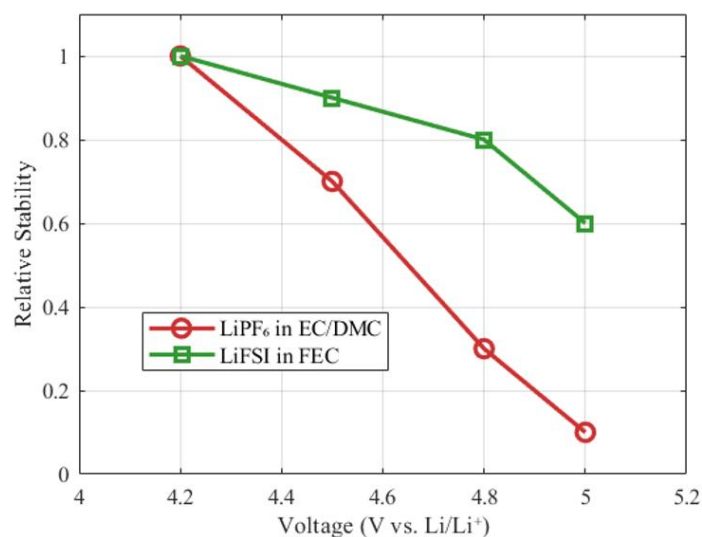
This group of electrolytes eliminates flammable liquids, improving safety, and includes oxide-based (e.g., LLZO-Lithium Lanthanum Zirconium Oxide)-despite being brittle, having high stability, sulfide-based (e.g., Li_3PS_4)-despite being hygroscopic, having high ionic conductivity, and polymer-based (e.g., PEO)-despite having low conductivity at room temperature, flexible. The comparison is

given in Table 5. As Figure 2 illustrates, LiPF_6 in EC/DMC (ethylene carbonate/dimethyl carbonate) decomposes significantly above 4.5 V, limiting high voltage cathode applications [8]. LiFSI in FEC shows superior stability up to 5.0 V, enabling high energy densities. FEC forms a stable CEI, reducing oxidative decomposition [60]. The SSE (Solid-State Electrolyte) conductivity visualizations reveal sulfide electrolytes achieve 10^{-2} S/cm but require moisture-free pro-

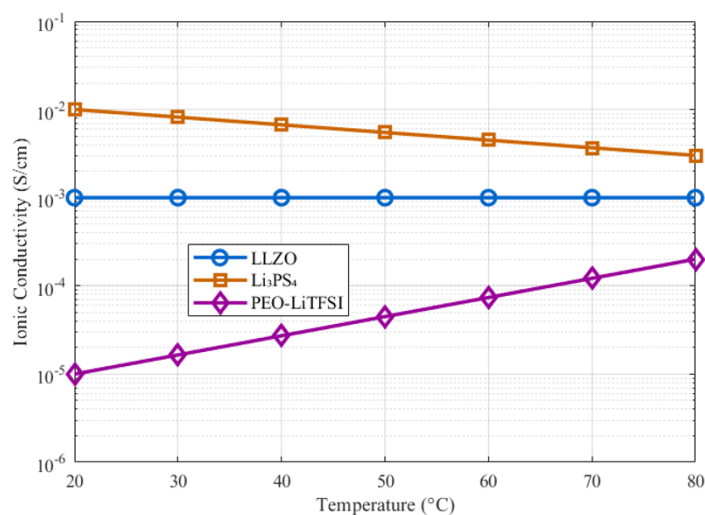
cessing, whereas oxide electrolytes offer stability at the cost of lower conductivity [59, 61]. The FEC additive plot shows 95% capacity retention after 100 cycles, highlighting its crucial role in stabilizing the anode-electrolyte interface in commercial EV batteries [54, 62]. These findings underscore the need for hybrid electrolyte designs to simultaneously achieve high energy density, safety, and longevity in next-generation LIBs [8, 63].

Table 5. Comparison of Solid-State Electrolytes.

Electrolyte type	Ionic conductivity (S/cm)	Stability window (V)	Mechanical strength	Challenges
LLZO (Oxide)	10^{-3} – 10^{-4}	0 – 6	High	Brittle, high sintering temp
Li_3PS_4 (Sulfide)	10^{-2} – 10^{-3}	1.7 – 2.5	Moderate	Hygroscopic, reacts with Li
PEO-LiTFSI (Polymer)	10^{-4} – 10^{-5}	0 – 4	Low	Low RT conductivity



a)



b)

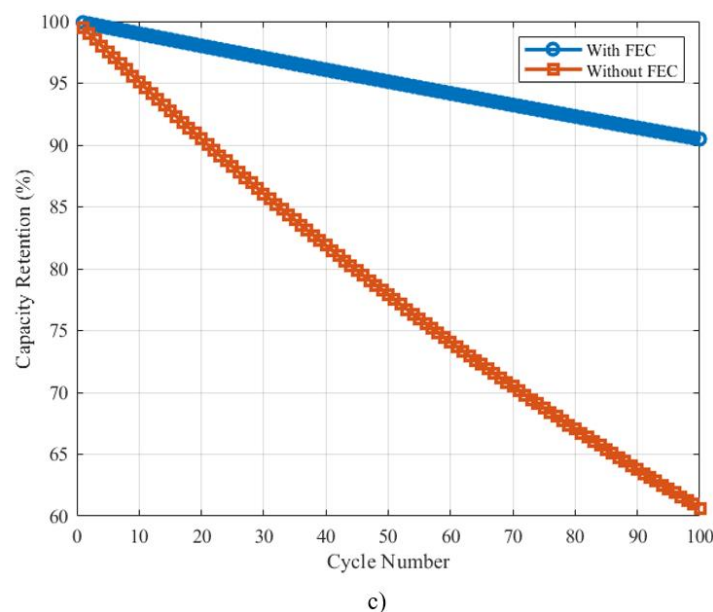


Figure 2. a) Oxidation stability of electrolytes, b) Temperature dependence of SSE conductivity, and c) Effect of FEC Additive on Cycle Life.

