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# Back to the future: towards the realization of lithium metal batteries using liquid and solid electrolytes

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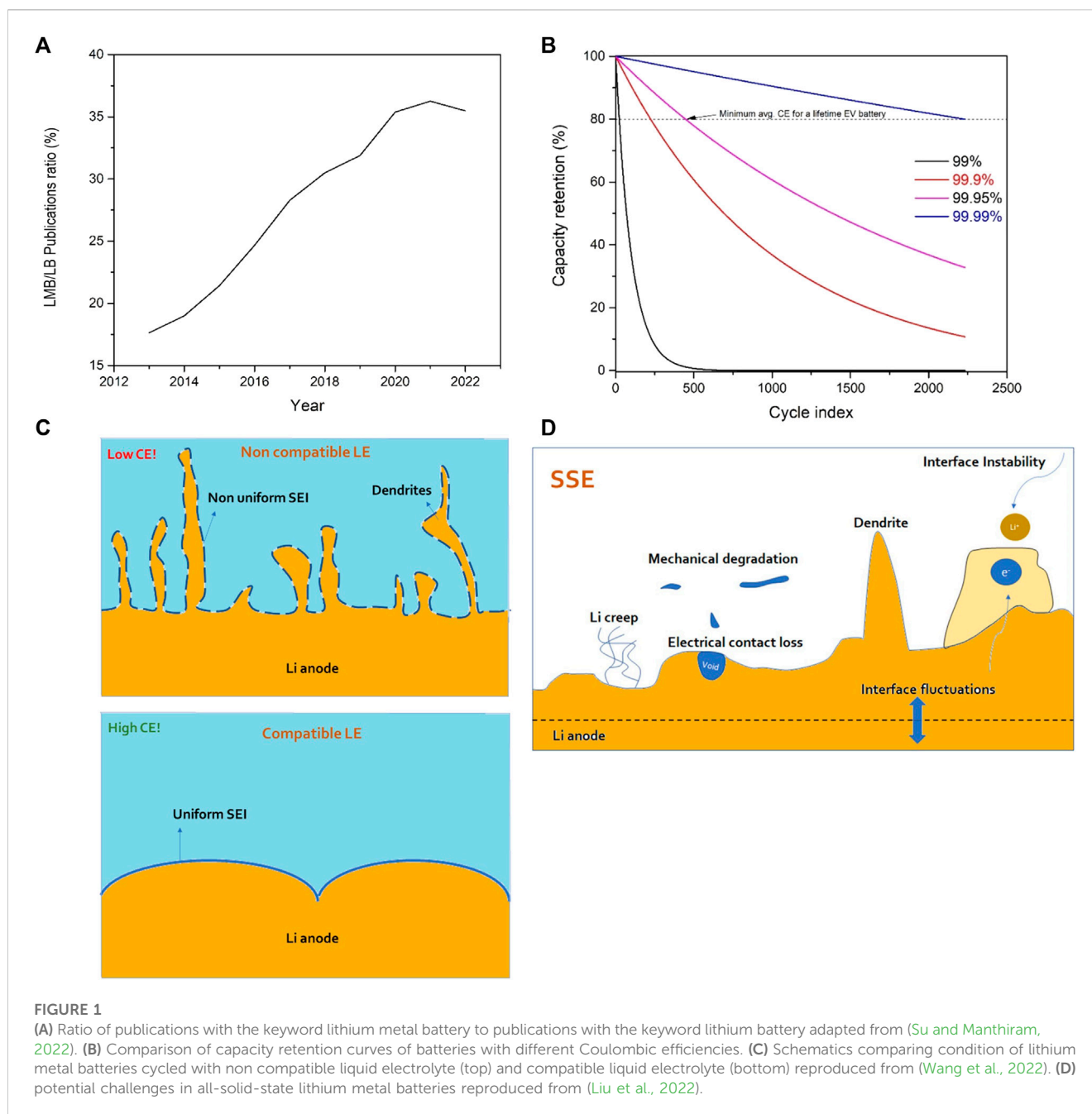
As the specific energy of traditional lithium-ion batteries (LIBs) approaches theoretical limits, the quest for alternatives intensifies. Lithium metal batteries (LMBs) stand out as a potential solution, promising substantially higher energy densities (~35% increase in specific energy and ~50% increase in energy density at the cell level). Historically, challenges with liquid electrolytes (LEs) in LMBs, such as dendrite growth and unstable solid electrolyte interphase (SEI) formation, led to skepticism about their compatibility and most of the focus was on solid-state electrolytes (SSEs) such as polymer electrolytes and recently inorganic electrolytes (oxides, sulphides halides). However, recent strides in LE engineering have repositioned LEs as viable candidates for LMBs, particularly with the strategic use of additives and the careful formulating of solvents. This review delves into the engineering of LEs for LMBs, highlighting their renewed potential and explores the realm of SSEs and report on the recent advancements in both fields. We aim to provide a comprehensive overview of the evolving landscape of LMB research.

