

Pushing the boundaries of chemistry? It takes #HumanChemistry

Make your curiosity and talent as a chemist matter to the world with a specialty chemicals leader. Together, we combine cutting-edge science with engineering expertise to create solutions that answer real-world problems. Find out how our approach to technology creates more opportunities for growth, and see what chemistry can do for you at:

evonik.com/career



Check for updates

Critical review on low-temperature Li-ion/metal batteries

Nan Zhang, Tao Deng, Shuoqing Zhang, Changhong Wang, Lixin Chen, Chunsheng Wang^{*} and Xiulin Fan^{*}

N. Zhang, S. Zhang, Prof. L. Chen, Prof. X. Fan

State Key Laboratory of Silicon Materials and School of Materials Science and Engineering Zhejiang University, Hangzhou 310027, China. E-mail: xlfan@zju.edu.cn

N. Zhang, Dr. T. Deng, Dr. C. Wang, Prof. C. Wang Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA.

E-mail: cswang@umd.edu

N.Z. and T.D. contributed equally to this work.

Keywords: low-temperature battery, electrolyte, desolvation energy, solid electrolyte interface, Li battery

With the highest energy density ever among all sorts of commercialized rechargeable batteries, Li-ion batteries (LIBs) have stimulated the upsurge utilization in 3C devices, electric vehicles, and stationary energy storage systems. However, a high performance of commercial LIBs based on ethylene carbonate electrolytes and graphite anodes can only be achieved at above -20 °C, which restricts their applications in harsh environments. In this review, we provided a comprehensive research progress and in-depth understanding of the critical factors leading to the poor low-temperature performance of LIBs, sorted out

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the <u>Version of Record</u>. Please cite this article as <u>doi:</u> 10.1002/adma.202107899.

the distinctive challenges on the anodes, electrolytes, cathodes and electrolyte-electrodes interphases, with a special focus on Li-ions transport mechanism therein. Finally, promising strategies and solutions for improving low-temperature performance were highlighted to maximize the working-temperature range of the next-generation high-energy Li-ion/metal batteries.

1. Introduction

Li-ion batteries (LIBs) with high energy/power density, long lifespan, environmental friendliness, and technological maturity have monopolized energy storage areas (such as 3C devices, electric vehicles (EVs)) after 30 years' rapid development.^[1-7] Despite of the significant advances, the issue of decayed performance of LIBs at low temperatures pops out, which becomes one of the main obstacles to restrict their applications at high altitudes or latitudes, and certain defense and space applications (**Figure 1**a).^[2,8] Once the temperature drops to -20 °C or lower, most commercial LIBs based on ethylene carbonate (EC) electrolytes suffer from severe capacity and energy loss due to significantly decreased ionic conductivity, sluggish interfacial charge transfer kinetics, and slow Li⁺ transport in SEI and inside electrodes. For a typical Panasonic 18650 Li-ion cell (Figure 1b), only ~5% of energy density can be retained at -40 °C, let alone the power density under low temperatures.^[9] Even worse, some prototype 18650 Li-ion cells cannot work at all because of the solidification of electrolytes at such a low temperature.^[10] Compared with other commercial batteries such as nickel-metal hydride (NiMH) batteries and Lead-acid batteries, LIBs based on graphite anodes suffer from more serious loss of energy and power density at the low temperature of below -30 °C.^[9] Besides, Li dendrites, which are easily formed during low-temperature charging, can bring about some safety concerns.

To enable the proper function of LIBs at low temperatures, internal or external thermal management systems are usually used in most LIBs-powered systems.^[11-13] A typical example is the application of radioisotope thermal generators (RTGs) in 2004 Mars Spirit and Opportunity rovers, which supported the normal operation of the battery packs under the ultra-low temperature of -100 °C on Mars.^[14] Given the additional cost, system complexity, and reduction in energy density, novel strategies for LIBs against low-temperature without functional accessories are highly appealed. Exciting is that significant advances are being achieved recently with a landmark energy density of ~140 Wh kg⁻¹ at an extremely low temperature of -60°C (Figure 1c).^[15,16] In light of these achievements in the performance, mechanisms and design principles of the low-temperature high-energy Lion/metal batteries, a critical and comprehensive review on this rapidly evolving area deems necessary and urgent. In this work, we first classified the substantial issues in the cell operation, and then tried to figure out the rate-limiting steps and underlying mechanisms on the poor low-temperature electrochemical performance. In the following section, we discussed the recent breakthroughs in

electrolytes, electrodes and cell configurations, and finally examined how these factors together determine the low-temperature chemistries. Considering the significant advances in high-energy Li metal batteries (LMBs) in the past five years, the discussion on low-temperature LMBs is also covered.

Figure 1d summarized the typical issues that restrict the electrochemical performance of LIBs at low temperatures: (1) the decline of the wettability and ion conductivity of liquid electrolyte resulting from its increased viscosity or solidification block the ion transport in electrolyte; (2) the increase of intrinsic grain-boundary resistance and sluggish Li⁺ diffusion within electrodes suppress the (de)lithiation reactions; (3) difficult Li⁺ desolvation and slow transport through solid electrolyte interphase (SEI) together with large charge-transfer resistance reduce battery kinetics; (4) severe Li plating on anode under low-temperature brings some safety concerns.^[17-19]



Figure 1. (a) Wide range of potential applications of LIBs under low-temperature external environments from above -20 to lower than -100 °C (b) Comparison of energy/power density of typical commercial batteries operated at 25, -20, and -30 °C. (c) Development on energy density for LIBs or

LMBs operated at low temperatures. The solid and dash lines represent the achievement of energy density at ultra-low temperatures of < -60 °C for LIBs and LMBs, respectively. The data were obtained from Ref.^[12,15,16,20-25] (d) Schematic of a typical LIB consisting of layered oxide cathode, graphite anode, and electrolyte, as well as the limiting factors for low-temperature operation.

1.1 Limiting process for low-temperature performance

To address the abovementioned challenges, designing novel electrolytes catering to the needs of lowtemperature circumstances is a prerequisite for cost-efficient and safe Li-based batteries. Since the 1990s, EC with high dielectric permittivity (ε, 89.78 at 25 °C) and good capability to passivate the graphite anodes has been regarded as an indispensable component of electrolytes for LIBs.^[26] The addition of acyclic carbonate or carboxylic esters, such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), or diethyl carbonate (DEC), reduces the viscosity of electrolytes and improves the overall ion transport kinetics in batteries.^[27,28]

The challenges for low-temperature batteries are how to achieve a high capacity without Li plating to ensure a long cycle life. The viscosity of electrolytes would increase with the dropping of temperature and electrolytes are even frozen due to relatively high melting points of carbonate solvents (*e.g.*, ~10 °C for EC/DMC 1:1 by mole^[29]), which leads to a sharp decrease in ionic conductivity.^[30] To ensure the normal function of LIBs at low temperatures, novel electrolytes should satisfy additional requirements: (1) keep the liquid state in a wide temperature range, *e.g.*, -80 to +60 °C; (2) maintain an acceptable ionic conductivity (at least 0.1 mS cm⁻¹) at low temperatures;^[31] (3) form stable SEI/cathode-electrolyte interphase (CEI) with low interfacial resistance in the whole operating temperature range.

When electrolytes could meet the above requirements, kinetic issues in the interior and/or surface of electrodes would probably turn up in defining the low-temperature properties of LIBs.^[32] For example, as shown in **Figure 2**a and b, the lithiation process of graphite was relatively difficult even at a very low current density (5.4% and 42.3% of discharge capacity retention for graphite and coke at 0.0095 mA cm⁻², respectively), although the delithiation process for graphite was achievable at -40 °C (87% and 86% of charge capacity retention for graphite and coke, respectively). Huang et al.^[32] ascribed the distinct low-temperature performance to the Li⁺ diffusivity discrepancy of 10⁻¹¹ cm² s⁻¹ for graphite *vs*. 10⁻⁹ cm² s⁻¹ for coke. Using electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration (GITT) techniques, Wang et al.^[33] revealed that the higher polarization in the lithiation process of graphite restricts the Li⁺ insertion to only Li_{0.2}C₆ (*vs*. LiC₆ at room temperature, RT), leading to a low capacity at -30 °C (Figure 2c). In the lithiation process, the Li-rich

phase would cover the Li-poor phase ($Li_{0.5}C_6$ on $Li_{0.33}C_6$ or LiC_6 on $Li_{0.5}C_6$). The increased diffusion distance of Li⁺ impedes the progress of further lithiation. When the LiC₆ phase appears and covers the $Li_{0.5}C_6$ phase, the $Li_{0.33}C_6$ core still exists in the electrode due to sluggish kinetics. The coexisting of different phases at a certain state of charge (SOC, the level of charge of an electric battery relative to its capacity) and discharge results in the asymmetry of Li⁺ diffusivity in graphite (Figure 2d) and the increase in reaction impedance.^[32,34]



Figure 2. The comparison of charge (a) and discharge (b) profiles of Li | graphite half-cell running at RT and -40 °C. The insert image in (a) is a schematic diagram of the Li⁺ diffusion during Li (de)intercalation. The insert image in (b) is the performance comparison of coke with various sizes at various temperatures (20, -20, -30 °C). (a) and (b) Reproduced with permission.^[32] Copyright 2000, The Electrochemical Society. (c) Open-circuit potential *vs.* Li content for graphite half-cell running at RT and low temperature (-30, 25 °C). Reproduced with permission.^[33] Copyright 2002, The Electrochemical

Society. (d) The comparison of diffusion coefficient during (de)lithiation process of graphite from a temperature range of -40 - 40 °C. Reproduced with permission.^[34] Copyright 2002, Elsevier.

Accepted Articl

Besides the diffusion issues within the graphite anode, the high interface resistance associated with Li⁺ desolvation and transport in SEI, and charge transfer also restricts the reversibility at low temperatures. In the commercial cells consisting of graphite anode, layered oxide cathodes and carbonate electrolytes, the charge transfer resistance (R_{ct}) increases fastest among all three parts of cell resistances as temperature decreases (Figure 3a-d),^[21] while little change occurred in cathode structure at low temperatures.^[35,36] As shown in Figure 3e, multi-steps, *i.e.* Li⁺ desolvation, Li⁺ migration through SEI, etc., could be tentatively separated in the Li⁺ intercalation process.^[37,38] Li et al.^[39,40] revealed that the Li⁺ desolvation process is the rate-controlling step at low temperatures instead of Li⁺ through the SEI or diffusion in electrode materials using the cell-components switching method. Li₄Ti₅O₁₂ (LTO) anode with a relatively high intercalation potential (~1.5 V vs. Li/Li⁺) is generally considered to be within the electrochemical window of carbonate-based electrolytes and therefore free from the SEI-forming process.^[41] Thus, as Equation (1)-(3) demonstrate, LTO ||LTO symmetric cells are ideal for examining the effect of desolvation at low temperatures without the interference from SEI resistance. Compared with LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA)||NCA and graphite||graphite cells, the LTO ||LTO symmetric cell should only exhibit the resistance of Li⁺ desolvation in the semicircle of EIS results.

$R_{NCA/NCA} = R_{ct} + R_{CEI of NCA} + R_{desolvation} + R_{b}$	(1)
$R_{graphite/graphite} = R_{ct} + R_{SEI of graphite} + R_{desolvation} + R_{b}$	(2)
$R_{LTO/LTO} = R_{ct} + R_{desolvation} + R_{b}$	(3)

However, the three symmetric cells presented almost identical impedance at -40 °C (Figure 3f), indicating that Li⁺ migration through SEI isn't the rate-determining step at low temperatures or SEI still exists on LTO. Since LTO ||LTO cells with different electrolytes exhibited distinct R_{ct} values due to the differences in solvation structures (Figure 3g), the stripping of the solvent sheath from Li⁺ at low temperatures did play a critical role in the rapidly increased R_{ct} (becoming predominant below -20 °C).

In the conventional EC-based electrolytes, the calculated activation energy barrier for Li⁺ desolvation on LTO surface falls in the range of 52 ± 3 kJ mol⁻¹, while the overall energy barrier at graphite/electrolyte interphase is calculated to be 60-70 kJ mol⁻¹.^[41-43] These results quantitatively confirmed that Li⁺ desolvation is the rate-limiting step during lithiation at low temperatures.



Figure 3. (a) Nyquist plots of charged Li-ion, lithiated graphite/graphite, and delithiated cathode/cathode cells at 20 °C. (b)-(d) A comparison of the temperature dependence of three kinds of resistances (R_b, R_{sl}, R_{ct}). The dash line represents the resistance of electrolytes calculated from the ionic conductivity. (a)-(d), Reproduced with permission.^[21] Copyright 2003, Elsevier. (e) Schematic of Li⁺ movement from the electrolyte into the layers of graphite, including desolvation and migration processes. Reproduced with permission.^[38] Copyright 2007, American Chemical Society.Comparison of EIS results derived from (f) symmetrical batteries with NCA, graphite, and LTO electrodes using E9 electrolyte (1.0 M LiPF₆ EC/PC/EMC (1:1:8 by wt.) + 0.05 M CsPF₆) at -40 °C, and (g) LTO||LTO cells with different carbonate electrolytes (EC/PC/EMC with different weight ratios (E1: 5:2:3; E2: 4:2:4; E3: 3:2:5; E4: 2:2:6; E5: 1:2:7; E9: 1:1:8) containing 1.0 M LiPF₆ and 0.05 M CsPF₆) at -40 °C. The insert image in (g) is the zoom-in at a low resistance area. (f) and (g), Reproduced with permission.^[40]

1.2 Li plating on graphite surface at a low-temperature

The high tendency of Li plating is another thorny problem when LIBs operate at low temperatures or high rates.^[44,45] The potential for Li⁺ intercalation into graphite is close to that for lithium plating (within 100 mV vs. Li/Li⁺).^[46] Once the overpotential of LIBs oversteps this potential gap, the Li⁺ tends to be reduced on the surface of graphite rather than intercalated into its layers due to the lower nucleation barrier.^[19,47-51] The plated Li could induce a series of parasitic reactions, generating thicker LIC. SEI and leading to "dead" lithium, which would severely consume the limited recyclable lithium in graphite directly (Figure 4e). (a) (b) 2.5 Simulation 0.2 0.4 0.6 0.8 ratio / % 2 Experiment Total reaction current Insertion reaction current 1.5 Ē lating reaction current -25°C 1 ā -3





This article is protected by copyright. All rights reserved.

Figure 4. (a) Lithium plating ratio for charging at 1.5 C and low temperatures of -25 °C and -20 °C, (b) the simulated currents for plating reaction, intercalation reaction, and the total reaction at -25 °C at different SOCs and (c) the simulated over-potential of plating reaction at the anode-separator interface at different SOCs when charged at -25 °C in graphite | NCM111 cells. (a)-(c), Reproduced with permission. from ref.^[51] Copyright 2017, The Electrochemical Society. (d) Voltage profiles of Li⁺ intercalation and Li plating of HOPG and the corresponding images of the edge plane of a HOPG particle at lithiation state 6, (e) the distribution of Li concentration in graphite based on phase separation model. 1, 2, 3L, 1L are four different lithiation phases of Li_xC₆ from high to low lithiation degree. The typical three potential plateaus during the lithiation of graphite occur in the phase transition between two consecutive phases of these four phases. (d) and (e), Reproduced with permission.^[52] Copyright 2021, CellPress.

It is generally believed that the improvement of the LIBs' low-temperature performance requires comprehensive consideration of various aspects such as electrolytes, electrodes, and battery structures. To maximize the low-temperature electrochemical performance of the LIBs, electrolytes with broadened liquid range and high ionic conductivity, which could ideally couple with the anodes and cathodes, are the prerequisite. These electrolytes should possess low Li-ion desolvation energy and good film-forming ability with low resistance.

2. Low-Temperature Electrolytes

2.1. Organic solvents for organic low-temperature electrolytes

To increase the ionic conductivity of electrolytes at low temperatures, early research focused on reducing the freezing point and viscosity of electrolytes by adding co-solvents or additives into ECbased electrolytes. Smart et al.^[53] reported that the equiproportionally ternary mixture of EC, DEC, and DMC containing 1 M LiPF₆ provided a conductivity of about 1 mS cm⁻¹ at -40 °C, ~10% higher than EC/DMC or DEC binary mixture, which contributes to more efficient Li intercalation-deintercalation at low temperatures. The graphite || LiCoO₂ (LCO) cells with EC/DEC/DMC electrolyte realized 85% of the room-temperature capacity (RTC) at 0.05 C/-20 °C and maintained over 85% of initial capacity after 600 cycles at -25 °C. Plichta et al.^[20,54] reported that the addition of a small amount of EMC could reduce the freezing point of EC/DMC mixtures without significantly decreasing the ionic conductivity. Li||LCO cells with an electrolyte of 1 M LiPF₆ EC/DMC/EMC (1:1:1 by vol.) reached 52% of RTC at -40 °C. Although propylene carbonate (PC) is regarded as a co-intercalated solvent for graphite, it is able to suppress EC crystallization and could be used as a decent ingredient for low-temperature electrolytes.^[55] At -20 °C, LIBs with graphite anode and lithium nickel-based layered oxide cathode using the electrolyte of 1 M LiPF₆ PC/EC/EMC (1:1:3 by wt.) held 83% of RTC. To get a full picture of freezing points of various carbonate mixtures, Ding et al.^[29,56] mapped several carbonate binary liquid/solid phase diagrams, including pairs of the five commonly used carbonates: EC, PC, DEC, DMC, EMC, and EMC-dimethyl ethylene carbonate (DMEC), EMC-isobutylene carbonate (iBC). Figure 5a displays a typical phase diagram between DEC and DMC mixture, and Figure 5b shows the phase behavior of EC/EMC mixture after adding different amounts of LiPF₆. These phase diagrams indicate that the pairing of carbonates with different freezing points and molecular structures is more likely to broaden the liquid range and paves the way to accurate modeling of DMC-EC, DMC-PC, and EC-PC binary systems.^[57]

Apart from these binary systems, ternary and quaternary carbonate solvents were investigated to further improve the low-temperature performance of LIBs. Smart et al.^[58] investigated several ternary or quaternary all-carbonate-based electrolytes, of which the most promising formulations consist of 1.0 M LiPF₆ EC/DEC/DMC/EMC (1:1:1:2 by vol.) and 1.0 M LiPF₆ EC/DEC/DMC/EMC (1:1:1:3 by vol.)