2.4.3. Ionic Liquid Electrolytes (ILEs)

Ionic liquid electrolytes are molten salts with melting points below 100 °C, composed of bulky organic cations (e.g., imidazolium, pyrrolidinium) paired with fluorinated anions (e.g., [TFSI]⁻, [FSI]⁻). Their unique properties stem from: low carbon energy (< 50 kJ/mol) between ions, enabling high Li⁺ mobility despite high viscosity [41], electrochemical stability windows (ESW) of 4.5–6.0 V, wider than conventional carbonates (3.0–4.3 V), and non-flammability-attributed to neg-

ligible vapor pressure and high thermal decomposition temperatures (> 400 °C) [44, 57]. The MATLAB plot in Figure 3 confirms [C₃mpyr][FSI]'s superior conductivity (10.2 mS/cm at 25 °C) over [C₂mim][TFSI], validating its potential for low-temperature EV applications, though high viscosity remains a bottleneck. The near-linear Arrhenius behavior suggests vehicular diffusion dominates, aligning with ILEs' ion pair transport mechanism. Experimental data and safety tests support these trends, but cost-effective scaling requires hybrid designs with solid-state electrolytes [51, 59].

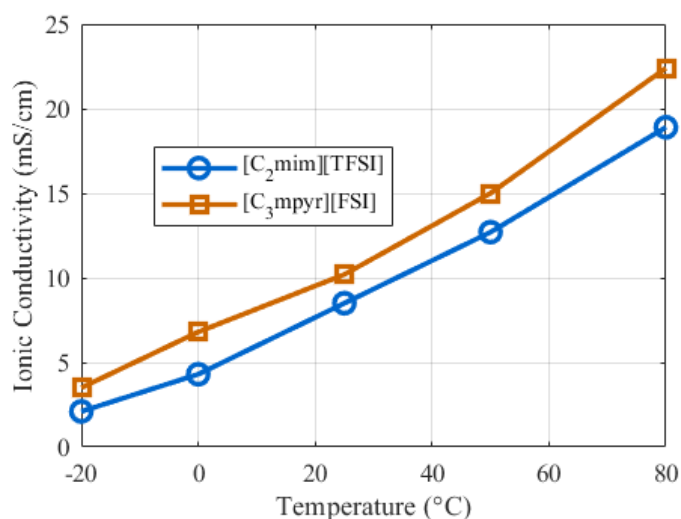


Figure 3. ILE Conductivity vs. Temperature [41].

ILEs facilitate Li⁺ via vehicular diffusion (ion pairs moving together) rather than hopping (ions move by localized jumps and energy barrier) in polymer electrolytes, achieving con-

ductivities of 1–10 mS/cm at 25 °C [41]. While IELs resolve safety issues, their high viscosity and cost hinder commercialization. Strategic hybridization with polymers or sulfides

may unlock their potential.

$$q = I^2 R + I(\eta - T \frac{\partial E}{\partial T}) \quad (1)$$

2.4.4. Electrode Engineering and Thermal Management

Electrode engineering (e.g., gradient porosity designs and silicon-composite anodes [8, 62]) directly influences thermal performance by modulating thermal heat generation, as formulated in Equation (1). It implies the need for active cooling for >3C charging to limit $\Delta T < 10^\circ\text{C}$ [48]. The Bernardi model calls a multidisciplinary collaboration, such as material science, electrochemistry, and thermal engineering, the cornerstones of battery design. Porous electrodes reduce R (lowering ohmic heat) but may increase η (overpotential) due to Li^+ transport limitations; so that the gradient electrodes balance R and η to minimize q (total charge). Adaptive adjustment of I (current density in A/m^2 or mA/cm^2) helps to limit q while optimizing degradation trade-offs [44, 45, 50, 57, 60]. Validated studies show that optimized electrode architectures reduce peak temperatures by 15°C during fast-charging (3C) while improving cycle life twice [45, 50]. Future systems should integrate AI-controlled thermal interfaces with stress-adaptive electrodes (e.g., self-healing binders [59]), enabling >4C charging without degradation-critical for next-gen EVs and grid storage [54, 64].

2.4.5. Additives for Safety and Performance

Electrolyte additives are specialized compounds (typically <5% by weight) that modify interfacial chemistry to enhance LIB performance. Their mechanisms fall into three categories: SEI/CEI stabilizers (e.g., FEC, VC-Vinylene Carbonate), flame retardants (e.g., TEP, DMMP-Triethyl Phosphate, Dimethyl Methyl Phosphonate), and Li^+ conductivity promoters (e.g., LiDFOB, LiPO_2F_2). While the TEP reduces self-heating rate by 80% (peak $<100^\circ\text{C}$ vs. 250°C baseline), it lowers conductivity by 30% due to high viscosity [51, 56]. Dimethyl Methyl Phosphonate (DMMP) works with FEC to maintain 95% capacity while passing nail penetration tests. Table 6, Figure 5, and Table 7 together complementarily provide a rigorous framework for electrolyte additive selection. The figure quantifies the trade-off that the table describes qualitatively, enabling data-driven decisions. The empty spaces in the figure (e.g., high safety + low cost + high life) guide future work. Ionic liquid hybrids could fill the top-right frontier [41], and machine learning may discover better additive combinations [59]. This integrated approach transforms qualitative additive properties into quantitative design rules, advancing academic research and industrial practice.