## KEYWORDS

lithium anode, lithium metal batteries, additives, fluorinated additives, composite cathodes, catholyte, solid electrolyte, liquid electrolyte

## Introduction

Lithium-ion batteries (LIBs) have revolutionized the realms of portable electronics and electric vehicles, offering transformative power storage solutions for a technologically-driven society (Chu et al., 2016). Their widespread adoption was driven by the high energy density as well as efficiency and versatility they introduced, which was notably absent in the battery technologies that preceded them (Liu et al., 2019a). Yet, the insatiable demand for even higher energy density and efficiency reveals that the potential of LIBs is nearing its limit, especially with graphite-based anodes reaching their theoretical energy threshold (Lin et al., 2017). Lithium metal batteries (LMBs) emerged as a promising alternative, offering much higher specific capacities (Liu et al., 2017). They were, in fact, commercialized even before LIBs but were shelved due to notable safety concerns and limited cyclability (Lin et al., 2017). Their potential to usher in an era of batteries with unparalleled specific energy has been acknowledged, given their impressive specific capacity and low reduction potential (Liu et al., 2017). By replacing the graphite electrode with lithium metal, there's a projected ~35% increase in specific energy and ~50% increase in energy density at the cell level, outlining a



promising route to meet the US Department of Energy's (DOE) electric vehicle pack benchmarks of  $235 \text{ Wh kg}^{-1}$ ,  $500 \text{ Wh L}^{-1}$ , and a cost of  $125 \text{ US\$ kWh}^{-1}$  (Albertus et al., 2017). However, despite these compelling advantages, LMBs face significant challenges, such as the growth of dendrites, which not only shorten battery life but also pose serious safety threats (Albertus et al., 2017).

A crucial aspect of lithium batteries, both LIBs and LMBs, is the choice and stability of the electrolyte used. Historically, ether-based electrolytes dominated the landscape due to their reductive stability (Peled, 1979). However, with the advent of high-voltage cathodes, there was a noticeable shift. The changing dynamics required a shift from ether solvents to carbonate-based, moderate-concentration electrolytes to ensure compatibility (Amanchukwu et al., 2020). Although these aligned with high-voltage cathodes, they exhibited

instability when paired with lithium metal, leading to issues like dendritic growth and reduced cycle life (Qian et al., 2015).

Considering these developments and challenges, the past decade saw researchers pioneering strategies that enhanced electrolyte concentrations and opened doors to more stable electrolytes that could work seamlessly with lithium metal anodes and high-voltage cathodes. However, the quest for the ideal LMB is ongoing, as the performance of current LMBs still falls short of practical application benchmarks (Louli et al., 2020). Figure 1A demonstrates the increased interest in LMBs in recent literature by showcasing the ratio of publications containing the keyword 'lithium metal batteries' to publications containing the more general keyword 'lithium batteries' calculated from numbers provided by Manthiram et al. (Su and Manthiram, 2022). This mini review

will delve deeper into the forefront of battery research. Firstly, we will discuss recent advances in lithium electrolyte (LE) engineering, shedding light on the innovations that have enhanced battery performance and safety. Subsequently, we will explore the strides made in enabling solid-state lithium metal batteries (SSLMBs). [Figure 1C, D](#) show schematics that summarize the challenges within LE enabled LMBs and solid-state electrolytes (SSEs) enabled LMBs. Finally, we gaze into the horizon of electrochemical energy storage, outlining our envisioned future targets and practical considerations for LMBs. We will explore pathways, informed by current research trends and technological gaps, on how we might traverse the journey from present achievements to future aspirations.

## Liquid electrolyte lithium metal batteries

### High concentration electrolytes (HCEs)

The pursuit of enhancing electrolyte concentrations for superior battery performance can be traced back to LIB research from the mid-1980s ([Yamada and Yamada, 2015a](#); [Wang et al., 2022](#)). McKinnon and Dahn's 1985 discovery showcased how saturated LiAsF<sub>6</sub> in propylene carbonate (PC) successfully circumvented the co-intercalation of PC into ZrS<sub>2</sub> electrodes ([McKinnon and Dahn, 1985](#)). Subsequent works by Jeong et al. extended these findings, highlighting the efficacy of concentrated solvents like LiClO<sub>4</sub>, LiPF<sub>6</sub>, and LiBETI in PC to suppress co-intercalation into graphite anodes. ([Jeong et al., 2003](#); [Jeong et al., 2008a](#)). Recently, Yamada et al. successfully extended their application to alternative solvents such as dimethyl sulfoxide (DMSO) and acetonitrile (AN), complemented with 3.2–4 M LiTFSI as the salt ([Yamada et al., 2010](#)). These high concentration electrolytes (HCEs) not only curtailed co-intercalation, but also significantly enhanced the electrolyte's reductive stability ([Yamada et al., 2014](#)). Additionally, Suo et al., 's 2015 adaptation of this approach to water-based electrolytes marked a pioneering venture into aqueous LIB chemistry ([Suo et al., 2015](#)).

HCE's potential in enhancing Li metal cycling came to the forefront with Jeong et al., 's 2008 exploration, which, while promising, highlighted the necessity for further optimization ([Jeong et al., 2008b](#)). A groundbreaking study in 2015 by Qian et al. detailed the success of 4 M LiFSI in DME, achieving impressive Li cycling columbic efficiency (CEs): 99.1% under 0.2 mA/cm<sup>2</sup> and 98.4% under 4 mA/cm<sup>2</sup> ([Qian et al., 2015](#)). Numerous subsequent investigations have further refined HCEs for LMBs, striving for optimal performance and stability ([Zeng et al., 2018a](#); [Fan et al., 2018b](#); [Suo et al., 2018](#); [Hagos et al., 2019](#); [Maeyoshi et al., 2019](#); [Chen et al., 2020](#); [Wang et al., 2022](#)). However, despite their merits, HCEs do possess shortcomings, including reduced ionic conductivity and increased viscosity, which necessitate specialized separators ([Yamada and Yamada, 2015b](#)). Moreover, the high concentration leads to substantial cost implications due to the predominant usage of expensive Li salts ([Zhang et al., 2020](#)).