(Figure 5c), providing high ionic conductivities of 1.21 mS cm⁻¹ and 1.32 mS cm⁻¹ at -40 °C, respectively. With the latter electrolyte, MCMB||LiNi_{0.8}Co_{0.2}O₂ cells delivered ~65% of the RTC at -40 °C. At a current rate of 0.1 C, 8.771 Ah (108 Wh kg⁻¹) and 7.555 Ah (84 Wh kg⁻¹) (charging at RT) were obtained for SAFT prototype DD-size (9 Ah) LIBs at -40 and -50 °C, respectively. Liao et al.^[59] investigated the rticl performance of LiFePO₄ (LFP)/C cathode in 1.0 M LiPF₆ EC/DMC/DEC/EMC (1:1:1:3, vol.) electrolyte, and found the Li||LFP/C cells could keep a capacity of 84.8%, 66.9% and 51.3% of RTC at 1 C at 0, -20, and -40 °C, respectively. The increase of viscosity and solidification at low temperatures tends to decrease the ionic conductivity of commercial electrolytes, thus leading to the rapid drop of cell capacity.^[60] Considering the high freezing point and viscosity of EC solvent, it is rational to develop EClean or even EC-free electrolytes for low-temperature applications. In addition, PC-based electrolytes have relatively low freezing points, and the addition of film-forming additives could make it possible for wide-temperature-range applications in existing battery systems. (a) (b) e of 9.61 M LiPF, of 0.77 M LIFF, of 0.98 M LIFF,



CCCDDI

This article is protected by copyright. All rights reserved.

Figure 5. A typical binary phase diagram of (a) DEC and DMC, (b) EC and EMC mixtures with various concentrations of LiPF₆. Reproduced with permission.^[29,56] Copyright 2000, 2001, The Electrochemical Society. (c) the discharge voltage profiles of MCMB–carbon/LiNi_{0.8}Co_{0.2}O₂ cells consisting of various binary, ternary, and quaternary carbonate electrolytes with different solvent ratios at -40 °C. Reproduced with permission.^[58] Copyright 2003, Elsevier.

To further reduce the viscosity and freezing point of electrolyte, a number of aliphatic esters were studied as co-solvents for low-temperature electrolytes, such as methyl formate (MF, melting point: -100 °C), methyl acetate (MA, -98 °C), methyl butyrate (MB, -84 °C), ethyl acetate (EA, -84 °C), ethyl propionate (EP, -73 °C). Table 1 summarizes the physical properties of these reported solvents. Due to the low freezing point and high polarity, Ein-Eli et al.^[61] first introduced MF into EC-based electrolytes. The binary mixtures of MF/EC (e.g., 1:1 and 3:1 by vol.) containing 1 M LiAsF₆ exhibited ion conductivities of 5.6 and 8.4 mS cm⁻¹ at -40 °C, respectively. Similar enhancement on ionic conductivity was also observed by using EA and MB as co-solvents.^[62] Graphite||LCO cells with EC/DMC/EA or EC/DMC/MB-based electrolytes retained more than 80% of the RTC at 0.5 C and -40 °C. Although the introduction of aliphatic esters with low chain lengths such as MA and MF helps to maintain higher initial capacities at low temperatures (e.g., 92% of RTC for graphite || LCO cells using EC/DMC/MA-based electrolytes at 0.2 C and -20 °C), however, the cycle performance was adversely affected with 33% capacity decayed after 200 cycles.^[63] By contrast, EC/DEC/EP (longer chain length) and EC/EMC/EP-based electrolytes enabled cells to maintain 87-89% of RTC and retain >80% after 300 cycles under the same testing conditions. As the chain length or molecular weight of aliphatic esters increases, electrolytes with them as co-solvent exhibit less improvement on ionic conductivity but better surface film-forming capability, which helps bolster up the low-temperature kinetics of LIBs.^[64] The poor cycle performance of low-chain length aliphatic esters could be improved by the addition of hydrocarbon such as toluene (tol).^[65] The good film-forming capability of tol restricts the adverse effects of aggressive MA or MF, leading to considerable improvement in low-temperature cycling performance. Smart et al.^[66] screened the low-temperature performance of multi-component electrolytes with the composition 1.0 M LiPF₆ EC/EMC/X (20:60:20 by vol.), where X = methyl propionate (MP), EP, MB, ethyl butyrate (EB), propyl butyrate (PB) and butyl butyrate (BB). As a prototype, the MCMB||LiNi_xCo_{1-x}O₂ cells with the electrolyte containing MP as co-solvent delivered a

capacity of over six times as much as those with the all-carbonate-based formulations at 0.1 C and -50/-60 °C. Besides, EA, EP and, EB as co-solvents were reported to improve the low-temperature performance of 18650-type graphite ||LiMn₂O₄ (LMO) cells.^[67] 1.0 M LiPF₆ EC/EMC/EA (1:1:2 by wt.) showed an ionic conductivity of 1.7 mS cm⁻¹, with which the highest capacity retention of 90% was achieved at -40 °C. Using EA as a co-solvent, the LTO||LMO cells passed the U.S. Advanced Battery Consortium cold rank test at -30 °C.^[68] Recently, it is reported that a high ionic conductivity of 2.48 mS cm⁻¹ could be obtained for 1.0 M LiPF₆-MP electrolyte even at -60 °C after introducing 10 vol.% fluoroethylene carbonate (FEC).^[25] The charge transfer kinetics was also facilitated at lithiation/delithiation process due to the formation of LiF-rich interface layer on both electrodes. As a result, graphite||NCM111 pouch cells showed increased rate performance and decent lowtemperature discharge capacity (109 mAh g⁻¹ for NCM111 at 0.1 C and -40 °C).

Table 1. Comparison of physical properties of some solvents for low-temperature electrolytes

Solvents	Freezing Point [°C]	Boiling Point [° C]	Viscosity [mPa s ⁻¹]	Dielectric constant
EC	36.4	248	1.93	89.78
PC	-48.8	242	2.52	64.92
DMC	4.6	91	0.589	3.107
EMC	-53	110	0.648	2.958
DEC	-74.3	126	0.753	2.805

	MF	-100	32	0.325	8.69
le	MA	-98	57	0.364	6.864
C	MP	-88	80	0.481	6.07
	EA	-84	77.1	0.423	6.05
	EP	-73	99.2	0.492	5.717
	MB	-84	102.8	0.539	5.432
	EB	-98	121.5	0.639	5.0046
)t(РВ	-95.2	143	0.832	4.3
	BB	-91.5	166	0.977	4.39
S	DME	-58	85	0.417	7.55
C	DOL	-95	78	0.588	7.34
	TEGDME	-45	216	3.31	7.79

DIOX	11.8	101	1.20	2.226
DMSO	18.5	189	2.02	46.64
SF	27.6	285	11.5	44
AN	-44	82	0.369	35.95

In addition to the solvents listed in Table 1, a number of novel solvents were also developed recently for low-temperature applications. Lu et al.^[69] explored 2,2,2-Trifluoroethyl N-caproate (TFENH) as a new co-solvent for low and high-temperature applications of LIBs, which increases the ionic conductivity and reduces the viscosity of electrolytes. A thin and stable SEI on the surface of graphite was demonstrated to reduce charge-transfer resistance and improve the cycling stability of LIBs. At a discharge current rate of 0.2 C, graphite anode with 0.75 M LiPF₆ EC/EMC/TFENH (15:60:25 by vol.) electrolyte maintained 92% of RTC at -50 °C.^[70] Liu et al.^[71] prepared a ternary mixture of 3-(2methoxyethoxy) propanenitrile(G1-CN), FEC and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl (F-EPE) with 1 M LiPF₆ salt as a non-flammable and low-temperature electrolyte. At -20 °C, the graphite || LMO cells with the G1-CN/F-EPE/FEC (10:30:60) electrolyte exhibited a reversible capacity of 52.9 mAh g⁻¹, corresponding to 57.1% of RTC. Due to the high dipole moment and low viscosity for facile Li-ion transport, isoxazole (IZ) solvent doubled the ionic conductivity compared to that of EC/EMC electrolytes at a temperature range of -20 to 20 °C.^[72-74] Coupled with FEC/EC cosolvent and lithium difluoro(oxalato)borate (LiDFOB) salt, IZ-based electrolyte (1 M LiDFOB FEC/IZ, 1:10 by vol.) exhibited an ionic conductivity of ~10 mS cm⁻¹ at -20 °C, in which the graphite anode demonstrated a high reversible capacity of 187.5 mAh g^{-1} at 0.1 C and -20 °C.

Since the function of the electrolytes is based on the solvents dissociating salts, determining the freezing point, ionic conductivity and SEI forming capability, the electrochemical and physical

properties of the solvents play a critical role in the low-temperature LIBs. Overall, no solo solvent could satisfy all the requirements for low-temperature batteries as discussed above. Yet, the merit for the electrolytes is that "cocktail strategy" could be applied in blending the electrolyte to maximize the electrochemical performance of the batteries, especially when coupled with the lithium salts and additives.

2.2. Lithium Salts for organic low-temperature electrolytes

In addition to "cocktail optimized" solvents with different ratios, Li salts critically affect the lowtemperature performance of electrolytes *via* altering the dissociation degree and SEI-formation capability of the anions. As the most commonly used salt in non-aqueous electrolytes, LiPF₆ would decompose into LiF and PF₅, forming LiF-rich SEI and also passivating of Al current collector on cathodes. However, its sensitivity to H₂O by forming HF, which destabilizes the anode and cathode, results in capacity fading during battery cycling.^[7,75] Therefore, as the alternatives of LiPF₆, new salts are intensively explored to further enhance the low-temperature performance of electrolytes.

The electrolyte of 1 M LiAsF₆ EC/EMC/MA/tol(1:1:1:1) exhibited 1.8 mS cm⁻¹ at -40 °C and 1 mS cm⁻¹ at -50 °C.^[65] EC/DMC/EMC/PC (15:37:38:10) containing 0.9 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) displayed a promising overall performance over the temperature ranged from -30 to 70 °C,^[30] which is worthy of further optimization. Besides, Zhou et al.^[76] prepared lithium pentafluoroethyltrifluoroborate (Li[C₂F₅BF₃], LiFAB) *via* a facile metathesis reaction. Compared to LiPF₆, LiFAB-containing electrolyte showed a low ionic conductivity (~8 mS cm⁻¹) at RT but a higher ionic conductivity of 2 mS cm⁻¹ at -40 °C due to the weaker coordinating ability of FAB⁻. Zhao et al.^[77] revealed that the addition of LiNO₃ to LiFSI-DOL transforms the electrolyte to a highly correlated but amorphous state, which led to high ionic conductivity of 1 mS cm⁻¹ at -50 °C.



Figure 6. (a) The correlation between the ionic conductivity (mS cm⁻¹) and LiTFSI concentration (M) for DOL-DME-TEGDME-based electrolytes at different temperatures from -40 to 60°C. Reproduced with permission.^[78] Copyright 2019, Hindawi. (b) Ionic conductivities of electrolytes with LiPF₆, LiTFSI, LiBF₄, and LiClO₄ salts in various carbonate-based solvents at temperatures ranging from -40 °C to 60 °C. Reproduced with permission.^[79] Copyright 2010, The Electrochemical Society.

Over a wide temperature range (-40 to 60 °C), the LiTFSI salt at 1.0-1.4 M exhibited the highest ionic conductivity in mixed ether solvents, including 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), and TEGDME (**Figure 6**a),^[78] which is the compromise of solvent viscosity, salt solubility and dissociation degree. Compared with the electrolytes containing LiPF₆, LiTFSI, and LiClO₄, LiBF₄-based electrolytes exhibit the lowest ionic conductivity at RT but a much slower downtrend as temperature decreases (Figure 6b).^[79] It should be pointed out that the ionic conductivity of electrolytes is not a decisive factor for the low-temperature performance of LIBs, providing that it could support the sufficient Li⁺ transport between the electrodes.^[80] Even though LiBF₄-based electrolyte possesses lower conductivities than LiPF₆ counterpart (0.9 vs. 1.5 mS cm⁻¹ at -20°C, 1 m (mol kg⁻¹ solvent) salt in EC/DMC/DEC, 1:1:1 by wt.), it breeds a decimated charge-transfer resistance for the charged graphite|| lithium nickel-based oxide full cells. The full cells with the electrolyte of 1 M LiBF₄ in PC/EC/EMC (1:1:3 by wt.) retained 86% of RTC at -30 °C, while the corresponding value was 72% for LiPF₆-based electrolyte.^[17] Although LiBF₄-based electrolytes showed great potential for low-

temperature LIBs, some features, including hydrolysis susceptibility, relatively low ionic conductivity, and inefficient SEI-formation capability, hindered its wide applications.^[81] To address these issues, LiBOB was proposed to improve SEI formation and thus effectively promoted graphite cycling at low temperatures.^[82] Yet, the poor solubility in linear carbonate solvents and relatively high viscosity of solutions restricted the extensive use of LiBOB in low-temperature LIBs.^[83] Combining the good ionic conductivity of LiBF₄ and decent SEI-formation capability from LiBOB, electrolyte using LiBF₄–LiBOB (90:10 by mole) salt mixture in PC/EC/EMC ternary solvents enhanced the cycling performance and rate performance of Li||LFP cells in a wide temperature range of -50 to 90 °C.^[84] The Li||LFP cell delivered up to 100 mAh g⁻¹ at 1 C and -10 °C and possessed improved rate performance in this bi-salts electrolyte.

LiDFOB synergistically combined the pros of LiBF₄ and LiBOB because of its chemical structure containing the half-molecular moieties of both, which helped lower the SEI/charge transfer resistances and maintained the robust SEI even with a high concentration of PC in a wide temperature range from -30~60 °C.^[85,86] Yang et al.^[87] designed 1.0 M LiDFOB PC/EC/EMC electrolyte to reduce the R_{ct} and enhance the low-temperature performance of NCM111 cathode. At -30 °C, the Li||NCM111 cells with LiDFOB-based electrolyte maintained 86% of RTC. Coupled with a series of sulfone and sulfite solvents (we will discuss their role in the following chapters), the reversible capacity of Li||LFP cells with 0.9 mol L⁻¹ LiDFOB sulfolane (SF)/ dimethyl sulfite (DMS) (1:1 by vol.) electrolyte remained 29.0% of RTC at -40 °C,^[88] corresponding to four times of that for LiPF₆ EC/DMC electrolytes. The Li||LFP cell with 0.9 mol L⁻¹ LiDFOB SF/diethyl sulfite (DES) electrolyte also showed decent cycling stability and rate performance at low temperatures.^[89] However, the low-temperature performance of pure LiDFOB based electrolytes was still not satisfactory due to the continuing SEI formation at low temperatures, leading to a high interface resistance. To address this issue, blended salts with LiDFOB were adopted to ameliorate the low-temperature performance. Compared with LiPF₆ EC/DEC/DMC/EMC electrolyte, the dual-salt electrolyte of 0.9 mol L⁻¹ LiDFOB/LiBF₄ (5.365:1 by wt.) EC/DMS/EMC (1:1:3 by vol.) showed a slightly lower but acceptable ionic conductivity of nearly 1 mS cm⁻¹ at -40 °C.^[90] At -20 °C, Li||LFP cells with dual-salt electrolyte showed 89.4% of RTC at -20 °C and retained 94.57% of the initial capacity after 50 cycles, in contrast to 53.7% and 46.03% for LiPF₆-based electrolyte, respectively. Zhang et al. studied the low-temperature performance of LiBF₄/LiDFOB dual-salt electrolytes with

different ratios in a wide temperature range.^[91] Due to the larger anionic radius and better ionic dissociation with solvents, electrolytes with LiDFOB showed increased ionic conductivities compared with pure LiBF₄-based electrolytes. LCO cathodes with LiBF₄/LiDFOB (8:2) PC/EC/EMC (1:1:3) + 5%FEC electrolyte exhibited an excellent cycling stability by presenting high capacity retention of 98.67% at - 20 °C after 300 cycles. Shangguan et al.^[92] synthesized lithium trifluoro(perfluoro-tertbutyloxyl)borate (Li[(CF₃)₃COBF₃], LiTFPFB) with bulky anion and investigated the low-temperature electrochemical behaviors of dual-salt electrolytes with LiTFSI in PC/EC/EMC. The addition of LiTFPFB effectively mitigated Al foil corrosion and suppressed the Li dendrites. At -20 °C and 0.1 C, NCM523 LMBs with electrolyte containing 1 M (LiTFSI)_{0.6}-(LiTFPFB)_{0.4} and 0.05 M LiPO₂F₂ additive presented a high capacity of 101.3 mAh g⁻¹ (93.7% of RTC) and retained a capacity of 96.8 mAh g⁻¹ (91.4%) after 50 cycles.

The anions of lithium salts exert substantial influences on the low-temperature performances of the cells, mainly due to the following three specific reasons: i) the anion derived SEI, ii) the dissociation degrees, and iii) possible parasitic reactions. Future new salt explorations or existing salt blends should balance these three features to ensure low interfacial resistance, high electrolyte conductivity and good interfacial stability.

2.3. Additives for organic low-temperature electrolytes

The adoption of additives is the most convenient and economical method to improve the performance of commercial LIBs and is highly accepted by the industry.^[93] Generally, the content of an additive in the electrolyte is at most 5% (wt.% or vol.%). The improvement of low-temperature performance for LIBs by additives has been intensively investigated recently. Due to the low freezing point and high dielectric constant, PC-based electrolytes showed great potential for low-temperature applications, yet the graphite exfoliation caused by PC co-intercalation hindered its possible applications. Recent investigations indicated that the exfoliation could be tackled by some film-forming additives.^[94,95] Sulfur-based additives (*e.g.*, 1,3,2-dioxathiolane-2,2-dioxide (DTD) and its derivatives) with smaller lowest unoccupied molecular orbital (LUMO) than that of PC can be reduced above the PC co-intercalation potential, forming a Li₂SO₃ and ROSO₂Li-riched protective film.^[96-101] Allyl sulfide (AS)-

added electrolytes were demonstrated to be spontaneously decomposed on the surface of soaked graphite and form a sulfur-containing inner layer SEI, which facilitated the charge-transfer process at low temperatures.^[102] Besides, the addition of 2 wt.% AS could also suppress Li plating, further enhancing the low-temperature performance of cells. Guo et al.^[103] reported that the graphite || NCM523 pouch cells with carbonate electrolyte (1 M LiPF₆ EC/EMC, 1:2 by wt.) containing 0.5 wt.% DMS exhibited superior low-temperature performance, outperforming the commercialized DTD additive (Figure 7a). The reduction products from DMS had a weak combination with Li⁺, which helped to form a more anion-derived SEI than that formed by DTD reduction. Phenyl methanesulfonate (PhMS) additive showed a similar film-forming capability to enhance the lowtemperature electrochemical behavior of graphite | NCM523 cells.^[104] Wotango et al. investigated the film-forming mechanisms on MCMB anode using an additive combination of 4-chloromethyl-1,3,2dioxathiolane-2-oxide (CMDO), EC, and FEC in 1.0 M LiPF₆ PC/DMC (1:1 by vol.) electrolyte.^[105] The MCMB half-cells with the electrolyte containing these additives (2 vol.% CMDO, 3 vol.% EC, and 5 vol.% FEC) presented significantly improved cycling performance with high initial Coulombic efficiencies (iCEs) of 77%, 92.5% at -10°C and RT, respectively. Such improvement was related to the high decomposition voltage of CMDO, which led to the formation of SEI with an inner layer containing sulfate derivatives (e.g., ROSO₂Li, Li₂SO₃, Li₂S, Li₂O, etc.), thus creating a thin, compact and Li-ion conductive SEI. Xu et al.^[106] blended an electrolyte with MA, tris(trimethylsilyl) phosphite (TMSP) and 1,3-propanediolcyclic sulfate (PCS) additives to enable a 5 V high-voltage LIB for a wide operation temperature range from -60 °C to 50 °C. Owing to the lower LUMO, the TMSP and PCS additives alleviated the reductive decomposition of MA and carbonate solvents by forming a high ionic conductive and stable SEI on the surface of MCMB anode (Figure 7b). At 0.3 C and -5 °C, MCMB||LiNi_{0.5}Mn_{1.5}O₄ (LNMO) cell with the electrolyte (BE (EC/DEC/EMC, 1:1:1 by vol.) + MA (same vol. as BE) +1 wt.% TMSP + 1 wt.% PCS) delivered an initial capacity of 101.7 mAh g^{-1} (99.7% retention of RTC), which is much higher than the cell without additives (74.3% of RTC) and with BE/MA (70.5% of RTC).