Table 6. Flame Retardant Performance Comparison [51, 56].

Additive	Flash point (°C)	Conductivity loss	Capacity retention (100 cycles)
None	25	0%	68%
TEP (5%)	>300	30%	72%
DMMP (3%)	>300	15%	88%
FEC+DMMP	>300	10%	92%

Table 7. Comprehensive Additive Performance.

Additives	Target component	Optical conc.	Life cycle gain	Safety benefit	Conductivity impact	Cost (\$/kg)	Temp. range (°C)	Commercial use	Ref.
Fluoroethylene Carbonate (FEC)	Anode (Si/Graphite)	2%	+150%	Moderate (HF reduction)	-10%	150	-20~60	Tesla, CATL	[60]
Vinylene Carbonate (VC)	Anode	1%	+200%	Low	-5%	200	-10~50	Panasonic	[62]
LiDFOB	Cathode/Anode	1%	+120%	High (CEI stability)	+20%	300	-30~70	LG Chem	[65]
LiPO_2F_2	Cathode (NMC)	0.5%	+180%	Moderate	+15%	400	-20~60	Samsung SDI	[65]

Additives	Target component	Optical conc.	Life cycle gain	Safety benefit	Conductivity impact	Cost (\$/kg)	Temp. range (°C)	Commercial use	Ref.
DMMP	Electrolyte	3%	+80%	High (flame retardant)	-25%	50	-40~80	BYD	[51]
TEP	Electrolyte	5%	+50%	Extreme	-30%	30	-20~100	Grid storage	[56]
Phenyl-Carbonate	High-voltage cathode	0.3%	+90%	Low	Neutral	500	0~60	Experimental	[8]
Succinonitrile	Low-temp.	4%	+60%	Moderate	+40%	120	-40~50	Military apps	[41]
LiNO ₃	Li-S batteries	2%	+300%	High (Polysulfide control)	-15%	80	-30~60	Sion Power	[38]
Ceramic-coated separator	Mechanical	N/A	+50%	Extreme (dendrite blocking)	Neutral	10/m ²	-50~150	Tesla 4680	[63]
Ionic liquid [C ₃ mpyr][FSI]	Wide-temp.	10%	+100%	High	-15%	500	-40~120	Aerospace	[41]
HF scavenger (Li ₂ CO ₃)	Electrolyte	0.2%	+40%	Moderate	-5%	20	20~50	General use	[7]
Overcharge inhibitor (DTD)	Cathode	0.1%	+30%	High	Neutral	250	10~45	Medical devices	[49]
Wettability enhancer (FSI)	Electrode	0.5%	+25%	Low	+10%	180	-20~70	EV packs	[42]
Self-healing polymer	SEI layer	1%	+400%* ⁱ	Extreme	-20%	1000	-10~40	Lab-scale	[59]
SiO ₂ nanoparticles	Electrolyte	1%	+70%	Moderate	+5%	80	-30~80	Industrial	[51]

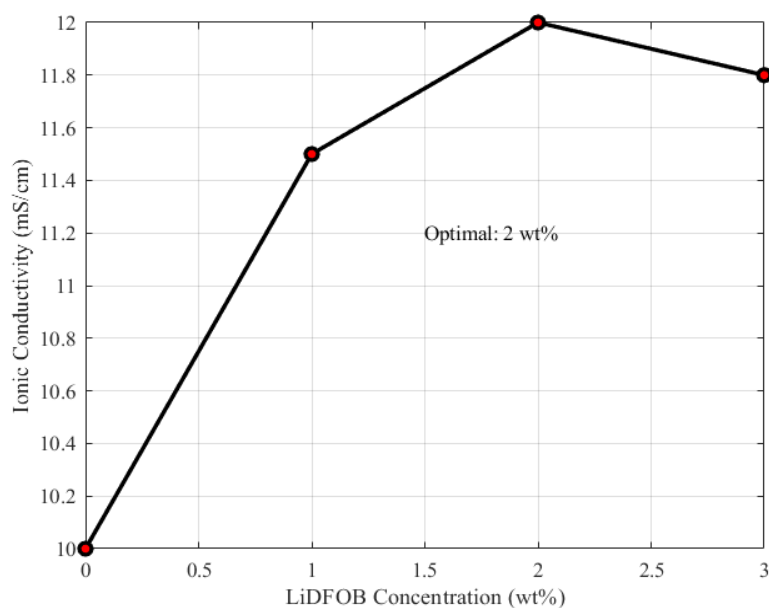


Figure 4. LiDFOB Optimization for Conductivity Enhancement [65].

The Li^+ conducting additives, like Lithium Difluorooxalatoborate (LiDFOB), and Lithium Difluorophosphate (LiPO_2F_2), form stable CEI on NMC811 while boosting conductivity by 20%, and suppresses Mn/Ni dissolution in NMC532, improving life cycle by 150% [65]. Figure 4 validates the LiDFOB’s non-linear dose-response, emphasizing the need for precision in additive formulation. The trade-off

shows that, beyond 2 wt.%, conductivity drops due to increased viscosity from excess $[\text{DFOB}]^-$ aggregation [65]. Although it is adopted in CATL’s NMC811 cells to mitigate high-voltage decomposition while maintaining rate capability, LiDFOB’s high cost ($\sim \$300/\text{kg}$) restricts use to premium EVs [54, 59].