### Localized high concentration electrolytes (LHCEs)

To circumvent HCEs' limitations, diluting HCEs with another solvent seemed to be a straightforward solution. However, the challenge lay in selecting a solvent that would not compromise the Li-ion solvation environment intrinsic to HCEs. Early work by

Dokko et al., in 2013 highlighted this potential, leveraging the benefits of diluting HCEs with solvents like 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) to enhance Li-S batteries' cyclability ([Dokko et al., 2013](#)). A slew of subsequent research has expanded on these findings, identifying optimal solvent ratios and candidates for dilution that ensure stability and performance ([Moon et al., 2015](#); [Ueno et al., 2016](#); [Doi et al., 2017](#); [Wang et al., 2022](#)).

Chen and co-workers' 2018 introduction of a Li metal CE of 99.3% in a unique electrolyte comprising 5.5 M LiFSI/dimethyl carbonate and bis(2,2,2-trifluoroethyl)ether highlighted the innovation in LHCEs ([Chen et al., 2018c](#)). A series of LHCEs followed, each honing in on the optimal molar ratios and solvents to maximize LMB performance ([Chen et al., 2018d](#); [Cao et al., 2019](#); [Fan et al., 2019](#); [Ren et al., 2019](#); [Wang et al., 2022](#)). The full potential of these electrolytes has yet to be validated.

### Electrolytes with novel additives

Electrolyte additives have etched a reputation for significantly impacting Li-based battery performance ([Xu, 2004](#); [Zhang et al., 2018c](#)). Historical research has presented a plethora of additives, from 2-methylfuran ([Abraham et al., 1984](#)) and CO<sub>2</sub> ([Aurbach et al., 1992](#); [Aurbach and Zaban, 1994](#)) to a wide range of inorganic metal ions ([Matsuda, 1993](#); [Yoon et al., 2008](#); [Vega et al., 2009](#); [Stark et al., 2011](#); [Wang et al., 2022](#)). Modern advancements, particularly over the past half-decade, have witnessed an influx of new organic/inorganic additives ([Wang et al., 2022](#)). Some notable mentions include solvents like vinylene carbonate, ([Stark et al., 2011](#); [Ren et al., 2018](#)), fluoroethylene carbonate, ([Stark et al., 2011](#); [Zhang et al., 2017](#)), and bis(2,2,2-trifluoroethyl) carbonate ([Louli et al., 2019](#)) salts like LiAsF<sub>6</sub>, ([Ren et al., 2018](#)), LiPF<sub>6</sub>, ([Stark et al., 2011](#)), and LiNO<sub>3</sub>, ([Li et al., 2015](#); [Zhang et al., 2018](#); [Yan et al., 2018](#); [Wang et al., 2019](#); [Yan et al., 2019](#); [Wang et al., 2022](#)), and innovative materials such as LiF, ([Lu et al., 2014](#)), nanodiamonds, ([Cheng et al., 2017](#)), LiPS, ([Li et al., 2015](#)), and tris(pentafluorophenyl) borane ([Li et al., 2020](#)). Among these, fluorinated chemicals, especially LiF, FEC, and CuF<sub>2</sub>, have proven to be particularly impactful. LiNO<sub>3</sub>'s widespread adoption further underscores its effectiveness, greatly enhancing Li metal's CE ([Wang et al., 2019](#)). In tandem, the integration of additives with electrolytes, as demonstrated by Lu and co-workers, ([Li et al., 2020](#); [Zhang et al., 2020](#)), showcases the vast potential inherent in additive candidates. These combinations and synergies underline the promise additives hold for enhancing LMBs' performance.

### Fluorinated electrolytes

Fluorinated electrolytes have emerged as a promising electrolyte due to their ability to form stable solid electrolyte interphase (SEI) or cathode electrolyte interphase (CEI) layers ([Yuan et al., 2023](#)). These electrolytes are derived by substituting hydrogen atoms in solvent molecules with fluorine atoms, which aids in forming LiF-rich SEI or CEI layers on both the cathode and Li metal ([Li et al., 2019](#)). This substitution also reduces the flammability of organic solvents ([Shadike et al., 2021](#); [Xu et al., 2021](#)). Wang et al. introduced an all-fluorinated electrolyte composed of 1 M LiPF<sub>6</sub> in a mixture of FEC, 3,3,3-fluoroethyl-methyl carbonate, and 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether. This electrolyte is nonflammable and forms F-rich SEI layers

(Shadike et al., 2021). With added lithium difluorooxaloborate salt, the interphase of the LiNiO<sub>2</sub> cathode is stabilized, enhancing electrochemical performance (Deng et al., 2019). It is also suitable for 5.3 V high-voltage cathodes by forming LiF-rich CEI layers (Chen et al., 2019). Yu et al. designed fluorine-substituted ether solvents, which after fluorine substitution, became highly stable against both Li-metal and high-voltage cathodes (Yu et al., 2020). They further synthesized fluorinated-1,2-diethoxyethanes, revealing that the position and amount of F atoms on 1,2-diethoxyethane significantly influence electrolyte performance (Kim et al., 2022). Fluorinated electrolytes also exhibit extended electrochemical windows, reaching up to 6 V, surpassing conventional carbonate electrolytes (Yang et al., 2021). However, they have higher viscosity and lower ionic conductivity, necessitating the use of co-solvents to optimize these properties.