Additives with fluorine groups could induce a thin and compact SEI layer with low resistance, therefore functioning well in low-temperature batteries. Difluoromethyl acetate (MFA) was reported to decompose on the surface of graphite to form a robust SEI, which prevents Li⁺ co-intercalation

effectively.^[94] Besides, evidenced by EIS technique, cells with MFA (1.0 M LiClO₄ EC/DEC/PC/MFA, 1:1:1:0.15 by vol.) showed improved charge-transfer kinetics. Liao et al.^[107] investigated the effect of FEC addition on the low-temperature performance of MCMB. Compared with the baseline electrolyte (EC/PC/EMC, 1:3:8 by vol.), a stable and highly Li*-conductive SEI was formed with 2% FEC addition upon the initial cycling, which facilitated the migration of Li* through SEI and thus promoted the electrochemical performance at low temperatures. The LUMO of fluorosulfonyl isocyanate (FI, -0.6182 eV) is much lower than those of EC (0.1306 eV) and DMC (0.0683 eV), which leads to a higher reduction potential (2.8 V vs. Li/Li*) than commonly used carbonate solvents.^[108] As a result, FI dominates the formation of SEI, which consists of an inorganics-rich inner layer and a thin organic outer layer. The low interfacial resistances due to the robust SEI boost the low-temperature and rate performance of the graphite anode. Polydimethylsiloxane (PDMS)-based copolymers such as poly[dimethylsiloxane-co-(siloxane-g-acrylate)] (PDMS-A), poly(dimethylsiloxane-co-phenylsiloxane)(PDMS-P), and poly[dimethylsiloxane-co-(siloxane-g-ethylene oxide)] (PDMS-EO) were studied as low-temperature additives for LIBs.^[109]

co-(siloxane-g-ethylene oxide)] (PDMS-EO) were studied as low-temperature additives for LIBs.^[109] The addition of PDMS-based additives with high electrochemical stability protects carbonate electrolytes from degradation and freezing, which effectively enhances the capacity retention and rate capability of graphite||LCO cells at low temperatures. Won et al.^[110] reported the joint adoption of PDMA-A (1 wt.%) and lithium-modified silica (1 wt.%) could improve both the room-temperature and low-temperature electrochemical behavior of commercial graphite||LCO cells due to the enhanced interfacial stability. At 0.1 C and -20°C, the electrolyte with these additives maintained higher initial capacity (~110 mAh g⁻¹) and improved 63.4% retention after 50 cycles.

Since SEI/CEI films formed by organic additives generally present low ionic conductivity and high interface impedance of full cells,^[111-114] inorganic salt-type additives were explored to lower the interface impedance. Wu et al.^[115] applied NaCl as a low-temperature film-forming additive for LFP cathode, which facilitates the formation of homogeneous CEI with high Li-ion conductivity for Li⁺ diffusion. The cells with NaCl additive also showed low polarization and improved lithium insertion/desertion kinetics. Li₂CO₃ as a film-forming ingredient for LFP cathode was reported to suppress the continual decomposition of electrolyte and accelerate Li⁺ migration, which led to improved electrochemical performance of Li||LFP cell at -40 °C by retaining 77.2 mAh g⁻¹ at the initial

cycles.^[116] Yang et al.^[117] investigated the effect of lithium difluorophosphate (LiPO₂F₂) on the electrochemical behavior of graphite ||NCM523 cell at low temperatures. The SEI enriched with LiF and Li₂CO₃ exhibited lower R_{ct}. As a result, the cell with 1 wt.% LiPO₂F₂ additive maintained 71.9% and 57.93% of RTC while only 49.4% and 9.6% were observed for cells with the blank electrolyte at -20 °C and -30 °C. Similar effects were also reported for the lithium difluorobis(oxalato) phosphate (LiDFBOP) additive.^[118]

Aforementioned synergetic effects of various additives were manifested incisively in the 0.05 M CsPF₆-containing 1 M LiPF₆ EC/PC/EMC electrolyte (baseline electrolyte).^[119] The co-addition of 0.5% FEC, tris(trimethylsily) phosphite (TTMSPi), and PS in baseline electrolyte helped to build highly conductive and dense CEI/SEI on the surface of cathodes (NCM or NCA) and anode (graphite), leading to superior cycle stability and improved low-temperature performance. Jones et al.^[120] investigated the effects of additives in the ester-rich electrolyte at low temperatures, including VC, LiBOB, LiDFOB, propane sultone (PS), and lithium bis(fluorosulfonyl)imide (LiFSI). Among these additives, LiFSI functions best. At a current density of 0.2 C and charge cut-off of 4.1 V, it was not until -40 °C that graphite||NCA cells with an electrolyte (1.0 M LiPF₆ EC/EMC, 1:1 by vol.). By contrast, cells with an electrolyte displayed Li-plating at ~-10 °C due to the increased SEI resistance. Representative low-temperature additives were summarized in **Table 2**, most of which take effects *via* building low resistant and high ionic conductive SEI/CEI layers on electrodes and endowing the electrolytes with low-temperature features.



Figure 7. (a) A comparison of the low-temperature cycling performance and corresponding possible SEI formations of MCMB||NCM811 cells using baseline electrolyte (1.0 M LiPF₆ EC/EMC, 1:2 by wt.), electrolyte with DMS additive and electrolyte with DTD additive. Reproduced with permission.^[103] Copyright 2019, American Chemical Society. (b) The possible working mechanism of TMSP and PCS as functional additives based on XPS analysis. Reproduced with permission.^[106] Copyright 2019, Elsevier.

Table 2. A summary of recently reported additives for improving the low-temperature performance of cells

Classificati	Additive	Baseline	anode cathode	Low-T	Ref.
on	S	electrolyte		Performan	
				ce	
		1.3 M LiPF ₆		-30 °C@0.05 C	
	2 wt.%	EC/EMC/DEC	Li graphite	~60 mAh	Jurng
		(3:2:5, vol.) 1.0 M LiPF₅		g ⁻¹ -10 ℃@0.2 C	et al. ^{[97}
	0.5 wt.%	EC/EMC (1:2,	graphite NCM523	82.13% of	Guo
Solvent	DING	wt.) 1.0 M LiPF ₆		RTC -10 °C@0.2 C	et al. ^{[98}
additives	1 wt.% PhMS	EC/EMC (1:2, wt.)	graphite NCM523	73.8% (50	Lin et al ^{[99}
	2 vol.% CMDO	1.0 M LiPF ₆		-10 °C@0.1 C	Wotan
	3 vol.% EC 5 vol.%	PC/DMC (1:1, vol.)	Li MCMB	~ 230 mAh g ⁻¹ (35	o et

	1 wt.% TMSP	1.0 M LiPF ₆		-5 °C@0.3 C	Xu
	1 wt.% PCS	MA/EC/DEC/EMC (3:1:1:1, vol.)	MCMB LiNi _{0.5} Mn _{1.5} O ₄	101.7 mAh g ⁻¹	et al. ^[101]
		1.0 M LiPF ₆		-20 °C@1 C	Liao
	2 vol.% FEC	EC/PC/EMC	Li MCMB	282.2 mAh g ⁻¹	et
		(1.3.8, VOL) 1.0 M LiPF ₆		C	al.[102]
	1 wt.%	EC/PC/EMC/DEC/VC/F EC		-20 °C@0.1 C	Kim
	PDMS- A	(20:5:55:20:2:5, vol.)	graphite LCO	89% (50 cycles)	et al. ^[104]
	1 wt.% PDMA-A	1.0 M LiPF ₆ EC/PC/EMC/DEC		-20 °C@1 C	Won
	1 wt.%	(20:5:55:20 vol.%) +	graphite LCO	~230 mAh g ⁻¹	et
	Li ₂ 0 ₂	VC (2 wt.%) + FEC (5 wt.%)		cycles)	al. ^[105]
C 1/	4 + 0/	1.0 M LiPF ₆ EC/PC/EMC		-30 °C@0.1 C	Wu
additives	4 wt.% Li ₂ CO ₃	(0.14:0.18:0.68)	Li LFP	51.5% of RTC	et al. ^[111]

Accepted Article

			0 °C@0.1 C	
1 wt %			123.5 mAh g ⁻¹	Yang
LiPO ₂ F ₂	EC/EMC/PC (4:7:1, wt.)	graphite NCM523	96.7% (50 cycles)	et al. ^[112]
1 wt %	1.0 M LiPF_{6}		-30 °C@0.2 C	Liao
LiDFBO P	EC/EMC (1:2, wt.)	graphite NCM523	49% of RTC	et al. ^[113]

2.4 Low-Temperature Organic Electrolytes for High Energy Battery Chemistries

Since the commercialization of LIBs in 1991, their energy density has escalated from ~80 Wh kg⁻¹ to ~280 Wh kg⁻¹, leaving little room for further optimization based on graphite anodes and layered cathodes. Besides, the close potentials between Li metal and graphite fundamentally restricted their low-temperature performance.^[9] Therefore, novel Li battery chemistries are intensively explored recently for low-temperature utilization.^[121] Some of the electrolytes for novel Li battery chemistries are compiled in **Table 3**.

Table 3. Electrolytes for novel low-temperature battery chemistries

Electrolyte categories	Formula	anode cathode	Low-T Performance	Ref.
	0.2 M LiTFSI		-60 °C@0.1 C	
	FM: CO ₂ (5 %)	Li LCO	60.6% of RTC	Meng et al. ^[117]
	1.2 M LiTFSI		-60 °C@1/15 C	
Fluorinated Electrolytes	AN/FM/CO ₂	Li NCM622	45% of RTC	Meng et al. ^[118]
	1.0 M LiPF ₆		-60 °C@0.2 C	
	MTFP/FEC	Li NCM811	133 mAh g ⁻¹	Holoubek et al. ^[15]
	1.28 M LiFSI		-85 °C@1/15 C	
LHCEs	FEC/FEMC– D2	Li NCA	45% of RTC	Fan et al. ^[119]

	5m LiTFSI/EA- DCM (1:4 by vol.)	Li PI	-70 °C@0.2 C	Dong et al. ^[120]
	1 M LiFSI DEE	Li SPAN	-60 °C@0.1 C 76% of RTC	Holoubek et al. ^[16]
ner.	2 mol kg ⁻¹ LiTFSI EA	PNTCDA PTPAn	-40 °C@0.2 C 69% of RTC	Dong et al. ^[121]
	2 M LiPF ₆ MP/FEC	graphite graphite	-60 °C@10 C 61.7% of RTC	Holoubek et al. ^[122]

Due to the highest theoretical specific capacity (3860 mAh g⁻¹) and the lowest electrochemical potential (-3.04 V vs. SHE), Li metal is regarded as the ultimate anode for energy storage systems.^[122] Meanwhile, Li metal anode also shows better low-temperature performance than graphite because of the relatively smaller nucleation barrier. Therefore, intensive investigations are focused on low-temperature LMBs. Meng and co-workers^[22] reported a hydrofluorocarbon-based liquefied gas electrolyte for LMB that showed a wide potential window (-3.23 - 2.47 V vs. Pt) over an extended temperature range from -78 to +65 °C (**Figure 8**a). With CO₂ as film formation additive, the LMB notably delivered a discharged capacity of >80 mAh g⁻¹ even at -60 °C, representing a breakthrough for the ultra-low temperature LMBs, thanks to the extremely low viscosity of fluoro-methane-based electrolyte, as well as the LiF-rich SEI. However, since the overall test was carried out in high-pressure stainless-steel cells, its application in conventional batteries still needs in-depth research. To further broaden the working temperature range, the authors introduced acetonitrile (AN) as a co-solvent and increased the salt concentration to a normal level. The modified liquefied gas electrolyte (1.2 M LiTFSI + 1 M AN in fluoromethane (FM): CO₂ = 19: 1) showed excellent stability to Li anode and enabled

Li||NCM622 cell with decent cycle stability from -60 °C to 55 °C.^[123] Owing to the good electrochemical stability of fluorinated interphases, all-fluorinated electrolytes were formulated to support high voltage LMBs.^[124] Holoubek et al.^[15] designed the electrolyte of 1 M LiPF₆ with a mixture of methyl 3,3,3-trifluoropionate (MTFP)/FEC (9:1 by vol.) for ultra-low-temperature application of LMBs (Figure 8b). The synergistic effect of MTFP with excellent oxidative stability (~5.8 V) and FEC with the good SEI forming capability leads to superior cycling stability for Li||NCM811 cells. At an ultra-low temperature of -60 °C, this electrolyte remained in a liquid state and provided an ionic conductivity of 0.75 mS cm⁻¹, making low-temperature application feasible. Discharge capacities of 161, 149, and 133 mAh g⁻¹ were obtained for Li||NCM811 full cells at -40, -50, and -60 °C, respectively. Li et al.^[125] developed a Li-CO₂ battery with DOL-based electrolytes working at -60 °C because of the electrolyte with low freezing point (-95 °C) and relatively high ionic conductivity (2.26 mS cm⁻¹ at -80 °C). In this work, Iridium was used for gas diffusion layer coating to facilitate CO₂ reduction reaction (CO₂ER), thus promoting the decomposition of the discharge products generated on the cathode. Due to the suppression of the parasite reactions, the cell delivered a stable capacity of ~500 mAh g⁻¹ for 150 cycles at -60 °C.

Ether-based electrolytes with a low Li⁺ desolvation energy show exceptional stability to Li metal anode because of low reduction potential and formation of anion-derived SEI.^[126-128] As a typical ether electrolyte, the DOL/DME-based electrolytes display a decent ionic conductivity in a wide range temperature, yet rampant lithium dendrites formation limits their utilization in low-temperature LMBs as evidenced by the plunged CEs at low temperatures (e.g., 45.4% and 27.5% at -40 °C and -60 °C for 1.0 M LiFSI in DOL/DME). In contrast, diethyl ether (DEE)-based electrolyte exhibited much higher CE retention at low temperatures (98.4% at -60 °C).^[16] This distinct feature is highly related to the solvation structures. The Li-desolvation process in DEE-based electrolytes is much easier than in DME-based electrolytes due to more contact-ion pairs (CIPs) and relatively lower binding energy (-280 kJ mol⁻¹ for Li⁺(DEE)_{1.8} vs. -414 kJ mol⁻¹ for Li⁺(DME)_{2.3}), resulting in lower R_{ct} and more homogenous Li deposition (Figure 8c). Coupled with sulfurized polyacrylonitrile (SPAN) cathode, the full cells kept 76% of the RTC at -60 °C and exhibited stable performance over 50 cycles. It is noted that this work utilized the low-temperature charge protocol, which is rarely reported in LMBs. Thenuwara et al.^[129] investigated the impact of FEC and EC additives on the low-temperature performance of ether-based

electrolytes (0.8 M LiTFSI and 0.2 M LiNO₃ in DOL/DME, 80:20) for LMBs. FEC could partially replace DOL in the first solvation shell of Li-ion, creating the formation of LiF, Li_2CO_3 -riched SEI on lithium metal anode, different from the only LiF for baseline electrolyte. Although the ionic conductivities of LiF and Li_2CO_3 are relatively low, the large space charge accumulation near the SEI tends to enhance the carrier concentration and Li-ion transport,^[130,131] thus leading to the formation of large Li particles as well as kinetics improvement at low temperatures.



Figure 8. (a) CV profiles of liquefied gas electrolytes at RT and low temperatures of -60 °C. Reproduced with permission.^[22] Copyright 2017, Science. (b) Schematic of F-rich interphases enabled all-fluorinated ester electrolytes operating at high-voltage and ultra-low temperatures. Reproduced with permission.^[15] Copyright 2020, American Chemical Society. (c) Schematic of low binding energy enabled facile desolvation and homogenous Li deposition in DEE-based electrolytes at low temperatures. Reproduced with permission.^[16] Copyright 2021, Nature.

As mentioned above, the sluggish Li⁺ desolvation process was believed to be the key hindrance to the low-temperature performances of LIBs.^[40,132,133] Therefore, reducing the Li⁺ desolvation energy is distinctly effective to improve the low-temperature performance. Low desolvation energy of Li+solvent could be achieved in localized high-concentration electrolytes (LHCEs) by adding non-polar or less-polar solvents. Li⁺ desolvation energy with solvents is correlated to the electrostatic potentials between them, as well as the chemical hardness of solvents.^[128] LHCEs could inherit the strong features of the HCEs (good stability to the cathodes, superior SEI formation capability, etc.), and meanwhile discard the shortcomings of the HCEs (high viscosity, high freezing points, etc.).^[134] Besides, by adding non-polar solvents, the overall affinity between the solvents and the Li⁺ could be reduced and therefore decrease the desolvation energy. Fan et al.^[23] introduced non-polar solvents tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane (D2) and methoxyperfluorobutane (M3) to all-fluorinated electrolytes, realizing the low-temperature applications of high-voltage Li-metal battery. The two electrolytes (1.28 M LiFSI FEC/FEMC-D2 and 0.7 M LiBETI FEC/DEC-M3) exhibited high ionic conductivity (>1×10⁻² mS cm⁻¹) at -80 °C and ultra-low freezing point (-125 °C and -132 °C, respectively). The low desolvation energy (Figure 9a, b) and LiF-rich SEI ensures the excellent cycling stability of Li||NCA batteries with a CE of 99.4% at RT and a discharged capacity of 56% RTC at -85 °C. Superior low-temperature performance was also demonstrated in the LHCE using 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluropropyl ether (TTE) as the dilute solvent .^[135] To conquer the narrow electrochemical window of EA (1.5~4.7 V vs. Li/Li⁺), LHCE was formulated using Dichloromethane (DCM, CH₂Cl₂) as the diluent.^[24] The LHCE 5 m LiTFSI EA/DCM (1:4 by vol.) presents a high ionic conductivity (0.6 mS cm⁻¹), low viscosity (0.35 Pa s) and a wide potential window (0~4.85 V) at -70 °C, endowing the Li | polyimide batteries with a high energy density of 178 Wh kg⁻¹ and superior rate performance as well as lowtemperature charging capability.