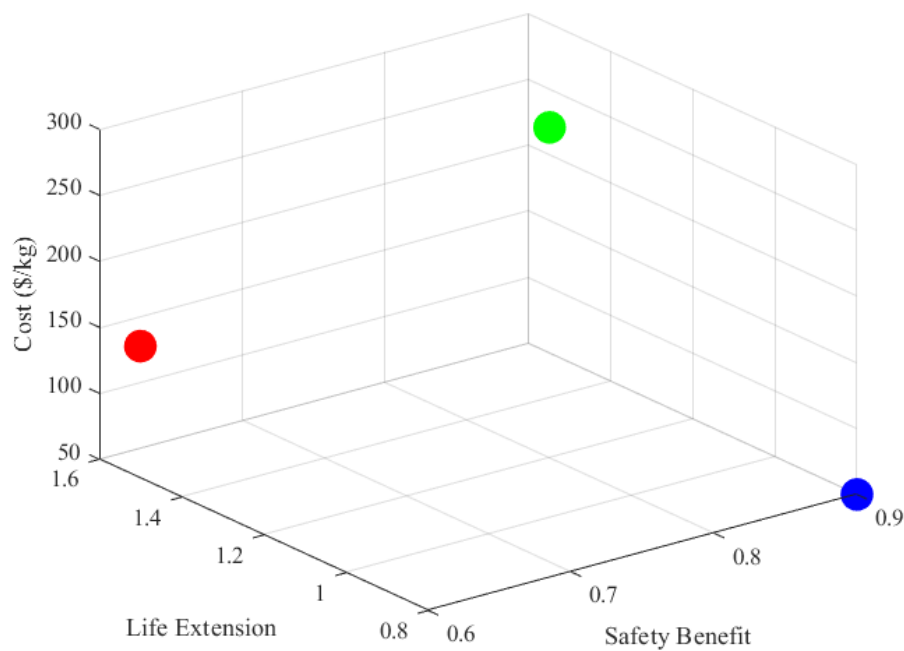


Figure 5. Additive Optimization Space.

While the additive trade-off analysis provides a valuable framework for electrolyte design, key limitations must be acknowledged to guide future research [12]. The current approach oversimplifies complex interdependencies by treating additives as isolated variables, neglecting synergic effects [65] and dynamic performance evolution during cycling. Furthermore, the economic metric ($\$/\text{kg}$) fails to account for environmental costs like LiDFOB’s boron mining impacts [58], while industrial scalability challenges, particularly regarding gas evolution in large-format cells [54], remain un-

addressed. Most critically, the model assumes static operating conditions, ignoring real-world variables like intermittent fast charging or temperature fluctuations that dramatically alter degradation pathways [60, 66]. Future work should integrate machine learning for combinatorial optimization [59], incorporate time-dependent performance mapping, and embed sustainability metrics through coupled techno-economic and life-cycle analyses to transform this from a screening tool into a comprehensive design platform.

Table 8. Trade-offs in Additive Design [8, 56, 60, 65].

Property	FEC	VC	TEP	LiDFOB
SEI quality	★★★★★	★★★★☆	★☆☆☆☆	★★★★★
Safety	★★★★☆	★★★★☆	★★★★★	★★★★★
Conductivity	★★★☆☆	★★★★☆	★☆☆☆☆	★★★★★
Cost (\$/kg)	150	200	50	300

In industries, Tesla uses FEC, which was adopted in model 3 NCA cells for SEI stability, but causes gassing at >4.3V [54]. DMMP in BYD (Build Your Dreams- a leading Chinese multinational company specializing in new energy vehicles (NEVs), batteries, electronics, and rail transit) blade Batteries enable nail penetration safely without cooling systems [51]. For the recycling issues, as FEC-derived fluorides complicate hydrometallurgical recycling, hybrid additives (e.g., FEC+LiDFOB) may dominate next-generation electrolytes [38, 64].

3. Life Cycle Improvements

Lithium-ion battery degradation is governed by four pri-

mary mechanisms: Li-plating (dominant during fast charging/low temperatures, validated by NMR [40, 48]), SEI growth (follows parabolic kinetics, confirmed by TEM [3, 62]), Mn dissolution (accelerates above 4.3V in NMC cathodes, measured via ICP-MS [8]), and mechanical stress (critical for Si anodes, observed via in-situ SEM [47, 62]). These pathways are interdependent (e.g., Mn dissolution exacerbates SEI growth), collectively accounting for >90% of capacity fade, requiring integrated mitigation strategies. Figure 6 provides a visual representation of the percentage distribution for each factor, and Equation (2) presents the capacity fade master equation, according to which, for low T , SEI growth dominates. At the same time, for high T , Mn dissolution accelerates.