### Phosphate-based electrolytes

Phosphate solvents, inherently non-flammable, have been explored as potential electrolyte solvents as well. These solvents, while employed in various applications as flame-retardant additives, unfortunately, exhibit instability towards the Li-metal anode. For instance, Wang et al. highlighted that even with an electrolyte containing 10 wt% tris(2,2,2-trifluoroethyl) phosphite additive, Li-S batteries failed after 700 cycles due to the Li-metal anode's degradation (Wang et al., 2014). Liu et al. delved into the stability of Li deposition in phosphate electrolytes with varying salt-to-solvent ratios. They found that a 1:1 ratio was essential to achieve an initial CE of 94.8% for Li deposition (Zeng et al., 2018b). Several strategies have been proposed to stabilize the Solid Electrolyte Interphase (SEI) between the Li-metal anode and phosphate solvents. These include designing ion-solvation phosphate-based electrolytes, preparing LHCEs, constructing nitride interphases, and developing inorganic-rich solid-state electrolytes (Shi et al., 2018). In high-concentration phosphate electrolytes, both the phosphate solvent and Li ions are surrounded by lithium salt anions. This configuration leads to the formation of inorganic-rich SEI layers during discharge, enhancing Li deposition's average CE to over 99% when the salt-to-solvent ratio is 1:2 (Zeng et al., 2018a). Additives have also shown promise in stabilizing the interphase in phosphate electrolytes. Guo et al. introduced LiNO<sub>3</sub> into the triethyl phosphate electrolyte, resulting in a nitride-rich interphase that improved the reversibility of Li deposition (Tan et al., 2019). Another effective additive, Li<sub>2</sub>O, has been shown to enhance the inorganic content in the SEI layer, improving its stability (Zhang et al., 2021; Kim et al., 2022).

### Ionic liquid electrolytes

Ionic liquids (IL), by virtue of their distinct physicochemical properties, have marked a significant advance in the electrolyte landscape for LMBs. Renowned for their nonflammability and negligible volatility, these liquids are poised to replace conventional carbonate-based solvents, enhancing the safety metrics of battery systems (Sun et al., 2020; Dong et al., 2022). The ionic liquids featuring FSI-/TFSI- anions have garnered attention due to their efficient ion transfer, with the reduced interaction between cations and anions boosting Li<sup>+</sup> fluidity (Wang et al., 2019). One such prominent example is the EM-5Li-Na IL electrolyte, composed of 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide ([EMIm]FSI)

mixed with 5 M lithium bis(fluorosulfonyl)imide (LiFSI) and 0.16 M sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) additive. This electrolyte showcases a low viscosity of 125 mPa s at ambient temperature, significantly lower than earlier ionic liquid formulations (Sun et al., 2020). Its ion conductivity stands at ~2.6 mS cm<sup>-1</sup> at 25°C, appreciably higher than other ionic liquids used in LMBs, and increases further with temperature (Sun et al., 2020). The LiCoO<sub>2</sub> (LCO)||Li cell employing this electrolyte demonstrates superior capacity retention and CE at moderate rates, in contrast to the rapid performance degradation seen with conventional electrolytes (Sun et al., 2020). Furthermore, the high concentration of LiFSI salts in the EM-5Li-Na IL electrolyte is linked to its enhanced battery performance, and the strategic inclusion of NaTFSI as an additive is a novel approach to LMB improvement (Sun et al., 2020). In essence, ionic-liquid electrolytes, with their broad electrochemical windows and superior safety profiles, could also offer a potential path forward for the development of high-voltage, high-safety LMBs.

## Solid electrolytes lithium metal batteries

Solid-state electrolytes (SSEs) are also a promising option as an electrolyte in LMBs. Monroe's report highlighted that a solid electrolyte with a shear modulus greater than 6.8 GPa effectively suppresses lithium dendrites (Monroe and Newman, 2005). It was also established that, aside from the modulus, other properties like Li<sup>+</sup> conductivity of the solid electrolyte have a role in dendrite suppression (Khurana et al., 2014). Optimal solid electrolytes share certain desired characteristics, (Wang et al., 2021), namely,

- High Li<sup>+</sup> ion conductivity at ambient temperature.
- Adequate mechanical strength to prevent dendrite growth.
- Compatibility at the interface with both electrodes.
- Chemical and electrochemical stability.

Among the various solid electrolytes researched, they can be broadly classified into ceramic electrolytes, polymer electrolytes, and hybrid inorganic/polymer solid electrolytes.