The kinetics of the low temperatures cell could be maximized if the Li⁺ do not experience the desolvation reactions. Dong et al.^[136] reported an organic electrodes-based battery using the low-temperature electrolyte of 2 mol kg⁻¹ LiTFSI EA with the 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA) as anode and polytriphenylamine (PTPAn) as cathode (Figure 9c). Differing from the conventional LIBs, the solvated Li⁺ could de/intercalate into the

organic electrode as a whole without desolvation on account of the surface groups and large interstitial space of the organic anode. As a result, the all-organic batteries with a rate of 5 C (*i.e.* 0.5 A g_{PTPAn}^{-1}) delivered a reversible capacity of 56 and 18 mAh g⁻¹ at -40 °C and -70 °C, corresponding to 64% and 21% of RTC, respectively (Figure 9d). Holoubek et al.^[137] designed a dual-graphite battery, where the desolvation barrier was theoretically avoided by decoupled solvation and desolvation (Figure 9e). MP was chosen to be the main solvent due to its low freezing point, while 10% of FEC was added to the electrolyte to stabilize the formed surface film on the anode and cathode. The prepared electrolyte of 2 M LiPF₆ MP/FEC(10%) exhibited an ionic conductivity of 1.50 mS cm⁻¹ at -60 °C, much higher than that of commercial electrolytes. The double-ionic batteries (DIB) showed superior low-temperature performance by maintaining 93.1% and 84.4% of RTC at -40 °C and -60 °C, respectively. When the rate was increased to 10 C, the cell still retained 61.7% of RTC at -60 °C. However, the energy density of DIBs is still limited since both of the stored Li⁺ and anions in the anodes and cathodes are from the electrolyte.^[138]



Figure 9. (a) Schematic of solvation structure of LHCEs and b) calculated Li⁺ solvation/desolvation energies in various electrolytes. Reproduced with permission.^[23] Copyright 2019, Nature. (c) Schematic of full cells with PTPAn cathode and PNTCDA anode and (d) the electrochemical performance of the

all-organic battery at a wide range of temperatures from -70 to 50 °C. Reproduced with permission.^[136] Copyright 2018, CellPress. (e) Operational schematics of graphite ||graphite dual-ion full-cells. Reproduced with permission.^[137] Copyright 2019, Wiley-VCH.

Lithium-sulfur (Li-S) batteries are expected to satisfy the growing demand for energy storage due to the high theoretical energy density (2600 Wh/kg), low cost, and environmental friendliness.^[139,140] However, conventional Li-S cells could only maintain 27% of RT capacity at -10 °C,^[141] which hinders the wide temperature range applications. It is reported that electrolyte containing 86:14 (by vol.) of DOL:DME might be a better choice for Li-S batteries instead of conventional one with 1:1 (by vol.).^[142] Ryu et al. introduced low freezing point additives of 1,3-dioxolane (DOXL) and MA to tetra(ethylene glycol) dimethyl ether (TEGDME) and improved the low-temperature electrochemical behavior of Li-S batteries.^[141] Cells with the optimum electrolyte formula of MA/TEGDME/DOXL (5:47.5:47.5) showed the lowest charge-transfer resistance and highest discharge capacity of 993 mAh g⁻¹ at -10 °C (74% of RTC).

2.5 Low-temperature Aqueous Electrolytes

Due to the higher safety and greater ionic conductivity compared with carbonate electrolytes, aqueous electrolytes were investigated to overcome the relatively high freezing point to meet low-temperature operation requirements. Ramanujapuram et al.^[143] tested the electrochemical behavior of LIBs with LCO cathode and aqueous electrolytes at subzero temperature. The melting point of the aqueous solution decreases substantially to between -45 and -50 °C for 16 mol kg⁻¹ LiCl, between -20 and -30 °C for 9 mol kg⁻¹ LiNO₃, between -30 and -35 °C for 3.5 mol kg⁻¹ Li₂SO₄, respectively. Compared to conventional organic electrolytes (1.0 M LiPF₆ EC/DEC), better low-temperature properties were achieved for LCO in the LiCl-saturated aqueous electrolytes, delivering 72% and 12% of RTC at -40 °C and -45 °C, respectively (**Figure 10**a). The dramatically reduced capacity at -45 °C is due to the significant increase of bulk electrolyte resistance and charge transfer resistance (R_{ct}) at the temperature close to freezing point. Nian et al.^[144] revealed that the intermolecular hydrogen bonds
Accepted Articl

(HBs) between dimethyl sulfoxide (DMSO) and water prevent the formation of HB grids among water molecules in ice crystals. As shown in Figure 10b and c, the freezing point of the aqueous solution containing DMSO (30% by mol) critically reduced to -130 °C (salt-free) and below -150 °C (saltcontaining), and the corresponding electrolyte showed a decent ionic conductivity, which is beneficial for ultra-low-temperature batteries. DMSO as an additive could also significantly improve the lowtemperature performance of other alkali (Na, K)-ion batteries. Tron et al.^[145] added antifreeze additive ethylene glycol (EtG) to aqueous electrolytes (1 M Li₂SO₄) for LIBs. The addition of EtG decreased the ionic conductivity of mixtures and expanded the electrochemical window but improved the chargetransfer process at low temperatures. LFP exhibited a capacity of ~90 mAh g⁻¹ at -10 °C and 1 C using electrolyte with 20 wt.% EtG, while the baseline electrolyte could not function due to the high freezing point of -4.6 °C. Chen et al.^[146] introduced acetonitrile (AN) to "water-in-salt electrolyte" (WiSE), which could exclude water molecules from the inner-Helmholtz layer of both anode and cathode, forming a protective SEI before water decomposition and expanding the electrochemical stability window to the range of 4.5 V (Figure 10d). The introduction of AN with low viscosity and low freezing point (-48 °C) extended the liquid temperature range, which supported its low-temperature application. The LTO||LMO full cells with AN-WiSE containing 15.3 mol kg⁻¹ LiTFSI delivered a capacity of 110 mAh g⁻¹ after 120 cycles at 0 °C, id est, 95% of RTC.



Figure 10. (a) Cycling performance of LCO using various aqueous and carbonate-based electrolytes at the temperature down to -45 °C, the rate was 0.2 C and 0.05 C. Reproduced with permission.^[143] Copyright 2018, Wiley-VCH. (b) differential scanning calorimetry (DSC) profile of water after adding 30% DMSO and (c) the temperature dependence of ionic conductivities of the 2 M NaClO₄ in pure H₂O (2M-0), H₂O/DMSO (2M-0.3, the molar ratio of DMSO is 3), and pure DMSO (2M-1) electrolytes. Reproduced with permission.^[144] Copyright 2019, Wiley-VCH. (d) The electrochemical stability windows of various high-concentration electrolytes and the physical state at low temperatures (0 and -20 °C, the insert figure). Reproduced with permission.^[146] Copyright 2020, Wiley-VCH.

2.6 Low-temperature Ionic Liquid Electrolytes

lonic liquids (ILs) with a wide operating temperature range are regarded as potential electrolytes for improving the low-temperature performance of LIBs.^[147,148] Due to the stable property and remarkable electrochemical performances, TFSI⁻-based ionic liquids were deeply studied for possible low-temperature applications,^[147,149-151] some of which display decent low-temperature ionic

conductivities and have been listed in Table 4. Some data about the ionic conductivity of pure ionic liquids without Li salts are also covered in Table 4. Fujie et al.^[152] combined (1-ethyl-3methylimidazolium) EMI-TFSI and MOF $(Zn(MeIM)_2, H(MeIM) = 2-methylimidazole, ZIF-8)$, creating a composite electrolyte with a higher ionic conductivity than bulk EMI-TFSI at low temperatures. Aguilera et al.^[153] introduced conventional electrolytes to N-butyl-N-methylpyrrolidinium (Pyr₁₄)-TFSI, leading to a similar conductivity to that of carbonate-based electrolytes at RT and a decreased freezing point. Similarly, Li et al.^[154] blended IL-decorated polymethyl methacrylate (PMMA) nanoparticles with a mixture of PC and MA containing 1 M LiTFSI, which exhibited an ionic conductivity of 0.915 mS cm⁻¹ at -40 °C. A stable and effective SEI film was observed on the surface of LTO anode, and reversible capacities of 107, 84, and 48 mAh g⁻¹ were obtained for Li||LTO cells at 0 °C, -20 °C, -40 °C, respectively. Xu et al.^[155] developed [BMIM][I]/[EA][N]/water/Lil mixture electrolytes, in which the hydrogen bonding donor (Water and [EA][N])-acceptor (iobide) network provided a much lower glass transition temperature (T_g, below -107 °C). Serving as a film-forming additive, EMI-BF₄ could decompose on the surface of both anode and cathode, constructing a stable and low-resistance SEI/CEI.^[156] Graphite || NCM523 cells with 1% EMI-BF4 exhibited a capacity retention of 93.8% after 150 cycles at -10 °C, while cells with blank carbonate electrolytes showed only 82.3% retention. In general, the ionic conductivity of IL-based electrolytes is highly related to the viscosity, which is largely affected by the sizes of anions and cations, as well as the strength of the electrostatic force between the anions and cations.^[157] Imidazolium-based ILs usually show a low viscosity and considerable high conductivity because of the relatively small cations.^[158,159] In addition, other factors should be considered when applying IL-based electrolytes for low-temperature applications. For example, the imidazolium-based ILs containing symmetric cations usually show higher melting points than those containing asymmetric cations.^[160] And the influence of anions and cations on the electrochemical window and Li⁺ transference number of the electrolytes should also be noticed.^[161,162]

Accepted Articl

Table 4. A summary of the low-temperature ionic conductivities for some ILs electrolytes

	Table 4. A summary
\mathbf{O}	Electrolytes
	0.3 M LiTFSI Pyr ₁₄ TFSI/I
ti	0.9 M LiTFSI DE
	0.8 m LiTFSI [EC:DMC]₀
	1 M LiTFSI PMM
C C	[BMIM][I]/[EA][N]/water/L
pt	(Pyr ₁₃ FSI) _{0,568} (Pyr
	EMI-TESI@7IE-
U U	
	2.7 Low-Temperatur Although the de

Electrolytes	Low-T ionic conductivities	Ref.
.3 M LiTFSI Pyr ₁₄ TFSI/PC (20%)	0.5 mS cm ⁻¹ at -40°C	Kühnel et al. ^[145]
0.9 M LiTFSI DEME-TFSI	0.8 mS cm ⁻¹ at 0°C	Sato et al. ^[146]
0.8 m LiTFSI [EC:DMC] _{0.24} [Pyr ₁₄ TFSI] _{0.76}	~1 mS cm ⁻¹ at 0 $^{\circ}$ C	Aguilera et al. ^[148]
M LITFSI PMMA-IL-TFSI/PC-MA	0.915 mS cm ⁻¹ at -40 °C	Li et al. ^[149]
BMIM][I]/[EA][N]/water/Lil	$\sim 1 \text{ mS cm}^{-1}$ at -40 °C	Xu et al. ^[150]
Pyr ₁₃ FSI) _{0.568} (Pyr ₁₄ TFSI) _{0.432}	0.1 mS cm ⁻¹ at -40 °C	Kunze et al. ^[142]
EMI-TFSI@ZIF-8	~0.1 mS cm ⁻¹ at 0 °C	Fujie et al. ^[147]

2.7 Low-Temperature Solid-State-Electrolytes

Although the development of all-solid-state batteries is a possible solution to improve the LIBs' safety, contacting issues between active materials and SSEs become more prominent at low temperatures. Therefore, it is difficult for all-solid-state batteries to achieve acceptable capacity at

low temperatures.^[163,164] Instead, polymer electrolytes, semi-solid electrolytes or gel electrolytes with high flexibility are more practical for low-temperature batteries than all-solid-state ones. In order to prevent the trapping of Li⁺ by three hydroxyl (-OH) of starch, Lin et al.^[165] developed an SSE host of y-(2,3-epoxypropoxy)propytrimethoxysilane (KH560) and boron (B) co-cross-linking with starch (B-Starch-Si, BStSi). Compared with PEO-based SSEs, much higher ionic conductivities of 0.123 mS cm⁻¹ and 0.03 mS cm⁻¹ were obtained for BStSi-based SSEs (50 wt.% LiTFSI mixed) at 0 °C and -20 °C, respectively. The LillLFP cells with the designed BStsi-SSE showed a high capacity of 113.8 (94.7% of RTC) and 55.9 mAh g⁻¹ (46.5% of RTC) after 200 cycles at 0 °C and -20 °C, respectively. The long cycle life under the low-temperature condition should be due to the small Li-ion transfer impedance and a compatible interface between the electrolyte and electrodes. Zhu et al.^[166] grafted trifluoromethanesulfonyl (Tf) into the UiO-66-NH₂ framework to form the metal-organic framework (MOF)-based single-ionic conducting SSE. The flexible electrolyte membrane was fabricated by adding 30% LiTFSI and 20% PVDF into the host (PL/UiOLiTFSI). Since the movement of Tf was anchored in the host, a high Li⁺ transference number of 0.84 was obtained. At 0 °C, Li||LFP cells with this electrolyte delivered a capacity of 56 mAh g⁻¹ at a current rate of 2 C and could restore to ~120 mAh g⁻¹ when returned to 0.1C. In addition, nearly 100% Coulombic efficiencies and high capacity retention (98.6% for 90 cycles at 0.2 C, 95.4% for 120 cycles at 0.5 C and 91.1% for 500 cycles at 1 C) were obtained. Due to the low production cost and high tap density, microsized Si is believed to be promising anode material for next-generation high energy density LIBs.^[126,167] Recently, Meng and co-workers reported that stable operation of microsized Si anode could be achieved by sulfide solid electrolytes.^[168] Unlike the conventional liquid electrolytes, solid-state electrolyte does not permeate through the porous microsized Si (μ Si) electrode and the interfacial contact area between the electrode and electrolyte is always two-dimensional. This strategy greatly reduced the continuous interfacial growth and irreversible lithium loss, leading to excellent cycle stability. In addition, the μ Si||NCM811 full cells with Li₆PS₅Cl electrolyte could also deliver ~40% of RTC at a low temperature of -20 °C.

Sufficiently high ionic conductivity is the prerequisite for the operation of low-temperature LIBs/LMBs. **Figure 11** compared ionic conductivities of a few typical electrolytes. If the effective Li-ion conductivity is above 0.1 mS cm^{-1[31]}, the ionic conductivity will not be a limiting factor. However, a higher ionic conductivity of electrolytes can reduce the cell polarization.





3. Electrodes for low-temperature batteries

3.1 Anodes

Graphite Considering the flat intercalation potential, favorable capacity, and long cycle life, graphite is undoubtedly the most successful anode material. However, as mentioned above, the intrinsic drawbacks of graphite, such as poor Li diffusion kinetics in the interlayers, relatively large interfacial resistance, and low intercalation potential, always restrict its applications in low-temperature conditions due to Li plating on graphite.^[170,171]

Reduction of lithiation overpotential and suppression of Li plating are critical for use of graphite in low-temperature batteries. Mild oxidation of graphite is a commonly used method to reduce the lithiation overpotential of graphite anodes. After thermal treatment^[172] or oxidation with concentrated nitric acid solution^[173], graphite usually exhibited better cycling performance at low temperatures, originating from the reduction of unsaturated carbon atoms at the edge planes, the decline of particle size, the creation of nanovoids, nanochannels, as well as the formation of chemically bonded SEI. The mildly oxidized graphite after mixing with 1 wt.% nanometric metal particles (Cu, Al, Sn) could deliver 30% of theoretical capacity at -30 °C and 0.2 C due to the catalytic effect of the metal in Li⁺ desolvation process.^[174,175] At -30 °C, compared with the pristine oxidized graphite electrode, oxidized graphite with Sn coating and dispersed Sn delivered a capacity of 152 and 94 mAh g⁻¹, respectively. This nanometal enhancement was echoed by Marinaro et a.^[176,177], who demonstrated copper nanoparticles on Super-P carbon (Cu/Super-P) as conductive additive effectively prompted the low-temperature performance of graphite and LTO anodes. Al₂O₃ coating on the graphite anode could also help to improve the low-temperature performance of graphite *via* Li-plating prevention.^[178]

The particle size reduction and structure modification are also effective methods to improve the low-temperature performance of graphite.^[179,180] Thin graphite sheets with through-holes (porous graphite nanosheets, PGN) and carbon nanotube (CNT) are good examples, which could shorten the diffusion path effectively.^[180] The dominant mesopores and micropores in PGN-CNT anodes facilitate the Li⁺ transport and lead to superior rate and low-temperature performance (**Figure 12** and b). The cell with the electrolyte of 0.75 M LiTFSI 1,3-dioxane (DIOX) retained 90% of capacity after 500 cycles at 4 C and RT and delivered 300 mAh g⁻¹ at 0.1 C and -20 °C. Raccichini et al.^[181] synthesized multilayer

crystalline graphene (GRAL) by ionic liquid-assisted microwave exfoliation of expanded graphite (Figure 12c). High surface area enabled a high-efficiency electrochemical reaction, as evidenced by the 3-4 times higher capacity for GRAL than commercial graphite at -30 °C (Figure 12d). Zhao et al.^[182] prepared the expanded meso-carbon microbeads (EMCMB) by oxidizing MCMB. The EMCMB with increased interlayer distance delivered a capacity of 130 mAh g⁻¹ and 100 mAh g⁻¹ at -10 °C and -40 °C, respectively.



Figure 12 (a) SEM images of PGN-CNT and (b) its electrochemical performance at high rates and low temperatures with DIOX-based and commercial electrolytes. (a) and (b), Reproduced with permission.^[180] Copyright 2019, Elsevier. (c) TEM images of GRAL anode and (d) the electrochemical comparison with SLP30 anode at -30 °C and 0.05/0.1 A g⁻¹. (c) and (d) Reproduced with permission.^[181] Copyright 2015, Elsevier.