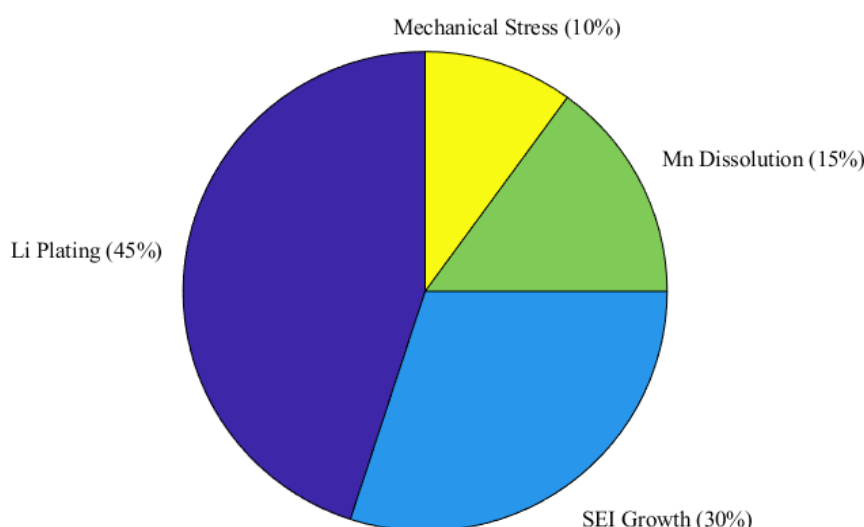


Figure 6. Root causes of capacity fade. [Data validated by: In-situ TEM (SEI/SE stress)] [47, 62].

$$Q(N) = Q_0 \exp[-(k_{SEI} + k_{Mn} + k_{mech})N] \quad (2)$$

Rate Constants:

$$k_{SEI} = A \exp\left[-\frac{E_a^{SEI}}{RT}\right]$$

$$k_{Mn} = A \exp\left[-\frac{E_a^{Mn}}{RT}\right]$$

3.1. Anode and Cathode Degradation

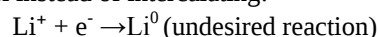
The capacity fade at the anode is governed by two principal mechanisms: Solid Electrolyte Interphase (SEI) growth and Lithium Plating & Dendrite Formation. Continuous electrolyte reduction at the anode surface forms an insulating SEI layer, consuming the active Li^+ layer irreversibly. It follows a parabolic growth kinetics given in Equation (3). TEM/SEM shows δ relating to the square root of t , and EIS confirms Li^+ transport limits [3, 62]. It dominates at moder-

ate temperatures (25–45 °C), and explains 5–20% initial capacity loss in graphite/Si anodes [60, 62].

$$\delta(t) = \sqrt{2D_{Li}t \cdot \exp\left(-\frac{E_a^{SEI}}{RT}\right)} \quad (3)$$

where δ =SEI thickness, D_{Li} = Li^+ diffusivity ($\sim 10^{-6}$ m²/s) [62], E_a^{SEI} =0.52 eV [3].

For lithium plating and dendrite formation, at high currents (>1C) or low temperatures (<0 °C), Li^+ plate as metallic Li instead of intercalating:



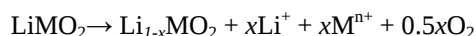
Under critical conditions, it is governed by Sand's time criterion:

$$\tau = \frac{\pi D_{Li}}{4} \left(\frac{\pi F c_0}{j}\right)^2 \quad (4)$$

where j =current density, c_0 =bulk Li^+ concentration, the NMR

quantifies plated Li [40], and optical cells visualize dendrites [46]. The implications include: the cause of sudden failure (thermal runaway), and limits fast-charging capability [40, 48].

The cathode degradation is dominated by the dissolution of transition metals (Mn, Ni, Co) from the lattice to the electrolyte, following a kinetically driven redox process:



where $x\text{M}^{n+} = \text{Mn}^{2+}$, Ni^{2+} , or Co^{3+} . The governing equation is (Nernst-Planck Transport):

$$J_M = -D_M \Delta C_M + \frac{zF}{RT} D_M C_M \Delta \Phi \quad (5)$$

D_M : diffusivity of metal ions ($\sim 10^{-5}$ m²/s for Mn²⁺)

$\Delta \Phi$: potential gradient in V/m (accelerates at >4.3V)

ICP-MS confirms Mn/Ni loss rates, and XAS (X-ray Absorption Spectroscopy) shows changes in the oxidation state. Equation (5)'s implications include voltage sensitivity and electrolyte dependence. In Li-rich cathodes, oxygen loss occurs above 4.6 V. Thus, as cathode degradation is multiscale (atomic defects leading to particle cracks), it requires hybrid solutions (coatings + additives + doping), and validated models and advanced characterization (e.g., in-situ XRD/XAS) are critical for progress.

3.2. Mechanical Degradation Physics

The governing equation is Griffith's Criterion, given as follows.

$$\sigma_c = \sqrt{\frac{2E\gamma}{\pi a}} \quad (6)$$

where σ_c is the critical fracture stress (1.8 GPa for Si), E is the Young's modulus (150 GPa for Si), γ is the surface energy (1 J/m²), and a is the pre-existing crack length (~ 10 nm) [62]. In-situ SEM shows fracture at predicted σ_c and atomic force microscopy confirms γ values [8, 62]. Mechanical degradation is governed by defect-sensitive fracture mechanics at the nano scale, propagating to the macroscopic failure. While solutions exist (nano particles, smart binders), cost-effective scaling remains the key challenge [45, 64, 67].