### Inorganic solid electrolytes

These are notable for their good Li<sup>+</sup> conductivity (>10<sup>-3</sup> Scm<sup>-1</sup>) and high elastic modulus, ranging from tens to hundreds of gigapascals (Xiong et al., 2020). Oxides (Li et al., 2019; Guo et al., 2019; Jiang et al., 2020) and sulfides (Zhao et al., 2020) have been explored as potential electrolytes in LMBs. However, their intrinsic brittleness and rigidity, combined with compatibility issues at the solid electrolyte/lithium interface, pose significant challenges for real-world applications. Interlayers between the solid electrolyte and lithium, like a membrane consisting of lithium perchlorate, poly(ethylene oxide) (PEO), and garnet particles, have been introduced to mitigate these problems (Pervez et al., 2019; Wen et al., 2019).

### Polymer solid electrolytes

Comprising of a blend of lithium salts and a polymer matrix, polymer solid electrolytes benefit from enhanced interface compatibility over their inorganic counterparts, thanks to their inherent flexibility (Li et al., 2019). PEO stands out as the primary material in this category. However, challenges arise due

**TABLE 1** Recently reported lithium metal batteries employing novel liquid and solid electrolytes along with their reported performance. Note: N/P is the ratio of negative to positive electrode capacity.

Cell configuration	Electrolyte	Electrochemical performance	Notes	References
Cu/LiTFSI-LiFSI-G3-HFE/NMC811+Li <sub>2</sub> O	1 M LiTFSI +1.5 M LiFSI/G3-HFE	0.375C–0.5D Capacity retention: 80% (300th cycle)	Anode free	Qiao et al. (2021)
Li/LiFSI-DME/NMC111	4 M LiFSI/DME	C/3 Capacity retention: 92% (500th cycle)	N/p = 60. N/P too high could impact energy density	Qian et al. (2016)
Cu/LiFSI-DME/NMC111		C/8 Capacity retention: 60% (50th cycle)	Anode-free	
Li/LiFSI-DMC-BTFE/NMC111	1.2 M LiFSI/DMC-BTFE	0.5C - 2D Capacity retention: 80% (700th cycle)	N/p = 45. N/P too high could impact energy density	Chen et al. (2018a)
Li/LiFSI-TEP-BTFE/NMC622	1.2 M LiFSI/TEP-BTFE	C/3–1D Capacity retention: 97% (600th cycle)	N/p = 56.25. N/P too high could impact energy density	Chen et al. (2018b)
Li/LiFSI-FDMB/NMC532	1 M LiFSI/FDMB	C/3 Capacity retention: 100% (210th cycle)	N/p = 2.5	Yu et al. (2020)
	1 M LiFSI/FDMB	C/5–D/3 Capacity retention: 80% (100th cycle)	Anode free	
Li/LiFSI-DME-FDMH/NMC532	1 M LiFSI/DME-FDMH	C/3 Capacity retention: 84% (250th cycle)	N/p = 1.6	Wang et al. (2021a)
Li/LiFSI-DME-FDMH/NMC811		C/2 Capacity retention: 76% (250th cycle)	N/p = 2	
		C/5–D/4 Capacity retention: 75% (120th cycle)	Anode free	
Li/LiPF <sub>6</sub> -FEC-FEMC-D2/NMC811	1 M LiPF <sub>6</sub> /FEC-FEMC-D2	C/2 Capacity retention: 95% (120th cycle)	N/p = 1	Fan et al. (2018a)
		C/4 Capacity retention: 50% (30th cycle)	Anode free	
Li/LiFSI-FSA/NMC622	1 M LiFSI/FSA	C/4 Capacity retention: 89% (200th cycle)	N/p = 7.6	Xue et al. (2020)
		C/10–D/3 Capacity retention: 50.8% (45th cycle)	Anode free	
Li/LiTFSI-LiDFPB-DME/NMC111	2 M LiTFSI +2 M LiDFOB/DME	C/3–1D Capacity retention: 79% (500th cycle)	N/p = 30	Jiao et al. (2018)
Li/LiPF <sub>6</sub> -EC-DEC-LiNO <sub>3</sub> /NMC111	0.5 M LiPF <sub>6</sub> /EC-DEC with LiNO <sub>3</sub>	1C Capacity retention: 80% (250th cycle)	N/p = 8.4	Liu et al. (2018)
Li/LiFSI-DME-LiNO <sub>3</sub> -CuF <sub>2</sub> /LFP	2.3 M LiFSI/DME with 20 mM of LiNO <sub>3</sub> and 20 mM of CuF <sub>2</sub>	0.2c Capacity retention: 100% (80th cycle)	N/p = 5	Yan et al. (2019)
Li/PPC-P(VDF-HFP)/LFP	PPC/P(VDF-HFP)	Initial discharge capacity: 140.0 mAh g <sup>-1</sup> (50 μA cm <sup>-2</sup> ) Capacity retention: 91.3% (300th cycle)	-	Lu et al. (2020)
Li/SN-CSSE/LCO	SN-CSSE	Initial discharge capacity: 160 mAh g <sup>-1</sup> (0.1C) Capacity retention: 99.98% (85th cycle)	-	Fu et al. (2021)
Li/LiTFSI-PEO@Ce-MOF/LFP	LiTFSI-PEO@Ce-MOF	Initial discharge capacity: 158 mAh g <sup>-1</sup> (1C) Capacity retention: 71% (2400th cycle)	-	Wu et al. (2021)
Li/P-IL/LFP	LAGP-PVDF-IL	Initial discharge capacity: 106 mAh g <sup>-1</sup> (0.5C) Capacity retention: 90.7% (196th cycle)	-	Lin et al. (2021)
Li/LLZO-PCL-LiTFSI/FCG78	LLZO-PCL-LiTFSI	Initial discharge capacity: 172.4 mAh g <sup>-1</sup> (0.5C) Capacity retention: 84.3% (200th cycle)	-	Tian et al. (2022)

(Continued on following page)

**TABLE 1 (Continued)** Recently reported lithium metal batteries employing novel liquid and solid electrolytes along with their reported performance. Note: N/P is the ratio of negative to positive electrode capacity.