Metal and Metal Oxide Anodes Spinel LTO has a theoretical capacity of 175 mAh g⁻¹ and superior cycling reversibility due to its SEI-free feature and zero volume change during the (de)lithiation process.^[41,183-185] As a result, LTO anodes were of particular interest for possible low-temperature applications. Yet, the low intrinsic electronic conductivity and sluggish interfacial reactions lead to

poor low-temperature performance.^[186-188] Recently, a combined strategy by decreasing the particle size and modifying the electrolyte-electrode interface was reported to improve the low-temperature performance of LTO.^[189-193] For example, the low-temperature performance for LTO was substantially improved after mixing with rutile TiO₂ (RTO).^[192,193] The pristine LTO could maintain 55.48% of RTC at 0.5 C and 43.62% of RTC at 1 C and -40 °C, while the LTO-RTO composite exhibited improved capacity retention of 69.7% and 51.6% under the same condition due to the shortened Li⁺ diffusion path. Huang et al.^[194] synthesized hierarchical porous dual-phase LTO-TiO₂ (HP LTO-TO) via a topochemical conversion method (Figure 13a-c). The morphology of ultra-thin nanosheets facilitated the Li⁺ intercalation reactions and reduced the electron/ion diffusion path. Compared with the capacity of 167 mAh g⁻¹ at RT, HP LTO-TO composites exhibited capacity retentions of 85.6%, 77.8%, and 56.3% at 0 °C, -10 °C, and -40 °C, respectively. However, this design of hierarchical porous structure critically reduced the energy density of the full cell. Zhang et al.^[195] effectively improved rate capability and low-temperature capacity of LTO after NH₄F etching. The NH₄F pre-treatment enlarged the surface area, induced the LiF formation on the surface, as well as enhanced the electronic/ionic conductivity via partial cation reduction from Ti⁴⁺ to Ti³⁺. As a result, the NH₄F pre-treat LTO exhibited much higher capacity retention of 63.3% at -40 °C, (vs. 40.0% for pristine LTO). Besides, the introduction of F effectively suppressed the gas generation by preventing the side reactions between anodes and electrolytes/moistures. Combined with low Li⁺ desolvation energy solvent DIOX, Xu et al.^[196] realized ~60% of RTC for nano-LTO anode at -80 °C, representing as one of the best low-temperature LTO anodes.

Special structures were designed for LTO to improve the low-temperature performance. Hu et al.^[197] reported a binder-free LTO electrode with aligned CNT nanosheets and Ag decorating. Benefiting from the high exposed surface area of LTO (aligned CNT nanosheets replaced the conventional binder) and low solvation energy for Li⁺ with DIOX-based electrolyte, LTO delivered a reversible capacity of 140 mAh g⁻¹ at 0.2 C and -60 °C, corresponding to 85% of its RTC. Zou et al.^[198] synthesized one-dimensional Li_{3.9}Cr_{0.3}Ti_{4.8}O₁₂ nanofibers and evaluated its lithium storage performance at a high rate and low temperatures. The nanofiber structure improved the Li⁺ diffusion, while high Ti³⁺ concentration and *in situ* Li₂CrO coating enhanced the intraparticle and interparticle electronic conductivities. The synergistic promotion from nanostructure and coating endows LTO a high capacity of 140 mAh g⁻¹ (10

C) and 91 mAh g⁻¹ (50 C) at RT, and a high capacity of 100 mAh g⁻¹ at 1 C and -20 $^\circ\text{C}$

Apart from the LTO anode mentioned above, other intercalation or alloying anodes were optimized for possible low-temperature applications. Marinaro et al.^[199] prepared nanosized rutile TiO₂ via a sol-gel method from an ethylene glycol-based titanium-precursor in the presence of a nonionic surfactant. The nano-TiO₂ was able to reversible insert/extract 0.7, 0.4 and 0.25 mol Li (1 mol equals 341 mAh g⁻¹) within the potential window of 0.1-3.0 V at 0 °C, -20 °C and -40 °C, respectively. Zhang et al.^[200] coupled (LiAlTiP)_xO_v and polyaniline as ionic conductors to decrease R_{ct} and increase the low-temperature capacity of the nano-Sn anode. Compared with the limited capacity (<100 mAh g^{-1}) of the pristine nano-Sn, nano-Sn-polyaniline-(15 wt.%) (LiAlTiP)_xO_v exhibited a reversible capacity of 545 mAh g⁻¹ at 5 mA g⁻¹ and -20 °C. Similar enhancement strategies for alloying anodes were also reported by Nobili et al.^[201], and Yan et al.^[202] Varzi et al.^[203] prepared Zn-rich porous Cu-Zn alloys as the anode materials using the dynamic hydrogen bubble template method (Figure 13d, e). The asprepared Cu₁₈Zn₈₂ anode presented a decent rate performance and cycling stability at -10 °C by delivering a capacity of 238 and 167 mAh g⁻¹ at 0.05 and 1 A g⁻¹, respectively. Compared with graphite composite anodes, amorphous monolithic columnar silicon anodes were reported to exhibit little capacity decay in 1.0 M LiPF₆ FEC/DMC (1:4 by wt.) electrolytes at -30 °C, which could be a promising material for the low-temperature applications.^[204]



Figure 13. (a) Schematic representation of the synthesis of HP LTO-TO and (b) its SEM image and (c) the low-temperature electrochemical performance using half cells at temperatures ranging from -40 – 25 °C. Reproduced with permission.^[194] Copyright 2018, Royal Society of Chemistry. (d) Schematic representation of the synthesis of Cu-Zn alloy anode and (e) the corresponding low-temperature performance at -20/-30 °C compared with commercial graphite. Reproduced with permission.^[203] Copyright 2018, Wiley-VCH.

3.2 Cathodes

Although cathodes are unlikely to be the critical factor for the low-temperature operation of LIBs, the large overpotential at low temperatures will require the electrolytes to have a high voltage stability thus have adverse impact on low-temperature operation. In general, solid-solution type cathodes (such as NCM) exhibit better low-temperature performance than phase-transformation counterparts (such as LFP), although both of these cathodes follow intercalation/deintercalation mechanisms.^[205]

Layered Oxide cathode Previous investigations indicated that high Li⁺ intercalation/deintercalation kinetics within the layered cathodes, such as LCO cathode^[143] and LMO cathode,^[68] were sufficient to support the operation of LIBs at low temperatures (e.g., -60 °C). Therefore, facilitating the interfacial reactions via particle size reduction and/or surface engineering are the main directions to further enhance the low-temperature performance of layered oxide cathodes. Sun et al.^[206] synthesized spherical NCM622 with controllable particle size, nanostructure, specific surface area, and pore distributions. Both the small particle size and the porous nanorod structure of the modified cathode improve the low-temperature performance. The spherical cathode (3 µm-size in diameter) delivered a capacity of 157 mAh g⁻¹ at 180 mA g⁻¹ and retained nearly 100% of initial capacity after 300 cycles at 0 °C. The AIF₃ coating prevented the attack of HF to the cathode and suppressed the parasitic reactions between electrolyte and cathode, leading to a stable R_{et} during the charge/discharge cycling.^[207] The AlF₃-coated NCA not only exhibited higher capacity (123 mAh g⁻¹ vs. 113 mAh g⁻¹ for un-coated NCA), better rate performance (62% vs. 54% capacity retention at 5 C) at RT, but also possessed good capacity retention at -10 °C without capacity loss at the first 20 cycles. As a reference, the uncoated NCA lost 14% of capacity after 20 cycles at the same test conditions. Sun et al.^[208] grafted NCM622 with benzenediazonium tetrafluoroborate ($C_6H_5N_2^+BF_4^-$) to form a polyphenylene-coated NCM622 and enhance the low-temperature performance (Figure 14a). At -20 °C, the polyphenylene-coated NCM622 delivered a capacity of 148 mAh g⁻¹ and 105 mAh g⁻¹ at rates of 0.1 C and 1 C, respectively. Full cells with the coated NCM622 cathode and exfoliated graphene (EG) anode exhibited excellent low-temperature cycling stability without capacity loss after 300 cycles at -30 °C (Figure 14b).^[209] Doping heteroatoms could also improve the cycling performance of layered oxide cathodes. At -20 °C, Ti-doped NCM111 cathode exhibited a discharging capacity of 122.4, 101.8, 78.5, and 51.3 mAh g⁻¹ at 0.1, 0.2, 1, and 5 C, in contrast to 118.8, 96.3, 67.7, and 30.1 mAh g⁻¹ of the pristine cathode, respectively.^[210] Ti doping at/near surface layer of NCM significantly altered the lattice parameters and reduced the impedance during the charge/discharge process, resulting in the enhancement of low-temperature electrochemical properties.

Owing to the high capacity of >250 mAh g⁻¹, the lithium-rich layered oxides (LLOs) cathodes have also been extensively studied at low temperatures recently.^[211-215] Takahashi et al.^[216] studied the electrochemical properties of LLOs at high and low temperatures. Both Mn and Ni atoms could

reversibly migrate from transition metal (TM) sites to lithium sites during the charge process in Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O₂ at high temperatures, which could provide vacancies for Li⁺ diffusion. However, such migration would become irreversible at low temperatures (-10 °C), which limits the Li⁺ diffusion and leads to fast capacity decay. The lithiated $Li_{1+x}(Co_{1/3}Ni_{1/3}Mn_{1/3})_{1-x}O_2$ cathode exhibited good compatibility with carbonate-based electrolyte even when the temperature decreased to less than -30 °C.^[217] High content of EC and high salt concentration improve the electrochemical performance of the cathode at RT but behave opposite at low temperatures with the demarcation line of -20 °C. Similar results were also reported by Li et al. in Li[Li_{0.2}Co_{0.4}Mn_{0.4}]O₂.^[218] Almost all Mn⁴⁺ can be activated at RT, but only a few can be achieved at -20 °C, resulting in relatively low capacity. Similar to the original layered oxide cathode, doping and surface coating could help improve the LLOs' lowtemperature performance.^[219,220] Li and Mo were introduced into NCM111 to form Li_{1+y}[Ni_{(1-x)/3}Mn₍₁₋ $_{x)/3}Co_{(1-x)/3}Mo_x]O_2$.^[220] Slight doping of Li (Li: M = 1.16, M = Ni_{(1-x)/3}Mn_{(1-x)/3}Co_{(1-x)/3}Mo_x) promoted the formation of ordered structure and enhanced the electrical conductivity, yet it would cause fast capacity decay once over-doping. At -30 °C, the cathode (Mo/M = 0.02, Li/M = 1.16) delivered a capacity of 65.41 mAh g⁻¹ at 750 mA g⁻¹ (5 C). Zhao et al.^[221] coated 2 wt.% AlF₃ onto Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ cathode to accelerate Li⁺ transport between adjacent particles and prevent side reactions between electrolyte and active materials. Paired with lithium metal anode, the coated Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ showed a doubled capacity retention (~45% vs. 20%) compared with the pristine cathode. The in situ formed LiAlO₂ on the cathode surface plays a critical role in the enhancement of electrochemical properties.



Figure 14. (a) The schematic of the preparation of polyphenylene/LNCM-3 cathode and the corresponding (b) low-temperature performance at 25, -10 and -20 °C, (c) EIS comparison of LNCM-3 between the pristine LNCM-3 and Polyphenylene/LNCM-3. Reproduced with permission.^[208] Copyright 2019, Wiley-VCH.

Lithium iron phosphate LiFePO₄ has been commercialized and widely utilized in EVs due to its good thermal stability, and low cost.^[222-226] Nonetheless, the pristine LFP presents inferior low-temperature and rate performance due to the deficient electronic conductivity of ~10⁻⁹ S cm⁻¹ ^[227] and poor Li⁺ diffusivity of ~10⁻¹⁴-10⁻¹⁶ cm² S⁻¹.^[228-231] Extensive work has focused on enhancing the electron/ion transport of LFP cathodes to improve the electrochemical performance at low temperatures. Particle size reduction and surface coating are proved to be the most effective methods. The reduced particle size of cathodes effectively improves the kinetics and low-temperature performance by shortening the diffusion path of electron and Li⁺ and providing a large specific surface area for the insertion/extraction of Li⁺.^[232-236] 80 nm LFP/C was synthesized by the sol-gel method using polyvinylpyrrolidone (PVP) and citric (**Figure 15**a).^[232] The nano-sized LFP/C displayed a high initial capacity of 126 mAh g⁻¹ (approximately 78.8% of RTC) and 97% of capacity retention after 500 cycles at -20 °C. Carbon coating not only improves the electrical conductivity but also significantly elevates

the interphase stability by reducing the side reactions.^[237-243] Zhou et al.^[243] employed spherical polystyrene as the carbon source to form a uniform carbon-coating on LFP. The derived LFP with 3.0 wt.% C showed the best low-temperature performance among all the coated LFP due to the increased electrical contact and shorter Li⁺ diffusion path. At -20 °C, LFP-3.0 wt.%C delivered an initial capacity of 147 mAh g⁻¹, 32 mAh g⁻¹ at 0.1 C and 5 C respectively, and maintained almost 100% of capacity retention after 100 cycles at 1 C. Zheng et al.^[244] reported a thin carbon-coated nano-LFP synthesized by using Tween60-Span60 composite as the surfactant and carbon source (Figure 15b). Surfactants help prevent the diffusion of reactants and the growth of LFP. As a result, the coated LFP displayed a capacity of 90.7% and 78.4% of RTC at 0.1 C at 0 °C and -20 °C, respectively. In addition to carbon, metals and other conductive materials were also utilized as coating ingredients to enhance the electronic conductivity of LFP.^[245-248] Ti₃SiC₂ (TSC) with high electrical conductivity (like metals) and superior mechanical property (like ceramics) was reported to modify the LFP/C composite in order to improve the low-temperature electrochemical performance.^[249] TSC and carbon co-coating shortened the diffusion path of Li⁺ and reduced polarization, resulting in significant enhancement of lowtemperature kinetics (Figure 15c). The 4 wt.% TSC coating LFP/C exhibited best cycle stability and rate performance at low temperatures, delivering 82.8% of RTC and maintaining 97% of initial capacity after 100 cycles at -20 °C. Xie et al.^[250] prepared spherical LFP with core/shell structure via coating polyacene (PAS), a specific planar conductive polymer with P-bond character. The LiFePO₄-PAS composite can reach a high electrical conductivity of a magnitude of 10 S cm⁻¹ and a higher tap density than the irregular sample (1.6 vs. 1.2 g cm⁻²). The as-prepared LFP@PAS delivered an initial capacity of 112 mAh g⁻¹ at 0 °C, *id est* 85% of RTC. Fluoflavin redox polymer (P1) displayed an oxidation potential of 3.7 V and a reduction potential of 3.3 V (vs. Li/Li⁺), sandwiching the potential of LFP (~3.4 V). Therefore, P1 could serve as an electrochemical mediator to accelerate the charge/discharge of LFP (Figure 15d). The charging capacity for LFP/P1 composite was around 80 mAh g⁻¹ compared with 50 mAh g⁻¹ for blank LFP at 30 C.^[251]

Accepted Articl



Figure 15. (a) Schematic of the preparation of nano-LFP/C and the corresponding SEM, TEM images. The low resistance and the enhanced low-temperature/rate performance are demonstrated by EIS

and Galvanostatic cycling. Reproduced with permission.^[232] Copyright 2013, Elsevier. (b) Schematic of the preparation of uniformly thin carbon-coated nano-LFP and the SEM images. Compared with the pristine sample, the LFP/C-TS showed greatly improved low-temperature and high-rate performance with greatly decreased resistance demonstrated by EIS. Reproduced with permission.^[244] Copyright 2015, Elsevier. (c) Schematic and SEM image of TSC-coating LFP/C. The corresponding low-temperature electrochemical properties of samples with various content of TSC are also shown. Reproduced with permission.^[249] Copyright 2015, Elsevier. (d) Schematic of ultrafast LFP cathode realized by the introduction of the redox mediator. SEM image of P1-coating LFP. CV profiles and high-rate performance of P1-coating LFP and the greatly reduced charge-transfer resistance. Reproduced with permission.^[251] Copyright 2020, American Chemical Society.

In addition to directly coating carbon or other conductive materials on LFP, 3D conducting network was also proposed to improve the electrical conductivity and low-temperature performance.^[253-256] Wu et al.^[257] combined carbon coating with graphitized conductive carbon to improve the low-temperature performance of nanoparticles LFP. Compared with pristine LFP, LFP@C, and LFP/CNT, dual-carbon modified LFP showed improved charge/discharge stability and high capacity retention of 71.4% RTC at -25 °C. Yang et al.^[258] synthesized LiMn_{0.8}Fe_{0.2}PO₄/C with DMSO assisting and PVP as an anti-agglomeration agent. The nano PVP-LMFP/C exhibited decent low-temperature properties with discharging capacity of 97 mAh g⁻¹ and a high capacity retention of 97% after 50 cycles at 0.1C at -15 °C. Li₃V₂(PO₄)₃ (LVP) with higher ionic and electrical conductivity was introduced to LFP together with graphene-like carbon coating.^[259] As reported, the 0.9LFP·0.1LVP@G was able to deliver a capacity of 118.4 mAh g⁻¹ at -20 °C at 0.2C.

By selective doping multi-valent cations into LFP, Li-deficient solid solutions with good electronic conductivity could be formed.^[260-262] $Li_{0.99}La_{0.01}Fe_{0.9}Mg_{0.1}PO_4/CA$ cathode was synthesized by doping plus carbon aerogel (CA) coating. La^{3+} and Mg^{2+} co-doped LFP/carbon aerogel (CA) exhibited excellent low-temperature cycling stability and rate capability, delivering a capacity of 120.3 mAh g⁻¹ (1 C) and 85.4 mAh g⁻¹ (10 C) at -20 °C.^[263] Li et al.^[262] investigated the effect of Ti doping on the low-temperature performance of LFP/C. The appropriate Ti⁺ doping reduced the size of primary particles, while the

surface carbon network increased the electrical conductivity. Such cathode materials exhibited a discharge capacity of 122.3 mAh g⁻¹ at 1 C and -20 °C, maintaining 76.3% of RTC. Some of the representative low-temperature electrochemical performances of LFP were summarized in **Table 5**.