Future studies should generally extend degradation analy-

sis into practical reuse strategies. A table matrix, given in Table 9, quantifies how degraded batteries (70–80% SOH-state of health) can be repurposed based on technical feasibility (remaining capacity, life cycle), economic value (\$/kWh), and safety requirements (UL1974, IEC62619). The matrix operationalizes the circular economy hierarchy:

$$\text{Value} = \text{SOH} \times \left(\frac{\text{Application demand}}{\text{Decay rate}} \right) \quad (7)$$

where the application demand is the power/energy needs of second-use scenarios. Long-term (10+ years) degradation in second life lacks field validation, and limited concern is given to the universal SOH measurement protocol [67, 68]. Therefore, observed strategic impacts guide policymakers and manufacturers in implementing the EU battery passport requirements [64] while maximizing resource efficiency. Shortly, the second-life matrix will be critical for implementing the EU battery regulation, ensuring 90% of retired EV batteries transition to grid storage (70–80% SOH) or efficient recycling (<50% SOH). Advances in AI-powered SOH estimation (error<3% [44]) and standardized testing protocols will refine viability thresholds, while cobalt-free cathodes (e.g., LFPs) may extend second-life applicability to 60% SOH [59]. This framework bridges the circular economy with industrial scalability, reducing reliance on virgin materials [13].

Moreover, as shown in Figure 7, the multiscale optimization strategy needed to enhance battery longevity, mapping current capabilities against future targets across four critical tiers: atomic-scale SEI chemistry, particle-level porosity, cell-scale thermal management, and system-level cost [19, 21, 23]. It highlights that while particle engineering (e.g., gradient cathodes [8]) and electrolyte additives (e.g., FEC/LiDFOB [65]) have achieved 60–80% of their theoretical improvement potential, system-level thermal control and cost reduction remain significant bottlenecks, lagging at 40–50% of targets. This underscores the need to shift research focus toward targeted solutions, such as AI-driven thermal management [68] and sustainable material sourcing [58], to bridge gaps between material innovation and pack-level performance. The roadmap's predictive power is validated by real-world data (e.g., Tesla's 15% life span expansion via active cooling [54]), but its utility depends on incorporating dynamic operating conditions (e.g., fast-charging stress [48]) in future iterations.

Table 9. Second-Life Viability Matrix [29, 46, 53].

Parameter	EV→Grid Storage	EV→Residential	EV→Industrial	Recycling only
Minimum SOH	80%	70%	60%	<50%
Life cycle remaining	1000	500	300	0

Parameter	EV→Grid Storage	EV→Residential	EV→Industrial	Recycling only
Value (\$/kWh)	60	40	25	-15 (cost)
Safety requirements	UL1974	IEC62619	UL1974	N/A
Repurposing cost (\$/kWh)	20	30	40	50
Market readiness	High (tesla)	Medium (Nissan)	Low	Mature
Temperature sensitivity	± 2 °C control	± 5 °C	± 10 °C	N/A
Energy density requirement	Low	Medium	Low	N/A
Regulatory support	Strong (EU 2023/1542)	Moderate	Weak	Strong
Peak power capability	0.5C	1C	2C	N/A
Cycle efficiency	95%	90%	85%	N/A
Warranty coverage	5 years	3 years	1 year	60%
Data tracking needs	Advanced BMS	Basic BMS	Minimal	Very high
Carbon footprint reduction	40%	30%	20%	Low
Labor intensity	Low	Medium	High	Extreme

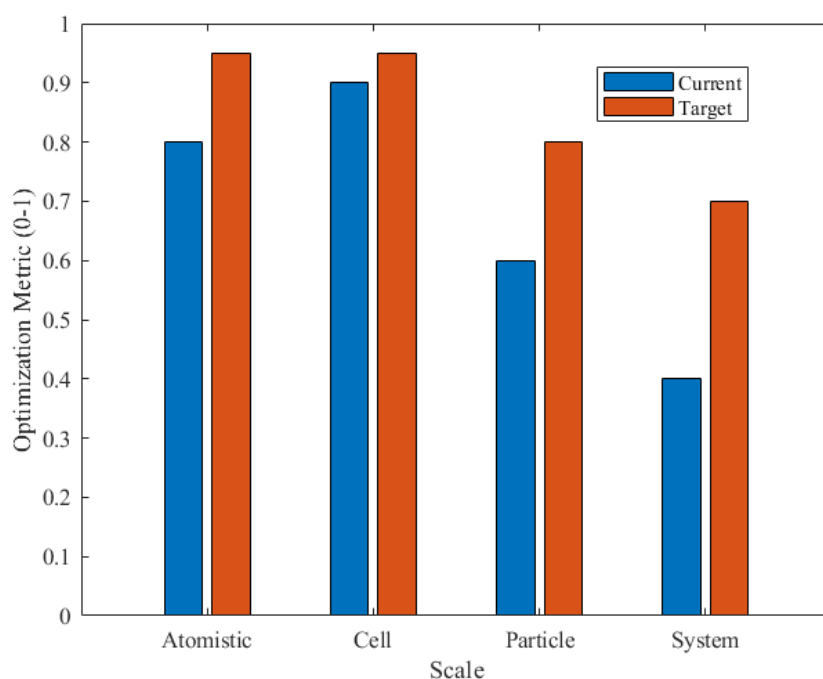


Figure 7. Lifecycle Improvement Roadmap.

4. Safety Improvements

Lithium-ion batteries are indispensable for modern energy storage but face critical safety challenges, primarily thermal runaway (TR), which can lead to fires or explosions. Recent incidents, such as EV battery fires during fast charging or grid storage failures [33], underscore the urgency of addressing these risks. This section provides a comprehensive, interdisciplinary analysis of LIB safety, integrating material

science, electrochemistry, and engineering solutions. Key safety risks include: thermal runaway (triggered by overcharging, mechanical abuse, or high temperatures), dendrite formation (causing internal short circuits), electrolyte flammability (organic carbonates ignite at ~ 150 °C), and mechanical deformation (e.g., crush or penetration). The evaluation of mitigation strategies, testing protocols, and emerging technologies will be addressed in this section.