Cell configuration	Electrolyte	Electrochemical performance	Notes	References
Li/TFA- LiPF <sub>6</sub> /LFP	TFA- LiPF <sub>6</sub> (deep eutectic salt)	Initial discharge capacity: 125 mAh g <sup>-1</sup> (0.1C) Capacity retention: 80% (60th cycle)	-	Mezzomo et al. (2023)
Li/LiPON-Mn/LiCoO <sub>2</sub>	Mn-doped LiPON	Initial discharge capacity: 130 μAh·cm <sup>-2</sup> μm <sup>-1</sup> (0.1C) Capacity retention: 93% (100th cycle)	-	Song et al. (2023)
Li/(LiTFSI-SN <sub>0.05</sub> -10 wt.% FEC)-15 wt.% PEO/NMC532	(LiTFSI-SN <sub>0.05</sub> -10 wt.% FEC)-15 wt.% PEO	Initial discharge capacity: 169 mA h g <sup>-1</sup> Capacity retention: 80% (120th cycle)	-	Liu et al. (2021a)
Li/PEO-LLZO nanofibers-LiTFSI/LFP	PEO/LLZO nanofibers/LiTFSI	Initial discharge capacity: 123.2 mA h g <sup>-1</sup> (1C) Capacity retention: 84% (200th cycle)	-	Zheng et al. (2021)
Li/Li <sub>3</sub> GaF <sub>6</sub> /LiFePO <sub>4</sub>	Li <sub>3</sub> GaF <sub>6</sub>	Initial discharge capacity: 137.5 mA h g <sup>-1</sup> (0.5C) Capacity retention: 90% (100th cycle)	-	Hu et al. (2020a)
Li/LiDGO-PEO-LiTFSI/LFP	LiDGO-PEO-LiTFSI	Initial discharge capacity: 156 mA h g <sup>-1</sup> (0.5C) Capacity retention: 98.7% (200th cycle)	-	Yang et al. (2021a)
Li/LLTO-PEO-LiTFSI/LFP	LLTO-PEO-LiTFSI	Initial discharge capacity: 144.6 mA h g <sup>-1</sup> (1C) Capacity retention: 96% (100th cycle)	-	Liu et al. (2020)
Li/PVDF-LSTHF-TMP-LiClO <sub>4</sub> /LFP	PVDF-LSTHF (10 wt.%)-TMP-LiClO <sub>4</sub>	Initial discharge capacity: 134 mA h g <sup>-1</sup> (1C) Capacity retention: 97.7% (300th cycle)	Li anode was coated with FEC	Dai et al. (2020)
Li/LMZP/LFP	LMZP	Initial discharge capacity: 140 mA h g <sup>-1</sup> (0.1C) Capacity retention: 90% (50th cycle)	-	Zhou et al. (2020)
Li/Li(IL)-UiO67/LFP- Li(IL)-UiO67	Li(IL)-UiO67	Initial discharge capacity: 149 mA h g <sup>-1</sup> (0.1C) Capacity retention: 94% (300th cycle)	Li(IL) comprises of LiTFSI dispersed in IL [EMIM][TFSI]; the Li(IL) was encapsulated in the UiO-67 MOF structure	Liu and Sun (2020)
Li/Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> -PVDF/LFP	Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> (80 wt.%)-PVDF	Initial discharge capacity: 150 mA h g <sup>-1</sup> (0.5C) Capacity retention: 98% (30th cycle)	-	Zhou et al. (2022)
Li/LLZT-PVDF/LiCoO <sub>2</sub>	LLZT-PVDF	Initial discharge capacity: 120.3 mA h g <sup>-1</sup> (2C) Capacity retention: 94.1% (200th cycle)	-	Sun et al. (2021)
Li/LIBOSS/TiS <sub>2</sub>	Li <sub>2</sub> S-B <sub>2</sub> S <sub>3</sub> -SiO <sub>2</sub> -LiI	Initial discharge capacity: 260 mA h g <sup>-1</sup> (0.1C) Capacity retention: 99% (130th cycle)	-	Kaup et al. (2020)
Li/TEP-FEC/LFP	TEP-FEC-PEGDA-HMPP-PVDF-LiTFSI-BA-EC/DMC	Initial discharge capacity: 139 mA h g <sup>-1</sup> (0.5C) Capacity retention: 93% (150th cycle)	A protective layer comprised of BA-PEGDA-PEO matrix and EC/DMC plasticizer is placed between the electrolyte and the anode because TEP is incompatible with Li anodes	Zhang et al. (2021a)
Li/LLZTO/NCM622	LLZTO (20 wt.%)-PPC-LiTFSI	Initial discharge capacity: 166 mA h g <sup>-1</sup> (0.5C) Capacity retention: 80% (100th cycle)	-	Chen et al. (2019a)
Li/PDOL-YSZ/NCM622	Polymerized 1,3-dioxolane (PDOL) -YSZ	Initial discharge capacity: 164.7 mA h g <sup>-1</sup> (0.5C) Capacity retention: 73% (800th cycle)	Li <sub>2</sub> ZrO <sub>3</sub> rich ion conductive layer forms on the surface of Li anode	Yang et al. (2022)
Li/PEO-LiTFSI/LiMn <sub>0.7</sub> Fe <sub>0.3</sub> PO <sub>4</sub>	PEO-LiTFSI (mole ratio EO/Li = 18)	Capacity retention: 90.3% (120th cycle)	-	Qiu et al. (2020)