Table 5. A summary of strategies for LFP to improve low-temperature performance

strategies	Electrolytes	Electrode configuration	Low-T Performance ^a	Ref.
	1.0 M LiPF ₆		-20 °C@0.1 C	
Nanosized	EC/DMC	nano-LFP/C	120 mAh g ⁻¹	Huang et al. ^[218]
	1.0 M LiPF ₆		-20 °C@0.1 C	
Carbon	EC/DMC/DEC/EMC	LFP-3 wt.% C	147 mAh g ⁻¹	Zhou et al. ^[229]
coating	1.0 M LiPF ₆		-20 °C@0.1 C	
coating	EC/DMC	LFP/C	78.4% of RTC	Zheng et al. ^[230]
	1.0 M LiPF ₆		0 °C@3 C	
Metal	EC/DMC	LFP/C-Sn	78 mAh g ⁻¹	Lin et al. ^[233]
	1.0 M LiPF ₆		-20 °C@0.1 C	
coating	EC/DMC	LFP/C-Ti ₃ SiC ₂	116 mAh g ⁻¹	Cai et al. ^[235]
	1.0 M LiPF ₆		0 °C@1 C	
	EC/EMC	LFP-PAS	112 mAh g ⁻¹	Xie et al. ^[236]

Wu et al.^[110]

Xie et al.^[239]

Yang et

al.^[240]

Yao et al.^[241]

Fan et al.^[242]

Zhang et

al.^[249]

Yang et

al.^[244]

Lv et al.^[247]

Li et al.^[248]

-25 °C@0.2 C

71.4% of RTC

-20 °C@0.1 C

124.4 mAh g⁻¹

-20 °C@10 C

78 mAh g⁻¹

-40 °C@0.1 C

87 mAh g⁻¹

-40 °C@0.5 C

~120 mAh g⁻¹

-20 °C@10 C

85.4 mAh g⁻¹

-15 °C@0.1 C

97 mAh g⁻¹

0 °C@10 C

86 mAh g⁻¹

-20 °C@1 C

122.3 mAh g⁻¹

LFP@C/CNT

LFP@Graphene

nanofibers

LFP/KB

LFP@carbon cage

LFP@coral-like

graphene

LFP/CA

La&Mg doping

nano-LiMn_{0.8}Fe_{0.2}PO₄/C

LiFe_{0.95}V_{0.05}PO₄/C

LFP/C Ti doping

		1.0 M LiPF ₆
		EC/EMC/DEC
		1.0 M LiPF ₆
		EC/DMC
()	conductive	
	polymers	1.0 M LiPF ₆
		EC/DMC
	3D	
	e otra alla	1.0 M LiPF ₆
	network	EC/DMC/EMC
r		1.0 M LiPF ₆
		EC/DMC/DEC/EMC
		1.0 M LiPF ₆
tec		1.0 M LiPF ₆ EC/DEC
otec		1.0 M LiPF ₆ EC/DEC
ptec		1.0 M LiPF ₆ EC/DEC 1.0 M LiPF ₆
eptec		1.0 M LiPF ₆ EC/DEC 1.0 M LiPF ₆ PC/EC/DEC
eptec	Multi-valent	1.0 M LiPF ₆ EC/DEC 1.0 M LiPF ₆ PC/EC/DEC
ceptec	Multi-valent	1.0 M LiPF ₆ EC/DEC 1.0 M LiPF ₆ PC/EC/DEC
ceptec	Multi-valent metal doping	1.0 M LiPF6 EC/DEC 1.0 M LiPF6 PC/EC/DEC
cceptec	Multi-valent metal doping	1.0 M LiPF ₆ EC/DEC 1.0 M LiPF ₆ PC/EC/DEC -
Accepted	Multi-valent metal doping	1.0 M LiPF6 EC/DEC 1.0 M LiPF6 PC/EC/DEC - 1.0 M LiPF6
Accepted	Multi-valent metal doping	1.0 M LiPF ₆ EC/DEC 1.0 M LiPF ₆ PC/EC/DEC - 1.0 M LiPF ₆ EC/DEC

^{a)} half cells with Li metal as the counter electrode

This article is protected by copyright. All rights reserved.

54

Other cathodes Thanks to the lower activation energy of Li⁺ intercalation in LVP than that in LFP,^[264] LVP cathode exhibits intrinsically better low-temperature performance. Carbon-coating further improves the low-temperature performance of LVP. ^[265-269] Some of the representative LVP/C cathodes are listed in **Table 6**. Qin et al.^[268] prepared pure phase LISICON structured LVP (r-LVP) *via* a Na-Li ion-exchange process. The fast 3D Li⁺ transport channel ensures the fast Li⁺ diffusion within r-LVP/C. As shown in **Figure 16**, r-LVP/C presented an initial capacity of 82 mAh g⁻¹ and 84% capacity retention after 5000 cycles at -10 °C and a current rate of 10 C. Tai et al.^[269] prepared a glucose/CNT modified LVP cathode. With the electrolyte of 1.2 M LiPF₆ in EC/DMC/EMC (1:1:1 by vol.) containing vinylene carbonate (VC) and propylene sulfite (PS) additives, the Li||LVP@CNT delivered a capacity of 116.2, 108.2, 103.7, 96.3, and 86.1 mAh g⁻¹ at -20 °C under the current rates of 0.5, 1, 2, 5, and 10 C, respectively. In addition, 97% of capacity retention after 300 cycles at -20 °C was realized, demonstrating the high low-temperature cycling stability. As the universal methods to promote the low-temperature performance, particle size reduction and surface coating are also applicable for V₂O₅,^[270] Se,^[271] Ni-based Prussian blue,^[272], *etc*.



This article is protected by copyright. All rights reserved.

Figure 16. (a) The advantages, (b) the low-temperature (ranging from -30 to 25 °C) rate (from 0.2 to 30 C) performance and (c) the long-term cycling stability of r-LVP at low temperatures (0 and -20 °C) at 10 C. Reproduced with permission.^[268] Copyright 2018, Royal Society of Chemistry.

Table 6. A summary of strategies for LVP modification to enhance the low-temperature performance

Electrolytes	Electrode configuration	Low-T Performance ^a	Ref.
		-30 °C@0.2 C	
1.0 M LIPF ₆ EC/DEC/DMC (1:1:1, vol.)	LVP/C	105.7 mAh g ⁻¹	Liu et al. ^[251]
1.0 M LiPF ₆ EC/DEC (1:1, vol.)		-20 °C@0.1 C	
	LVP/C	118.9 mAh g ⁻¹	Qiao et al. ^[252]
		-20 °C@0.2 C	
1.0 M LiPF ₆ EC/DMC (1:1, vol.)	LVP/C	120.7 mAh g ⁻¹	Teng et al. ^[253]
		97.2% (80 cycles)	-
1.0 M LiPF ₆ EC/DEC/DMC (1:1:1, vol.)		-30 °C@0.2 C	
	r-LVP	90 mAh g⁻¹	Qin et al. ^[254]
1.2 M LiPF ₆ EC/DMC/EMC (1:1:1, vol.) +VC&PS additive		-20 °C@10 C	
	LVP/CNT	86.1 mAh g ⁻¹	Tai et al. ^[255]

^{a)} half cells with Li metal as the counter electrode

4. Other strategies for low-temperature batteries

Due to the high cell resistance at low temperatures, substantial electrical energy of the LIBs would convert to thermal energy when a current is applied. Therefore, the heat generated by the electrochemical process can be potentially used for the internal heating of the batteries.^[273] The effective utilization of internal heat can be optimized through the modification of the battery structure.

Wu et al.^[274] investigated the relationship among the discharge rate, heating time, and power consumption during constant-current discharge (CCD). Both the heating time and the power consumption decreased exponentially as the discharge rate increased. Under a 2C discharge rate, the commercial 18650 LIBs were heated from -10 °C to 5 °C in 280 s with less than 15% power consumption. When a 1 C current was applied, the heating time increased to 1080 s and the power consumption reached 30%. Wang et al.^[12] firstly reported a novel LIB structure with a self-heating module to achieve a controllable temperature by embedding a thin nickel foil inside the cell (Figure 17a), representing a breakthrough for the low-temperature battery configuration without changing the battery chemistries. This module possessed a certain resistance and acted as an internal heating device, which could warm the cell from -30 °C to 0 °C within 30 seconds by consuming only 5.5% of cell capacity. Under an external environment of -30 °C, the so-called "all-climate" battery (ACB, or selfheating lithium-ion battery, SHLB) can deliver a discharge/regeneration power of 1061/1425 W kg⁻¹ at a 50% SOC. In the designed cell, one of the tabs of nickel foil is electronically connected to the anode terminal, welded to the negative tabs, while the other tab is extended to the outside of battery to form the activation terminal (ACT). The working mechanism of ACB is shown in Figure 17b.^[275] The surface temperature of the cell controls the switch connecting of ACT. At low temperatures the switch remains closed, which allows electrons to flow through the metal foil, thus generating large amounts of Ohmic heat to internally warm up the whole battery. Once the cell surface temperature reaches the target value, ACT switches to open, and the heating process will be terminated. In this case, the current bypasses the metal foil, and the battery can be used as a traditional LIB without the disruption of its performance. In the preheating process of ACB, the heat mainly originated from the Ohmic heat of metal foil, accounting for 78% of the overall cell heat generation on average.^[276] Zhang et al.^[277] studied the uniformity of the internal temperature of the battery during the heating process. Due to the insufficient heat transferring, the cell exhibited a large temperature gradient from the metal foil

to the cell surface vertically. For example, when the outer surface temperature of the battery reached 0 °C at the end of preheating, the internal metal foil has been 30 °C, which caused uneven current distribution and an increase in heating time and power consumption. Yang et al.^[276] added more nickel foils in the battery and formed a multi-sheet SHLB to abate the temperature gradient (Figure 17c). With this method, less than 5 °C temperature difference could be achieved from nickel foil to the outer surface of the cell. Three-sheet SHLB showed an increased heating efficiency by decreasing 30% of heating time and 27% of power consumption. Lei et al.^[278] further proposed an intermittent SHLB heating method of periodical activation and deactivation, which was proved more efficient to decrease the temperature gradient from 10-11 K to 2-3 K. Compared to conventional low-temperature batteries, the rapid heating feature of such design makes the SHLB battery performance more prominent due to: (1) the preservation of fast charge/discharge performance at low temperatures. After the short preheating time, a 9.5 Ah 170 Wh kg⁻¹ SHLB structure cell can be charged to 80% SOC in 15 min at a low temperature of -50 °C.^[279] (2) Improved cycle life without Li plating. Due to the mild temperatures within the SHLBs, lithium plating is fundamentally eliminated. Such lithium plating-free battery withstood 4500 cycles at 3.5 C with <20% of capacity fade at 0 °C.^[279] As a promising lowtemperature LIB, SHLB exhibited rapid preheating progress, low power consumption, long cycle lifespan and high-rate ability.

Similarly, Song et al.^[280] proposed a self-heating strategy by utilizing engineered black plasmonic air electrodes, which can effectively harvest solar energy and convert it into heat for all-solid-state lithium-air batteries in harsh environments. Under solar light irradiation conditions, the cell resistances could be significantly reduced even at -73 °C, and the corresponding lithium-air batteries showed a decent cycle performance, representing an innovative photothermal strategy for lithium-air batteries operating at low-temperature conditions.



Figure 17. (a) The schematic of self-heating "all-climate" batteries. Reproduced with permission.^[12] Copyright 2016, Nature. (b) The working mechanism of self-heating "all-climate" batteries. Reproduced with permission.^[275] Copyright 2016, Elsevier. (c) Sketch of multi-sheet designs for self-heating lithium-ion battery with two-sheet design (left) and three-sheet design (right). Reproduced with permission.^[276] Copyright 2016, Elsevier.

5. Conclusion and Outlook

In summary, the recent research progress on low-temperature Li-ion/metal batteries, including both the underlying mechanisms and promising strategies, has been reviewed comprehensively. A consensus has been reached that four crucial challenges significantly restrict the performance of LIBs at low temperatures: (1) the decline of wettability and ionic conductivity of electrolytes; (2) slow interfacial reaction kinetics including Li⁺ desolvation, charge transfer, and Li⁺ transport in SEI; (3) sluggish Li⁺ diffusion in electrodes; (4) Li plating on the anode surface, which may cause "short circuits". To overcome these tough issues, promising strategies are proposed: (i) rationally tailoring solvents, lithium salts, and additives to elevate the low-temperature ionic conductivities, reduce the

desolvation energy and form thin inorganic-rich SEI; (ii) doping, surface coating as well as electrodestructure design, *etc.* to boost the Li⁺ diffusion; (iii) suppressing Li plating on anodes and Li dendrite growth; (iv) other strategies, such as self-heating and/or battery configuration optimization, to enhance the low-temperature performance.

With decades of efforts dedicated to low-temperature Li batteries, remarkable progress has been achieved. Some scientific or/and engineering challenges remain to be unveiled, leaving a broad room for future developments. Some critical frontiers are envisioned as follows:

(1) It is vital to deeply understand the interfacial processes within LIBs/LMBs as the temperature decreases, including the Li⁺ desolvation, diffusion crossing SEI, charge transfer and inside/outside the bulk of electrode particles. Some advanced *in situ* characterization methods and theoretical calculations may help to gain atomic-level knowledge of these processes, such as *in situ* Raman, nuclear magnetic resonance, cryo-electron microscopy, *etc.* Special attention should be given to the desolvation process, which is recognized as the main culprit for the sluggish kinetics at low temperatures recently.

(2) Exploring advanced low-temperature electrolytes is one of the most effective methods for commercial battery chemistries. The low-temperature electrolytes should have a high ionic conductivity at low temperatures, low desolvation energy to reduce the charge-transfer resistance and form inorganic-rich SEI, which can suppress Li plating and dendrite growth at low temperatures due to the low activation energy and high interface energy against Li of inorganic SEI. In the commercial LIBs configurations, Li⁺ conductivity, areal specific resistance (ASR) of SEI, and the graphite interfacial resistance at low temperatures dominate the performance of the LIBs, all of which are highly related to the electrolytes. How to balance the desolvation energy, freezing temperature, ionic conductivity and ASR of SEI should be the hot topics for low-temperature LIBs. Inorganic-rich SEI showed a low ASR due to the high ratio of ionic conductivity to electronic conductivity of LiF. In addition, inorganic-rich SEI is highly lithiophobic, which suppresses the Li dendrite growth even if Li is deposited on the graphite surface at low temperatures. Therefore, inorganic-rich SEI is preferred for low-temperature electrolytes.

(3) Building novel battery chemistries, in which the solvated Li⁺ participate in the reactions as a whole without desolvation, is also a promising direction for maximizing the low-temperature performance. Yet, the energy density should be carefully considered for these new chemistries.

Accepted Article

(4) Engineering innovations on battery configuration are also possible or even more feasible shortcuts to improve the low-temperature performance, and therefore should be paid attention to. Effective utilization of the heat generated in battery operation can help the battery to operate in a favorable temperature range at low external temperatures. How to arrange the heating configurations to minimize the cost and maximize the effect is the crux of engineering innovations.

With the optimization of the electrolytes, special design of electrode materials, plus the configuration of cell structure, the working temperature range of Li batteries has been extensively widened. Some of the batteries have satisfied the application requirements at low (-20 - -40 °C) or ultra-low (such as < -60 °C) temperature conditions, although sacrificing some other properties. We believe that the target-oriented low-temperature Li batteries will profit from the niche market as the technology advances.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (22072134), Natural Science Foundation of Zhejiang Province (LZ21B030002), the Fundamental Research Funds for the Zhejiang Provincial Universities (2021XZZX010), the Fundamental Research Funds for the Central Universities (2021FZZX001-09), and "Hundred Talents Program" of Zhejiang University. This work was partially supported by the Assistant Secretary for Energy Efficiency and Renewable Energy,

Vehicle Technology Office of the U.S. DOE through Applied Battery Research for Transportation (ABRT) program under contract No. DE-SC0012704.

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

References

- [1] J. Hou, M. Yang, D. Wang, J. Zhang, *Adv. Energy Mater.* **2020**, 10, 1904152.
- [2] M. Armand, J. M. Tarascon, *Nature* **2008**, 451, 652.
- [3] M. R. Palacin, Chem. Soc. Rev. 2009, 38, 2565.
- [4] B. Scrosati, J. Hassoun, Y. K. Sun, *Energy Environ. Sci.* **2011**, 4, 3287.
- [5] L. Lu, X. Han, J. Li, J. Hua, M. Ouyang, J. Power Sources **2013**, 226, 272.
- [6] R. Schmuch, R. Wagner, G. Horpel, T. Placke, M. Winter, *Nat. Energy* **2018**, 3, 267.

[7] G. Zhu, K. Wen, W. Lv, X. Zhou, Y. Liang, F. Yang, Z. Chen, M. Zou, J. Li, Y. Zhang, W. He, *J. Power Sources* **2015**, 300, 29.

- [8] A. Gupta, A. Manthiram, *Adv. Energy Mater.* **2020**, 10, 2001972.
- [9] A. Fly, I. Kirkpatrick, R. Chen, *Appl. Therm. Eng.* **2021**, 189, 116750.
- [10] G. Nagasubramanian, J. Appl. Electrochem. **2001**, 31, 99.
- [11] W. Wu, S. Wang, W. Wu, K. Chen, S. Hong, Y. Lai, *Energy Convers. Manag.* 2019, 182, 262.

[12] C. Wang, G. Zhang, S. Ge, T. Xu, Y. Ji, X. Yang, Y. Leng, *Nature* **2016**, 529, 515.

[13] T. A. Stuart, A. Hande, J. Power Sources 2004, 129, 368.

[14] M. C. Smart, B. V. Ratnakumar, R. C. Ewell, S. Surampudi, F. J. Puglia, R. Gitzendanner, *Electrochim. Acta* **2018**, 268, 27.

[15] J. Holoubek, M. Yu, S. Yu, M. Li, Z. Wu, D. Xia, P. Bhaladhare, M. S. Gonzalez, T. A. Pascal, P. Liu, Z. Chen, ACS Energy Lett. 2020, 5, 1438.

[16] J. Holoubek, H. Liu, Z. Wu, Y. Yin, X. Xing, G. Cai, S. Yu, H. Zhou, T. A. Pascal, Z. Chen, P. Liu, *Nat. Energy* **2021**, 6, 303.

[17] S. S. Zhang, K. Xu, T. R. Jow, *Electrochem. Commun.* **2002**, 4, 928.

[18] J. Qin, Q. Lan, N. Liu, Y. Zhao, Z. Song, H. Zhan, *Energy Storage Mater.* **2020**, 26, 585.

[19] T. Waldmann, M. Wilka, M. Kasper, M. Fleischhammer, M. Wohlfahrt-Mehrens, *J. Power Sources* **2014**, 262, 129.

[20] E. J. Plichta, M. Hendrickson, R. Thompson, G. Au, W. K. Behl, M. C. Smart, B. V. Ratnakumar,
 S. Surampudi, J. Power Sources 2001, 94, 160.

[21] S. S. Zhang, K. Xu, T. R. Jow, J. Power Sources 2003, 115, 137.

[22] C. S. Rustomji, Y. Yang, T. K. Kim, J. Mac, Y. J. Kim, E. Caldwell, H. Chung, Y. S. Meng, *Science* **2017**, 356.

[23] X. Fan, X. Ji, L. Chen, J. Chen, T. Deng, F. Han, J. Yue, N. Piao, R. Wang, X. Zhou, X. Xiao, L.
 Chen, C. Wang, *Nat. Energy* **2019**, 4, 882.

[24] X. Dong, Y. Lin, P. Li, Y. Ma, J. Huang, D. Bin, Y. Wang, Y. Qi, Y. Xia, *Angew. Chem. Int. Ed.* 2019, 58, 5623.

[25] Y. G. Cho, M. Li, J. Holoubek, W. Li, Y. Yin, Y. S. Meng, Z. Chen, ACS Energy Lett. 2021, 6, 2016.

[26] R. Fong, U. Vonsacken, J. R. Dahn, J. Electrochem. Soc. **1990**, 137, 2009.

- [27] K. Xu, Chem. Rev. **2004**, 104, 4303.
- [28] K. Xu, Chem. Rev. **2014**, 114, 11503.
- [29] M. S. Ding, K. Xu, T. R. Jow, J. Electrochem. Soc. 2000, 147, 1688.
- [30] B. K. Mandal, A. K. Padhi, Z. Shi, S. Chakraborty, R. Filler, J. Power Sources 2006, 162, 690.
- [31] J. B. Goodenough, Y. Kim, Chem. Mater. 2010, 22, 587.