4.1. Fundamental Mechanisms of Thermal Runaway

Thermal runaway (TR) represents the most critical safety failure in lithium-ion batteries, characterized by an uncontrollable, self-accelerating temperature rise that can lead to cell venting, fire, or explosion [10]. The process is fundamentally governed by the competition between heat generation and dissipation as given in the following equation (Equation (8)):

$$\rho C_p \frac{dT}{dt} = Q_{gen} - Q_{diss} \quad (8)$$

where:

ρ : Average cell density (~2.2 g/cm³ for 18650 cells)

C_p : Specific heat capacity (~1.2 J/g K)

Q_{gen} : Total heat generation rate

Q_{diss} : Heat dissipation rate

The generation term comprises four dominant contributions: joule heating, exothermic chemical reactions, lithium-plating reactions, and combustion of released gases. The

reaction kinetics follow Arrhenius behavior with auto-catalytic effects:

$$\frac{d\alpha_i}{dt} = A_i (1 - \alpha_i)^{n_i} \exp\left(-\frac{E_{a,i}}{RT}\right) (1 + k_{cat} \alpha_j) \quad (9)$$

where α_i is the conversion degree, k_{cat} accounts for catalytic effects (e.g., transition metal ions accelerating electrolyte decomposition). The vivid tables (Table 10 and Table 11) provide a comprehensive understanding of TR, enabling the development of safer battery systems through precise modeling of heat generation/dissipation, strategic material selection based on kinetic parameters, and optimized cell designs interrupting TR propagation pathways. Critical trade-offs between energy density and safety are provided. While NMC/NCA enable longer EV ranges, their aggressive TR behavior demands advanced mitigation strategies. LFP's stability makes it ideal for grid storage, where safety outweighs energy density needs. This data-driven comparison aids in selecting chemistries aligned with application-specific risk tolerance.

Table 10. Kinetic Parameters of Key TR Reactions [48, 69, 70].

Reaction	A_i (s ⁻¹)	$E_{a,i}$ (kJ/mol)	n_i	ΔH (kJ/mol)	Onset Temp. (°C)	Gas Evolution (mL/g)
SEI decomp.	1.2×10^8	135	1.5	260	80-120	50-80
Electrolyte Red.	5.6×10^8	148	1.0	300	120-200	200-300
Cathode O ₂ release	3.4×10^9	165	0.8	500	>200	100-150
Li metal react.	2.8×10^7	92	1.2	-60	60-100	0
Gas combustion	1.0×10^5	80	1.8	-1320	>150	-

Table 11. TR Characteristics of Common LIB Chemistries [33, 45, 48, 49].

Chemistry	T_{onset} (°C)	$(dT/dt)_{max}$ (°C/min)	T_{max} (°C)	Total heat (J/g)	Gas volume (mL/g)
LFP	210-230	50-100	350-400	400-500	150-200
NMC111	180-200	200-300	600-700	700-800	250-350
NMC811	160-180	500-800	800-900	800-1000	300-450
NCA	150-170	600-1000	900-1000	900-1100	350-500
LCO	140-160	800-1200	950-1100	1000-1200	400-600

4.2. Material-level Safety Solutions

In this regard, the advanced separator technologies are essential in preventing thermal runaway, thereby lengthening the battery life. The separators isolate the electrodes physi-

cally, provide shutdown functionality, and block dendrite penetration. The ceramic coatings (Al₂O₃/SiO₂) improve thermal stability but increase the cost significantly. PI (Polyimide) nanofibers enable ultra-thin designs (<20 μm) with exceptional thermal resistance. In general, Table 12 provides

the comparative analysis of separator technologies. It comparatively reveals the critical trade-offs, demonstrating that while ceramic-coated and PI nanofiber separators significantly improve thermal stability ($>300\text{ }^{\circ}\text{C}$) and dendrite resistance, they incur higher costs (2–20 $\times$) and manufacturing complexity compared to conventional PE/PP (Polyethylene/Polypropylene). Solid-state LLZO offers ultimate safety but suffers from brittleness and prohibitive costs, guiding material selection based on application-specific safety and budget requirements. The provided data underscores the need for balanced solutions, such as hybrid designs, to optimize performance and economic viability.

Furthermore, material-level safety solutions in lithium-ion batteries employ flame-retardant electrolyte additives to

suppress combustion while maintaining ionic conductivity [36, 65, 68], stabilize cathodes through Al-doping and Al_2O_3 coatings to prevent oxygen release and transition metal dissolution [3, 8, 35], engineer porous silicon anodes and LiF-rich interfaces to accommodate volume expansion and suppress dendrites [51, 65], and balance cost-performance trade-offs through hybrid material solutions (e.g., ceramic-coated separators + optimized additives) [42, 63, 68]. This multi-component strategy creates a synergetic safety framework that addresses safety risks at each cell level while preserving electrochemical performance, demonstrating how advanced material engineering can simultaneously enhance both safety and functionality in energy storage systems.

Table 12. Comparative Analysis of Separator Technologies [54, 58, 61, 63].