(Continued on following page)

**TABLE 1 (Continued)** Recently reported lithium metal batteries employing novel liquid and solid electrolytes along with their reported performance. Note: N/P is the ratio of negative to positive electrode capacity.

Cell configuration	Electrolyte	Electrochemical performance	Notes	References
Li/PAN-LAGP/NMC622	PAN-LAGP 80 wt.%	Initial discharge capacity: 180 mA h g <sup>-1</sup> (0.1C) Capacity retention: 81.5% (270th cycle)	-	Duan et al. (2019)
Li/PAN-LLZTO/LFP	PAN-LLZTO-Mg(ClO <sub>4</sub> ) <sub>2</sub> (30 wt.%)	Initial discharge capacity: 150 mA h g <sup>-1</sup> (0.5C) Capacity retention: 99% (300th cycle)	-	Qiu and Sun (2020)
Li/PVDF-HFP-LiTFSI/TiO <sub>2</sub>	PVDF-HFP-LiTFSI (1:1.1 weight ratio)	Initial discharge capacity: 227.5 mA h g <sup>-1</sup> (0.2C) Capacity retention: 86.8% (800th cycle)	-	Liu et al. (2021b)
Li/PEO-LiTFSI-DBDPE-PI/LFP	PEO-LiTFSI-DBDPE-PI	Initial discharge capacity: 143 mA h g <sup>-1</sup> (0.5C) Capacity retention: 98% (300th cycle)	Decabromodiphenyl ethane (DBDPE) was incorporated to make the electrolyte fireproof	Cui et al. (2020)
Li/LGPS/LiCoO <sub>2</sub>	Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub> (LGPS)	Initial discharge capacity: 131 mA h g <sup>-1</sup> (0.1C) Capacity retention: 86.7% (500th cycle)	LiH <sub>2</sub> PO <sub>4</sub> protective layer employed at the Li/electrolyte interface to improve chemical stability and stabilize cycling	Zhang et al. (2018a)
Li/PI-LLZTO-PVDF/NCM	PI-LLZTO nanoparticles-PVDF	Initial discharge capacity: 152.6 mA h g <sup>-1</sup> (0.1C) Capacity retention: 94.8% (80th cycle)	-	Hu et al. (2020b)
Li/LiTFSI- Pyr1,3FSI/LiCoO <sub>2</sub>	LiTFSI- Pyr1,3FSI (mass ratio 1:1)	Initial discharge capacity: 160 mA h g <sup>-1</sup> (0.2C) Capacity retention: 94.2% (60th cycle)	-	Zhang et al. (2018b)
Li/Li (DME) <sub>0.7</sub> FSI-PEO <sub>0.6</sub> /NMC	Polymer in quasi-ionic liquid Li (DME) <sub>0.7</sub> FSI-PEO <sub>0.6</sub>	Initial discharge capacity: 127 mA h g <sup>-1</sup> (1C) Capacity retention: 88.4% (300th capacity with 4.2 V charge cutoff voltage)	-	Wu et al. (2019)
Li/PVDF-HFP/LFP	PVDF-HFP-LiPF <sub>6</sub> -EC-DEC	Initial discharge capacity: 125 mA h g <sup>-1</sup> (2C) Capacity retention: 86% (200th cycle)	Asymmetric gel polymer electrolyte is proposed	Li et al. (2020a)

to its low modulus (below 400 MPa) and insufficient ion conductivity at ambient temperature (Balo et al., 2018; Ding et al., 2019). Strategies to enhance Li<sup>+</sup> transport dynamics include the introduction of plasticizers such as IL, (Balo et al., 2018), incorporation of inorganic fillers, (Zhao et al., 2020), and fabricating cross-linked polymer electrolytes (Khurana et al., 2014). Recent innovations in this space include ILE@MOF electrolyte, which offers enhanced ionic conductivity by anchoring anions of the electrolyte salt (Chen et al., 2019).

### Inorganic/polymer hybrid solid electrolytes

Merging the benefits of both inorganic and polymer solid electrolytes, this category has garnered significant attention. Various polymer matrices (like PEO, (Li et al., 2020), polyethylene glycol (PEG), (Pan et al., 2020), and polycaprolactone (Zhang et al., 2019)) and inorganic fillers (e.g., lithium aluminium germanium phosphate (Zhang et al., 2019), lithium germanium phosphorus sulfide (Liu et al., 2019b; Pan et al., 2020), and lithium lanthanum zirconium oxide (Li et al., 2019)) have been combined to strike a balance between flexibility, conductivity, and rigidity. For instance, an LAGP-PEO hybrid solid electrolyte demonstrated commendable stability attributed to its impressive Li<sup>+</sup> conductivity and flexural modulus, reinforced by LAGP particles in the PEO matrix (Li et al., 2020).