[32] C. K. Huang, J. S. Sakamoto, J. Wolfenstine, S. Surampudi, *J. Electrochem. Soc.* 2000, 147, 2893.

[34] S. S. Zhang, K. Xu, T. R. Jow, *Electrochim. Acta* **2002**, 48, 241.

[35] H. P. Lin, D. Chua, M. Salomon, H. C. Shiao, M. Hendrickson, E. Plichta, S. Slane, *Electrochem. Solid-State Lett.* **2001**, 4, A71.

[36] A. Senyshyn, M. J. Muhlbauer, O. Dolotko, H. Ehrenberg, J. Power Sources 2015, 282, 235.

[37] K. Xu, J. Electrochem. Soc. **2007**, 154, S9.

[38] K. Xu, Y. F. Lam, S. S. Zhang, T. R. Jow, T. B. Curtis, J. Phys. Chem. C 2007, 111, 7411.

[39] Q. Li, S. Jiao, L. Luo, M. S. Ding, J. Zheng, S. S. Cartmell, C. M. Wang, K. Xu, J. G. Zhang, W. Xu, *ACS Appl. Mater. Interfaces* **2017**, 9, 18826.

[40] Q. Li, D. Lu, J. Zheng, S. Jiao, L. Luo, C. M. Wang, K. Xu, J. G. Zhang, W. Xu, *ACS Appl. Mater. Interfaces* **2017**, 9, 42761.

[41] K. Xu, A. von Cresce, U. Lee, *Langmuir* **2010**, 26, 11538.

[42] Y. Yamada, Y. Iriyama, T. Abe, Z. Ogumi, *Langmuir* **2009**, 25, 12766.

[43] K. Xu, A. von Cresce, J. Mater. Res. 2012, 27, 2327.

[44] V. Zinth, C. von Luders, M. Hofmann, J. Hattendorff, I. Buchberger, S. Erhard, J. Rebelo-Kornmeier, A. Jossen, R. Gilles, *J. Power Sources* **2014**, 271, 152.

[45] Y. Li, K. Qian, Y. He, Y. V. Kaneti, D. Liu, D. Luo, H. Li, B. Li, F. Kang, *J. Power Sources* 2017, 342,
24.

[46] M. C. Smart, B. V. Ratnakumar, J. Electrochem. Soc. 2011, 158, A379.

[47] G. Park, N. Gunawardhana, H. Nakamura, Y. S. Lee, M. Yoshio, *J. Power Sources* 2012, 199, 293.

[48] M. Petzl, M. Kasper, M. A. Danzer, J. Power Sources **2015**, 275, 799.

[49] M. C. Smart, B. V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S. G. Greenbaum, A. Hightower, C. C. Ahn, B. Fultz, *J. Electrochem. Soc.* **1999**, 146, 3963.

[50] T. Rauhala, K. Jalkanen, T. Romann, E. Lust, N. Omar, T. Kallio, J. Energy Storage 2018, 20, 344.

[51] H. Ge, T. Aoki, N. Ikeda, S. Suga, T. Isobe, Z. Li, Y. Tabuchi, J. Zhang, J. Electrochem. Soc. 2017, 164, A1050.

[52] T. Gao, Y. Han, D. Fraggedakis, S. Das, T. Zhou, C. N. Yeh, S. Xu, W. C. Chueh, J. Li, M. Z. Bazant, *Joule* **2021**, 5, 393.

[53] M. C. Smart, B. V. Ratnakumar, S. Surampudi, J. Electrochem. Soc. 1999, 146, 486.

[54] E. J. Plichta, W. K. Behl, *J. Power Sources* **2000**, 88, 192.

[55] S. S. Zhang, K. Xu, J. L. Allen, T. R. Jow, *J. Power Sources* **2002**, 110, 216.

[56] M. S. Ding, K. Xu, S. S. Zhang, T. R. Jow, J. Electrochem. Soc. 2001, 148, A299.

[57] Z. K. Liu, J. Electrochem. Soc. 2003, 150, A359.

[58] M. C. Smart, B. V. Ratnakumar, L. D. Whitcanack, K. B. Chin, S. Surampudi, H. Croft, D. Tice, R. Staniewicz, *J. Power Sources* **2003**, 119, 349.

[59] X. Liao, Z. Ma, Q. Gong, Y. He, L. Pei, L. Zeng, *Electrochem. Commun.* **2008**, 10, 691.

[60] A. J. Ringsby, K. D. Fong, J. Self, H. K. Bergstrom, B. D. McCloskey, K. A. Persson, J. *Electrochem. Soc.* **2021**, 168, 080501.

[61] Y. Ein-Eli, S. Thomas, R. Chadha, T. Blakley, V. Koch, J. Electrochem. Soc. 1997, 144, 823.

[62] S. Herreyre, O. Huchet, S. Barusseau, F. Perton, J. M. Bodet, P. Biensan, *J. Power Sources*2001, 97-98, 576.

[63] S. V. Sazhin, M. Y. Khimchenko, Y. N. Tritenichenko, H. S. Lim, J. Power Sources 2000, 87, 112.

[64] M. C. Smart, B. V. Ratnakumar, S. Surampudi, J. Electrochem. Soc. 2002, 149, A361.

[65] H. C. Shiao, D. Chua, H. P. Lin, S. Slane, M. Salomon, *J. Power Sources* **2000**, 87, 167.

[66] M. C. Smart, B. V. Ratnakumar, K. B. Chin, L. D. Whitcanack, *J. Electrochem. Soc.* 2010, 157, A1361.

[67] S. Hong, J. Li, G. Wang, Z. Zhang, Y. Lai, *T. Nonferr. Metal. Soc.* **2015**, 25, 206.

[68] K. Chen, Z. Yu, S. Deng, Q. Wu, J. Zou, X. Zeng, J. Power Sources 2015, 278, 411.

[69] W. Lu, K. Xie, Z. Chen, S. Xiong, Y. Pan, C. Zheng, J. Power Sources 2015, 274, 676.

[70] W. Lu, S. Xiong, K. Xie, Y. Pan, C. Zheng, *Ionics* **2016**, 22, 2095.

[71] Y. Liu, S. Fang, P. Shi, D. Luo, L. Yang, S. I. Hirano, J. Power Sources 2016, 331, 445.

[72] Z. Li, I. Carmichael, S. Ptasinska, *Phys. Chem. Chem. Phys.* **2018**, 20, 18271.

[73] S. Tan, U. N. D. Rodrigo, Z. Shadike, B. Lucht, K. Xu, C. Wang, X. Q. Yang, E. Hu, *ACS Appl. Mater. Interfaces* **2021**, 13, 24995.

[74] N. D. Rodrigo, S. Tan, Z. Shadike, E. Hu, X. Q. Yang, B. L. Lucht, J. Electrochem. Soc. 2021, 168.

[75] N. Zhang, C. Sun, Y. Huang, C. Zhu, Z. Wu, L. Lv, X. Zhou, X. Wang, X. Xiao, X. Fan, J. Mater. Chem. A 2021, 9, 1812.

[76] Z. Zhou, M. Takeda, T. Fujii, M. Ue, J. Electrochem. Soc. 2005, 152, A351.

[77] Q. Zhao, X. Liu, J. Zheng, Y. Deng, A. Warren, Q. Zhang, L. Archer, *Proc. Natl. Acad. Sci. U.S.A.* **2020**, 117, 26053.

[78] R. Dharavath, A. Murali, A. W. Tarapathi, B. T. Srinivasan, R. Kammili, *Int. J. Electrochem.* 2019, 2019, 8192931.

[79] D. Yaakov, Y. Gofer, D. Aurbach, I. C. Halalay, J. Electrochem. Soc. **2010**, 157, A1383.

[80] S. S. Zhang, K. Xu, T. R. Jow, J. Solid State Electrochem. 2003, 7, 147.

[81] S. S. Zhang, J. Power Sources 2007, 163, 713.

- [82] S. S. Zhang, K. Xu, T. R. Jow, J. Power Sources 2006, 156, 629.
- [83] K. Xu, S. S. Zhang, U. Lee, J. L. Allen, T. R. Jow, J. Power Sources 2005, 146, 79.
- [84] S. S. Zhang, K. Xu, T. R. Jow, J. Power Sources 2006, 159, 702.
- [85] S. S. Zhang, ECS Trans. 2007, 3, 59.
- 86] S. S. Zhang, *Electrochem. Commun.* **2006**, 8, 1423.

[87] C. Yang, Y. Ren, B. Wu, F. Wu, Adv. Mat. Res. 2012, 455, 258.

[88] S. Li, W. Zhao, X. Cui, Y. Zhao, B. Li, H. Zhang, Y. Li, G. Li, X. Ye, Y. Luo, *Electrochim. Acta* 2013, 91, 282.

[89] S. Li, W. Zhao, Z. Zhou, X. Cui, Z. Shang, H. Liu, D. Zhang, ACS Appl. Mater. Interfaces 2014, 6,
4920.

90] S. Li, X. Li, J. Liu, Z. Shang, X. Cui, *Ionics* **2015**, 21, 901.

[91] L. Zhang, Y. Sun, Y. Zhou, C. Hai, S. Hu, J. Zeng, Y. Shen, S. Dong, G. Qi, F. Li, *Ionics* **2018**, 24, 2995.

[92] X. Shangguan, G. Xu, Z. Cui, Q. Wang, X. Du, K. Chen, S. Huang, G. Jia, F. Li, X. Wang, D. Lu, S. Dong, G. Cui, *Small* **2019**, 15, e1900269.

93] S. S. Zhang, J. Power Sources 2006, 162, 1379.

[94] R. Chandrasekaran, M. Koh, Y. Ozhawa, H. Aoyoma, T. Nakajima, J. Chem. Sci. 2009, 121, 339.

[95] B. Han, Y. Zou, G. Xu, S. Hu, Y. Kang, Y. Qian, J. Wu, X. Ma, J. Yao, T. T. Li, Z. Zhang, H. Meng, H.
 Wang, Y. Deng, J. Li, M. Gu, *Energy Environ. Sci.* **2021**, 14, 4882.

[96] R. Wang, X. Li, Z. Wang, H. Zhang, *Nano Energy* **2017**, 34, 131.

[97] G. Wan, F. Guo, H. Li, Y. Cao, X. Ai, J. Qian, Y. Li, H. Yang, ACS Appl. Mater. Interfaces 2018, 10, 593.

[99] X. Zuo, X. Deng, X. Ma, J. Wu, H. Liang, J. Nan, J. Mater. Chem. A 2018, 6, 14725.

[100] A. Sano, S. Maruyama, J. Power Sources 2009, 192, 714.

[101] P. Janssen, R. Schmitz, R. Muller, P. Isken, A. Lex-Balducci, C. Schreiner, M. Winter, I. Cekic-Laskovic, R. Schmitz, *Electrochim. Acta* **2014**, 125, 101.

[102] S. Jurng, S. Park, T. Yoon, H. S. Kim, H. Jeong, J. H. Ryu, J. J. Kim, S. M. Oh, *J. Electrochem. Soc.* **2016**, 163, A1798.

[103] R. Guo, Y. Che, G. Lan, J. Lan, J. Li, L. Xing, K. Xu, W. Fan, L. Yu, W. Li, *ACS Appl. Mater. Interfaces* **2019**, 11, 38285.

[104] Y. Lin, X. Yue, H. Zhang, L. Yu, W. Fan, T. Xie, *Electrochim. Acta* **2019**, 300, 202.

[105] A. S. Wotango, W. N. Su, A. M. Haregewoin, H. M. Chen, J. H. Cheng, M. H. Lin, C. H. Wang, B. J. Hwang, ACS Appl. Mater. Interfaces 2018, 10, 25252.

[106] G. Xu, S. Huang, Z. Cui, X. Du, X. Wang, D. Lu, X. Shangguan, J. Ma, P. Han, X. Zhou, G. Cui, *J. Power Sources* **2019**, 416, 29.

[107] L. Liao, P. Zuo, Y. Ma, Y. An, G. Yin, Y. Gao, *Electrochim. Acta* **2012**, 74, 260.

[108] J. Shi, N. Ehteshami, J. Ma, H. Zhang, H. Liu, X. Zhang, J. Li, E. Paillard, *J. Power Sources* **2019**, 429, 67.

[109] K. M. Kim, N. V. Ly, J. H. Won, Y. G. Lee, W. I. Cho, J. M. Ko, R. B. Kaner, *Electrochim. Acta* 2014, 136, 182.

[110] J. H. Won, H. S. Lee, L. Hamenu, M. Latifatu, Y. M. Lee, K. M. Kim, J. Oh, W. I. Cho, J. M. Ko, J. *Ind. Eng. Chem.* **2016**, 37, 325.

[111] B. Liao, M. Xu, P. Hong, H. Li, X. Wang, Y. Zhu, L. Xing, W. Li, J. Appl. Electrochem. 2017, 47, 1161.

[112] J. Pires, A. Castets, L. Timperman, J. Santos-Pena, E. Dumont, S. Levasseur, C. Tessier, R. Dedryvere, M. Anouti, *J. Power Sources* **2015**, 296, 413.

[113] W. Huang, L. Xing, R. Zhang, X. Wang, W. Li, J. Power Sources 2015, 293, 71.

[114] R. Chen, Y. Zhao, Y. Li, Y. Ye, Y. Li, F. Wu, S. Chen, J. Mater. Chem. A 2017, 5, 5142.

[115] B. Wu, Y. Ren, D. Mu, X. Liu, G. Yang, Z. Sun, Solid State Ionics 2014, 260, 8.

[116] B. Wu, Y. Ren, D. Mu, C. Zhang, X. Liu, F. Wu, Int. J. Electrochem. Sci. 2013, 8, 8502.

[117] B. Yang, H. Zhang, L. Yu, W. Fan, D. Huang, *Electrochim. Acta* **2016**, 221, 107.

[118] B. Liao, H. Li, M. Xu, L. Xing, Y. Liao, X. Ren, W. Fan, L. Yu, K. Xu, W. Li, *Adv. Energy Mater.* **2018**, 8, 1800802.

[119] B. Liu, Q. Li, M. H. Engelhard, Y. He, X. Zhang, D. Mei, C. Wang, J. G. Zhang, W. Xu, ACS Appl.
 Mater. Interfaces 2019, 11, 21496.

[120] J. P. Jones, M. C. Smart, F. C. Krause, R. V. Bugga, J. Electrochem. Soc. 2020, 167.

[121] X. Fan, C. Wang, *Chemical Society Reviews* **2021**, 50, 10486.

[122] F. Shi, A. Pei, A. Vailionis, J. Xie, B. Liu, J. Zhao, Y. Gong, Y. Cui, *Proc. Natl. Acad. Sci. U.S.A.* **2017**, 114, 12138.

[123] Y. Yang, Y. Yin, D. M. Davies, M. Zhang, M. Mayer, Y. Zhang, E. S. Sablina, S. Wang, J. Z. Lee, O. Borodin, C. S. Rustomji, Y. S. Meng, *Energy Environ. Sci.* 2020, 13, 2209.

[124] X. Fan, L. Chen, O. Borodin, X. Ji, J. Chen, S. Hou, T. Deng, J. Zheng, C. Yang, S. C. Liou, K. Amine, K. Xu, C. Wang, *Nat. Nanotechnol.* **2018**, 13, 715.

[125] J. Li, L. Wang, Y. Zhao, S. Li, X. Fu, B. Wang, H. Peng, Adv. Funct. Mater. 2020, 30, 2001619.

[126] J. Chen, X. Fan, Q. Li, H. Yang, M. R. Khoshi, Y. Xu, S. Hwang, L. Chen, X. Ji, C. Yang, H. He, C.M. Wang, E. Garfunkel, D. Su, O. Borodin, C. Wang, *Nat. Energy* **2020**, 5, 386.

[127] J. Chen, Q. Li, T. P. Pollard, X. Fan, O. Borodin, C. Wang, Mater. Today 2020, 39, 118.

[128] M. Okoshi, Y. Yamada, A. Yamada, H. Nakai, J. Electrochem. Soc. 2013, 160, A2160.

[129] A. C. Thenuwara, P. P. Shetty, N. Kondekar, S. E. Sandoval, K. Cavallaro, R. May, C. T. Yang, L. E.
 Marbella, Y. Qi, M. T. McDowell, ACS Energy Lett. 2020, 5, 2411.

[130] Q. Zhang, J. Pan, P. Lu, Z. Liu, M. W. Verbrugge, B. W. Sheldon, Y. T. Cheng, Y. Qi, X. Xiao, *Nano Lett* **2016**, 16, 2011.

[131] J. Pan, Q. Zhang, X. Xiao, Y. T. Cheng, Y. Qi, ACS Appl. Mater. Interfaces 2016, 8, 5687.

[132] X. Dong, Y.-G. Wang, Y. Xia, Acc. Chem. Res. 2021, 54, 3883.

[133] J. Ming, J. Zhang, Q. Li, G. Liu, H. Cheng, Q. Sun, Chem. Eur. J 2021, 27, 1.

[134] S. Chen, J. Zheng, D. Mei, K. S. Han, M. H. Engelhard, W. Zhao, W. Xu, J. Liu, J. G. Zhang, Adv. Mater. 2018, 30, e1706102.

[135] X. Zhang, L. Zou, Y. Xu, X. Cao, M. H. Engelhard, B. E. Matthews, L. Zhong, H. Wu, H. Jia, X. Ren, P. Gao, Z. Chen, Y. Qin, C. Kompella, B. W. Arey, J. Li, D. Wang, C. Wang, J. Zhang, W. Xu, *Adv. Energy Mater.* **2020**, 10, 2000368.

[136] X. Dong, Z. Guo, Z. Guo, Y. Wang, Y. Xia, Joule 2018, 2, 902.

[137] J. Holoubek, Y. Yin, M. Li, M. Yu, Y. S. Meng, P. Liu, Z. Chen, *Angew. Chem. Int. Ed.* 2019, 58, 18892.

[138] J. R. Dahn, J. A. Seel, J. Electrochem. Soc. 2000, 147, 899.

[139] H. Peng, J. Huang, X. Cheng, Q. Zhang, Adv. Energy Mater. 2017, 7, 1700260.

[140] M. Rana, S. A. Ahad, M. Li, B. Luo, L. Wang, I. Gentle, R. Knibbe, *Energy Storage Mater.* 2019, 18, 289.

[141] H. S. Ryu, H. J. Ahn, K. W. Kim, J. H. Ahn, K. K. Cho, T. H. Nam, J. U. Kim, G. B. Cho, *J. Power Sources* **2006**, 163, 201.
[142] Y. V. Mikhaylik, J. R. Akridge, J. Electrochem. Soc. 2003, 150, A306.

[143] A. Ramanujapuram, G. Yushin, Adv. Energy Mater. 2018, 8, 1802624.