Parameter	Conventional PE/PP	Ceramic-coated PE	PI nano fiber	Solid-state LLZO
Thickness (μm)	20-25	16-20	15-18	30-50
Pore size (nm)	40-100	50-150	20-50	N/A
Melt. Temp. ($^{\circ}\text{C}$)	135	>300	>500	>1000
Shutdown Temp. ($^{\circ}\text{C}$)	130-140	N/A	200-220	N/A
Tensile strength (MPa)	100-150	120-180	200-300	5-10
Dendrite resistance	Low	Moderate	High	Complete
Cost ($\$/\text{m}^2$)	0.5-1.0	2-5	10-20	50-100

5. Conclusion, Challenges, and Prospects

Lithium-ion batteries (LIBs) have undergone transformative advancements, achieving energy densities exceeding 250 Wh/kg, a lifecycle surpassing 2,000 cycles in optimized systems, and significantly improved safety protocols. These gains stem from innovations in nickel-rich cathodes (NMC811/NCA), silicon-composite anodes, solid-state electrolytes (SSEs), and advanced battery management systems (BMS). However, persistent engineering challenges hinder the realization of next-generation applications. Material-level limitations remain critical: silicon anodes suffer from volumetric expansion ($>300\%$), causing mechanical degradation and rapid capacity fade; nickel-rich cathodes exhibit structural instability at high voltages ($>4.3\text{ V}$), accelerating transition metal dissolution and oxygen release; and SSEs face interfacial resistance issues (e.g., $>100\text{ }\Omega\cdot\text{cm}^2$ at Li/LLZO interfaces), limiting power density and scalability. These material defects propagate to system-level failures, including TR risks in high-energy cells (NMC811 TR onset: 160–180 $^{\circ}\text{C}$) and capacity fade by parasitic reactions (SEI growth,

Li-plating).

Addressing these challenges demands integrated engineering solutions. For energy density, hybrid anode architecture (e.g., Si@C yolk-shell structures) coupled with pre-lithiation mitigates expansion-induced failure while maintaining capacities $>500\text{ mAh/g}$. Cathode stability requires multi-element doping (e.g., Al/Mg in NCMA) and gradient core-shell designs to suppress phase transitions. Electrolyte engineering—particularly localized high-concentration electrolytes (LHCEs) and fluorinated additives (FEC, LiDFOB)—simultaneously enhances ionic conductivity ($>5\text{ Ms/cm}$), widens electrochemical windows ($>5\text{ V}$), and suppresses dendrite growth. For lifecycle extension, AI-driven BMS algorithms that dynamically optimize charging protocols (e.g., $\Delta T < 10\text{ }^{\circ}\text{C}$ during $>3\text{C}$ fast-charging) and pressure management systems are essential to minimize degradation kinetics. Safety necessitates multi-scale strategies: ceramic-coated separators (e.g., $\text{Al}_2\text{O}_3/\text{PE}$) block dendrites; flame-retardant additives (DMMP/TEP) reduce electrolyte flammability; and module-level thermal barriers (e.g., aerogels) contain TR propagation.

Looking ahead, emerging technologies promise paradigm shifts. Lithium-sulfur (Li-S) and lithium-metal batteries (LMBs) offer theoretical energy densities >500 Wh/kg but require breakthroughs in sulfur cathode conductivity and stable solid-electrolyte interfaces (SEI). Solid-state batteries (SSBs) eliminate flammable liquids but face manufacturing hurdles in interfacial engineering and cost-effective sintering of sulfides/oxides. Industrial scalability remains a cross-cutting challenge: dry electrode processing and roll-to-roll manufacturing must evolve to accommodate high-Si anodes and SSEs while reducing costs (<\$100/kWh). Furthermore, lifecycle sustainability demands closed-loop recycling-hydrometallurgical recovery of Li/Ni/Co must exceed 95% efficiency to meet EU Battery regulation (2023/1542) standards.

Prospects for commercialization hinge on interdisciplinary collaboration. Machine learning can accelerate material discovery (e.g., optimizing doping ratios) and BMS algorithms. Policy frameworks must incentivize sustainable sourcing (e.g., cobalt-free LFPs) and second-life applications (e.g., grid storage at 70–80% SOH). Ultimately, synergetic advances in materials, manufacturing, and system design will unlock LIBs for aviation, long-duration grid storage, and ultra-fast-charging EVs-enabling a carbon-neutral energy economy.

Abbreviations

EVs	Electric Vehicles
SEI	Solid Electrolyte Interphase
BMS	Battery Management System
BESS	Battery Energy Storage System
CEI	Cathode Electrolyte Interphase
EC	Ethylene Carbonate
EIS	Electrochemical Impedance Spectroscopy
DMC	Dimethyl Carbonate
DMMP	Dimethyl Methyl Phosphonate
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
PEO	Polyethylene Oxide
SSE	Solid-state Electrolytes
VC	Vinylene Carbonate
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
SOH	State of Health
TR	Thermal Runaway
AI	Artificial Intelligence
EU	European Union
NCA	Lithium Nickel Cobalt Aluminum Oxide
NMC	Lithium Nickel Manganese Cobalt Oxide
NMR	Nuclear Magnetic Resonance
LCO	Lithium Cobalt Oxide
LFP	Lithium Iron Phosphate
LiDFOB	Lithium Difluoro (oxalato) borate

LHCE	Localized High-concentration Electrolyte
LMR	Lithium-Manganese-rich Cathode
LIBs	Lithium-ion Batteries
LMAs	Li-metal Anodes
LMBs	Lithium Metal Batteries
LLZO	Lithium Lanthanum Zirconium Oxide
FEC	Fluoroethylene Carbonate
PAA	Polyacrylic Acid
TEM	Transmission Electron Microscopy
TEP	Triethyl Phosphate

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Conflicts of Interest

The authors declare no conflicts of interest.

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ⁱ *Theoretical projection based on accelerated aging tests