Despite the advancements in solid electrolyte technologies, there remain substantial challenges. The interfacial resistances documented in several studies are notably high, resulting in relatively low current densities when used in batteries (Al-Salih et al., 2022; Al-Salih et al., 2024). One of the paramount issues in solid-state lithium batteries is the uncontrollable dendrite growth at high current densities, which can result in short circuits or diminished capacity. Dendrite formation might be influenced by the nonuniform contact between the solid electrolyte and lithium metal, but the underlying mechanisms in solid-state batteries remain underexplored (Tsai et al., 2016). Some studies, like that by Aguesse et al., have shed light on potential reasons, such as lithium clusters in cavities and pores of the garnet solid electrolyte or lithium metal accumulation in the pores leading to electrolyte failure (Aguesse et al., 2017). Yet, a comprehensive understanding of dendrite formation in solid electrolytes is still elusive. Considering the rapid advancements and evident challenges of SSEs, continuous research is crucial. While we've made progress, the onus is on the scientific community to further unravel the intricacies of solid-state lithium batteries, ensuring that we harness their full potential in the evolving landscape of energy storage solutions.

Table 1 lists examples of impressive high performing lithium metal batteries reported in the literature in the past few years.

## Discussion and outlook

Drawing upon the extensive analysis of practical considerations for LMB electrolytes, several aspects emerge that warrant critical discussion that takes into account industry, consumer, and market perspectives. The future of LMB technology is undoubtedly reliant on the interplay between battery materials' chemistry, their structural/performance relationship and their validation in industrial cells under real life application conditions. Let's delve into some of these aspects more deeply.

### Economic feasibility and environmental sustainability

The commercial feasibility of LMBs is inextricably linked to the cost-effectiveness of the electrolyte. However, emphasizing cost-effectiveness should not be at the expense of environmental considerations. In fact, the integration of green chemistry and atom economy must be central to future endeavors. Leveraging techniques such as organic-solvent-free methods for salt synthesis, like ball milling, or employing organic synthetic procedures that yield fewer byproducts can help bridge the gap between commercial viability and eco-responsibility.

### Calendar and cycle life

The spotlight on the cycle life of LMB electrolytes has inadvertently dimmed the attention towards the calendar life of these batteries. Even though recent electrolytes have made strides in cycling efficiency, there is still much ground to cover in terms of calendar life, with factors like SEI thickening playing a dominant role in capacity loss. Drawing parallels with the solid electrolytes for all-solid-state lithium batteries (ASSLBs), it becomes evident that while much progress has been made, the understanding of the nuanced mechanisms at play, like ion solvation and SEI formation pathways, is still in its infancy. The promise of anode-free LMBs heralds a transformative phase in energy density optimization. However, this promise is deeply intertwined with achieving exceptionally high CE. If a future electric vehicle (EV) is designed to journey 1,000 km per charge cycle, it necessitates a CE of at least 99.95% (see [Figure 1B](#)). This would ensure the battery's capability to power the vehicle for a staggering 400,000 km, harmonizing with the typical lifespan of many other car components. Such a CE threshold, while ambitious, positions the battery pack as a beacon of durability, potentially outpacing most other vehicle parts in longevity. For the auto industry, this paints a future where the battery is not the limiting factor but a benchmark of resilience and reliability, setting a realistic yet pioneering goal for future EVs.

### Battery safety

Just as the interfacial resistance in solid-state batteries (SSBs) is a challenge, safety stands out as a paramount concern for LMBs. While non-flammable solvents or additives show promise, their true safety merits can only be adjudicated under realistic conditions, such as nailing or heating tests. This necessity is highlighted by Ouyang et al.'s findings, which suggest that even assumed non-flammable electrolytes like trimethyl phosphate-based HCE can combust under the most rigorous conditions.

### Wide temperature range operation

The ability of LMBs to function efficiently across a broad temperature spectrum is a pertinent challenge that mirrors the need for SSEs to maintain stable contact with electrodes across varying conditions. Whether it is high-temperature performance, contingent on the robustness of SEI and CEI, or low-temperature operation, reliant on innovative solutions such as liquified gas electrolytes or weakly solvating solvents, both spectrums necessitate rigorous research and innovation.

To conclude, the realization of optimized LMBs requires a confluence of materials chemistry, engineering, safety protocols, and an understanding of real-world operational challenges. The path forward necessitates researchers from academia, government labs, and industry alike work hand-in-hand to prioritize cost-effectiveness, eco-friendliness, safety, and operational versatility to meet the demands of a dynamic marketplace. Embracing novel chemistries, for the components of the liquid electrolytes and solid electrolyte, at the vanguard of innovation. As we continue to expand our knowledge and develop more sophisticated strategies, the promise of LMBs as an advanced energy storage solution becomes increasingly tangible, paving the way for their integration into the sustainable energy storage landscape.

## Author contributions

HA-S: Conceptualization, Investigation, Software, Writing—original draft, Writing—review and editing. HK: Data curation, Formal Analysis, Writing—review and editing. EB: Project administration, Resources, Writing—review and editing. YA-L: Funding acquisition, Investigation, Resources, Visualization, Writing—review and editing.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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