[144] Q. Nian, J. Wang, S. Liu, T. Sun, S. Zheng, Y. Zhang, Z. Tao, J. Chen, *Angew. Chem. Int. Ed.* 2019, 58, 16994.

[145] A. Tron, S. Jeong, Y. D. Park, J. Mun, ACS Sustainable Chem. Eng. 2019, 7, 14531.

[146] J. Chen, J. Vatamanu, L. Xing, O. Borodin, H. Chen, X. Guan, X. Liu, K. Xu, W. Li, Adv. Energy Mater. 2020, 10, 1902654.

[147] M. Kunze, S. Jeong, G. B. Appetecchi, M. Schonhoff, M. Winter, S. Passerini, *Electrochim. Acta* **2012**, 82, 69.

[148] M. Galiński, A. Lewandowski, I. Stępniak, *Electrochim. Acta* **2006**, 51, 5567.

[149] G. B. Appetecchi, M. Montanino, D. Zane, M. Carewska, F. Alessandrini, S. Passerini, *Electrochim. Acta* **2009**, 54, 1325.

[150] R.-S. Kühnel, N. Böckenfeld, S. Passerini, M. Winter, A. Balducci, *Electrochim. Acta* 2011, 56, 4092.

[151] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 2004, 138, 253.

[152] K. Fujie, K. Otsubo, R. Ikeda, T. Yamada, H. Kitagawa, Chem. Sci. 2015, 6, 4306.

[153] L. Aguilera, J. Scheers, A. Matic, *Phys. Chem. Chem. Phys.* **2016**, 18, 25458.

[154] Y. Li, K. W. Wong, Q. Dou, W. Zhang, K. M. Ng, ACS Appl. Energy Mater. 2018, 1, 2664.

[155] Y. Xu, W. J. Lin, M. Gliege, R. Gunckel, Z. Zhao, H. Yu, L. L. Dai, *J. Phys. Chem. B* 2018, 122, 12077.

[156] W. Wang, T. Yang, S. Li, W. Fan, X. Zhao, C. Fan, L. Yu, S. Zhou, X. Zuo, R. Zeng, J. Nan, *Electrochim. Acta* **2019**, 317, 146.

[157] P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorganic chemistry* **1996**, 35, 1168.

[158] Y. Preibisch, F. Horsthemke, M. Winter, S. Nowak, A. S. Best, Chem. Mater. 2020, 32, 2389.

[159] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, *Journal of physical and chemical reference data* 2006, 35, 1475.

[160] H. Ohno, M. Yoshizawa, Solid State Ionics 2002, 154, 303.

[161] S. P. Ong, O. Andreussi, Y. Wu, N. Marzari, G. Ceder, Chem. Mater. 2011, 23, 2979.

[162] T. Fromling, M. Kunze, M. Schonhoff, J. Sundermeyer, B. Roling, *The Journal of Physical Chemistry B* **2008**, 112, 12985.

[163] M. T. F. Rodrigues, G. Babu, H. Gullapalli, K. Kalaga, F. N. Sayed, K. Kato, J. Joyner, P. M. Ajayan, Nat. Energy 2017, 2, 1.

[164] I. Osada, H. de Vries, B. Scrosati, S. Passerini, Angew. Chem. Int. Ed. 2016, 55, 500.

[165] Z. Lin, J. Liu, *RSC Adv.* **2019**, 9, 34601.

[166] F. Zhu, H. Bao, X. Wu, Y. Tao, C. Qin, Z. Su, Z. Kang, ACS Appl. Mater. Interfaces 2019, 11, 43206.

[167] N. Zhang, C. Sun, Y. Huang, L. Lv, Z. Wu, C. Zhu, X. Wang, X. Xiao, X. Fan, L. Chen, *Dalton Transactions* **2021**, 50, 8322.

[168] D. H. S. Tan, Y.-T. Chen, H. Yang, W. Bao, B. Sreenarayanan, J.-M. Doux, W. Li, B. Lu, S.-Y. Ham,
B. Sayahpour, J. Scharf, E. A. Wu, G. Deysher, H. E. Han, H. J. Hah, H. Jeong, J. B. Lee, Z. Chen, Y. S.
Meng, *Science* **2021**, 373, 1494.

[169] G. Liu, W. Weng, Z. Zhang, L. Wu, J. Yang, X. Yao, Nano Lett. 2020, 20, 6660.

[170] W. Cai, Y. Yao, G. Zhu, C. Yan, L. Jiang, C. He, J. Huang, Q. Zhang, *Chem. Soc. Rev.* 2020, 49, 3806.

- [172] X. Cao, J. H. Kim, S. M. Oh, *Electrochim. Acta* 2002, 47, 4085.
- [173] Y. P. Wu, C. Jiang, C. Wan, R. Holze, J. Power Sources 2002, 111, 329.

[174] F. Nobili, S. Dsoke, T. Mecozzi, R. Marassi, *Electrochim. Acta* **2005**, 51, 536.

[175] F. Nobili, M. Mancini, S. Dsoke, R. Tossici, R. Marassi, J. Power Sources 2010, 195, 7090.

[176] M. Marinaro, M. Mancini, F. Nobili, R. Tossici, L. Damen, R. Marassi, *J. Power Sources* 2013, 222, 66.

[177] M. Marinaro, F. Nobili, A. Birrozzi, S. K. E. Moorthy, U. Kaiser, R. Tossici, R. Marassi, *Electrochim. Acta* **2013**, 109, 207.

[178] A. Friesen, S. Hildebrand, F. Horsthemke, M. Borner, R. Klopsch, P. Niehoff, F. M. Schappacher,
 M. Winter, *J. Power Sources* 2017, 363, 70.

[179] Y. Ji, Y. Zhang, C. Wang, J. Electrochem. Soc. 2013, 160, A636.

[180] J. Xu, X. Wang, N. Yuan, B. Hu, J. Ding, S. Ge, J. Power Sources **2019**, 430, 74.

[181] R. Raccichini, A. Varzi, V. S. K. Chakravadhanula, C. Kubel, A. Balducci, S. Passerini, *J. Power Sources* **2015**, 281, 318.

[182] G. Zhao, Z. Wei, N. Zhang, K. Sun, Mater. Lett 2012, 89, 243.

[183] E. Ferg, R. J. Gummow, A. Dekock, M. M. Thackeray, J. Electrochem. Soc. 1994, 141, L147.

[184] T. Ohzuku, A. Ueda, N. Yamamoto, J. Electrochem. Soc. 1995, 142, 1431.

[185] L. Aldon, P. Kubiak, M. Womes, J. C. Jumas, J. Olivier-Fourcade, J. L. Tirado, J. I. Corredor, C. P. Vicente, *Chem. Mater.* **2004**, 16, 5721.

- [186] L. Zhao, Y. S. Hu, H. Li, Z. Wang, L. Chen, Adv. Mater. 2011, 23, 1385.
- [187] Y. Wang, L. Gu, Y. Guo, H. Li, X. He, S. Tsukimoto, Y. Ikuhara, L. Wan, J. Am. Chem. Soc. 2012,

134, 7874.

[188] D. P. Abraham, J. R. Heaton, S. H. Kang, D. W. Dees, A. N. Jansen, *J. Electrochem. Soc.* **2008**, 155, A41.

[189] J. L. Allen, T. R. Jow, J. Wolfenstine, J. Power Sources 2006, 159, 1340.

[190] E. Pohjalainen, T. Rauhala, M. Vakeapaa, J. Kallioinen, T. Kallio, J. Phys. Chem. C 2015, 119, 2277.

[191] T. Yuan, X. Yu, R. Cai, Y. Zhou, Z. Shao, J. Power Sources 2010, 195, 4997.

[192] Q. Huang, Z. Yang, J. Mao, Sci. Rep. 2017, 7, 15292.

[193] Q. Huang, Z. Yang, J. Mao, *lonics* **2017**, 23, 803.

[194] C. Huang, S. Zhao, H. Peng, Y. Lin, C. Nan, G. Cao, J. Mater. Chem. A 2018, 6, 14339.

[195] Y. Zhang, Y. Luo, Y. Chen, T. Lu, L. Yan, X. Cui, J. Xie, ACS Appl. Mater. Interfaces 2017, 9, 17145.

[196] J. Xu, X. Wang, N. Yuan, J. Ding, S. Qin, J. M. Razal, X. Wang, S. Ge, Y. Gogotsi, *Energy Storage Mater.* **2019**, 23, 383.

[197] B. Hu, X. Zhou, J. Xu, X. Wang, N. Yuan, S. Ge, J. Ding, *Chemelectrochem* **2020**, 7.

[198] H. Zou, H. Xiang, X. Liang, X. Feng, S. Cheng, Y. Jin, C. Chen, J. Alloys Compd. 2017, 701, 99.

[199] M. Marinaro, M. Pfanzelt, P. Kubiak, R. Marassi, M. Wohlfahrt-Mehrens, *J. Power Sources* **2011**, 196, 9825.

[200] X. Zhang, C. Wang, A. J. Appleby, J. Power Sources 2003, 114, 121.

[201] F. Nobili, I. Meschini, M. Mancini, R. Tossici, R. Marassi, F. Croce, *Electrochim. Acta* 2013, 107, 85.

[202] Y. Yan, L. Ben, Y. Zhan, X. Huang, *Electrochim. Acta* **2016**, 187, 186.

[203] A. Varzi, L. Mattarozzi, S. Cattarin, P. Guerriero, S. Passerini, *Adv. Energy Mater.* **2018**, 8, 1701706.

- [204] E. Markevich, G. Salitra, D. Aurbach, J. Electrochem. Soc. 2016, 163, A2407.
- [205] S. Hou, T. Gao, X. Li, C. Wang, *Nano Energy* **2020**, 67, 104254.
- [206] Z. Sun, L. Jiao, Y. Fan, F. Li, D. Wang, D. Han, L. Niu, *RSC Adv.* **2016**, 6, 97818.
- [207] B. C. Park, H. B. Kim, H. J. Bang, J. Prakash, Y. K. Sun, Ind. Eng. Chem. Res. 2008, 47, 3876.

[208] Z. Sun, Z. Li, L. Gao, X. Zhao, D. Han, S. Gan, S. Guo, L. Niu, *Adv. Energy Mater.* **2019**, 9, 1802946.

[209] Z. Sun, Z. Li, X. Wu, M. Zou, D. Wang, Z. Gu, J. Xu, Y. Fan, S. Gan, D. Han, L. Niu, *ACS Appl. Energy Mater.* **2019**, 2, 486.

[210] G. Li, Z. Huang, Z. Zuo, Z. Zhang, H. Zhou, J. Power Sources 2015, 281, 69.

[211] Z. Lu, L. Y. Beaulieu, R. A. Donaberger, C. L. Thomas, J. R. Dahn, *J. Electrochem. Soc.* **2002**, 149, A778.

[212] J. H. Kim, Y. K. Sun, J. Power Sources 2003, 119, 166.

[213] C. S. Johnson, J. S. Kim, C. Lefief, N. Li, J. T. Vaughey, M. M. Thackeray, *Electrochem. Commun.***2004**, 6, 1085.

[214] Y. J. Park, Y. S. Hong, X. Wu, M. G. Kim, K. S. Ryu, S. H. Chang, J. Electrochem. Soc. 2004, 151, A720.

[215] Z. Chen, Y. K. Sun, K. Amine, J. Electrochem. Soc. 2006, 153, A1818.

[216] I. Takahashi, K. Fukuda, T. Kawaguchi, H. Komatsu, M. Oishi, H. Murayama, M. Hatano, T. Terai, H. Arai, Y. Uchimoto, E. Matsubara, *J. Phys. Chem. C* **2016**, 120, 27109.

[217] M. C. Smart, J. F. Whitacre, B. V. Ratnakumar, K. Amine, J. Power Sources 2007, 168, 501.

[218] Z. Li, Y. Wang, X. Bie, K. Zhu, C. Wang, G. Chen, Y. Wei, *Electrochem. Commun.* 2011, 13, 1016.
[219] J. Kou, L. Chen, Y. Su, L. Bao, J. Wang, N. Li, W. Li, M. Wang, S. Chen, F. Wu, *ACS Appl. Mater. Interfaces* 2015, 7, 17910.

- [220] X. Wei, Y. Ren, *Electrochim. Acta* **2015**, 180, 323.
- [221] B. Zhao, J. Xie, H. Zhuang, X. Liu, W. Li, X. Hu, Y. Jiang, J. Zhang, Solid State Ionics 2020, 347.
- [222] O. K. Park, Y. Cho, S. Lee, H. C. Yoo, H. K. Song, J. Cho, *Energy Environ. Sci.* 2011, 4, 1621.
- [223] A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, J. Electrochem. Soc. 1997, 144, 1188.
- [224] Y. Wang, Y. Wang, E. Hosono, K. Wang, H. Zhou, Angew. Chem. Int. Ed. 2008, 47, 7461.
- [225] Y. Wu, Z. Wen, J. Li, Adv. Mater. 2011, 23, 1126.
- [226] L. Yuan, Z. Wang, W. Zhang, X. Hu, J. Chen, Y. Huang, J. B. Goodenough, *Energy Environ. Sci.***2011**, 4, 269.
- [227] S. Y. Chung, Y. M. Chiang, *Electrochem. Solid-State Lett.* **2003**, 6, A278.
- [228] P. P. Prosini, M. Lisi, D. Zane, M. Pasquali, Solid State Ionics 2002, 148, 45.
- [229] M. Contestabile, G. J. Offer, R. Slade, F. Jaeger, M. Thoennes, *Energy Environ. Sci.* **2011**, 4, 3754.
- 230] S. W. Kim, D. H. Seo, H. Kim, K. Y. Park, K. Kang, Phys. Chem. Chem. Phys. 2012, 14, 3299.
- [231] C. Li, N. Hua, C. Wang, X. Kang, T. Wumair, Y. Han, J. Alloys Compd. 2011, 509, 1897.
- [232] G. Huang, W. Li, H. Sun, J. Wang, J. Zhang, H. Jiang, F. Zhai, *Electrochim. Acta* **2013**, 97, 92.
- [233] A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, W. van Schalkwijk, Nat. Mater. 2005, 4, 366.
- [234] S. Bae, H. D. Song, I. Nam, G. P. Kim, J. M. Lee, J. Yi, Chem. Eng. Sci. 2014, 118, 74.
- [235] N. Zhao, Y. Li, X. Zhao, X. Zhi, G. Liang, J. Alloys Compd. 2016, 683, 123.

[236] X. Wang, L. Wen, Y. Zheng, X. Ren, Y. Li, G. Liang, *Ionics* **2020**, 26, 4433.

[237] K. Edstrom, T. Gustafsson, J. O. Thomas, *Electrochim. Acta* 2004, 50, 397.

[238] A. V. Churikov, *Electrochim. Acta* **2001**, 46, 2415.

[239] D. Aurbach, E. Zinigrad, Y. Cohen, H. Teller, *Solid State Ionics* **2002**, 148, 405.

[240] H. C. Shin, K. W. Nam, W. Y. Chang, B. W. Cho, W. S. Yoon, X. Q. Yang, K. Y. Chung, *Electrochim. Acta* **2011**, 56, 1182.

[241] Y. H. Nien, J. R. Carey, J. S. Chen, J. Power Sources 2009, 193, 822.

[242] Z. Chen, J. R. Dahn, J. Electrochem. Soc. 2002, 149, A1184.

[243] Y. Zhou, C. Gu, J. Zhou, L. Cheng, W. Liu, Y. Qiao, X. Wang, J. Tu, *Electrochim. Acta* 2011, 56, 5054.

[244] F. Zheng, C. Yang, X. Ji, D. Hu, Y. Chen, M. Liu, J. Power Sources 2015, 288, 337.

[245] C. H. Mi, Y. Cao, X. G. Zhang, X. B. Zhao, H. L. Li, *Powder Technol.* 2008, 181, 301.

[246] J. Morales, R. Trocoli, E. Rodriguez-Castellon, S. Franger, J. Santos-Pena, *J. Electroanal. Chem.***2009**, 631, 29.

[247] Y. Lin, Y. Lin, T. Zhou, G. Zhao, Y. Huang, Z. Huang, J. Power Sources **2013**, 226, 20.

[248] Y. H. Yin, X. N. Li, X. X. Mao, X. L. Ding, S. T. Yang, J. Mater. Sci. Technol. 2013, 29, 937.

[249] G. Cai, R. Guo, L. Liu, Y. Yang, C. Zhang, C. Wu, W. Guo, H. Jiang, *J. Power Sources* 2015, 288, 136.

[250] H. Xie, R. Wang, J. Ying, L. Zhang, A. Jalbout, H. Yu, G. Yang, X. Pan, Z. Su, *Adv. Mater.* 2006, 18, 2609.

[251] K. Hatakeyama-Sato, T. Akahane, C. Go, T. Kaseyama, T. Yoshimoto, K. Oyaizu, ACS Energy Lett.2020, 5, 1712.

[252] Y. H. Huang, K. S. Park, J. B. Goodenough, J. Electrochem. Soc. 2006, 153, A2282.

[253] D. Xie, G. Cai, Z. Liu, R. Guo, D. Sun, C. Zhang, Y. Wan, J. Peng, H. Jiang, *Electrochim. Acta***2016**, 217, 62.

[254] X. Yang, Y. L. Xu, H. Zhang, Y. Huang, Q. Jiang, C. Zhao, *Electrochim. Acta* **2013**, 114, 259.

[255] B. Yao, Z. Ding, J. Zhang, X. Feng, L. Yin, J. Solid State Chem. 2014, 216, 9.

[256] Q. Fan, Y. Zhang, Q. Xu, J. Wang, L. X. Lei, Y. Sun, P. D. Lund, *Energy Storage Mater.* 2019, 21, 457.

[257] X. Wu, Y. Guo, J. Su, J. Xiong, Y. Zhang, L. Wan, Adv. Energy Mater. 2013, 3, 1155.

[258] W. Yang, Y. Bi, Y. Qin, Y. Liu, X. Zhang, B. Yang, Q. Wu, D. Wang, S. Shi, *J. Power Sources* 2015, 275, 785.

[259] Q. Hu, J. Liao, B. Zou, M. Yu, Z. Tang, Z. Wen, C. Chen, *J. Solid State Electrochem.* 2018, 22, 797.

[260] S. Y. Chung, J. T. Bloking, Y. M. Chiang, *Nat. Mater.* **2002**, 1, 123.

[261] Y. Lv, B. Huang, J. Tan, S. Jiang, S. Zhang, Y. Wen, *Mater. Lett* **2018**, 229, 349.

[262] Z. Li, X. Ren, Y. Zheng, W. Tian, L. W. An, J. Sun, R. Ding, L. Wen, G. Liang, *Ionics* **2020**, 26, 1599.

[263] H. Zhang, Y. Xu, C. Zhao, X. Yang, Q. Jiang, *Electrochim. Acta* 2012, 83, 341.

[264] X. Rui, Y. Jin, X. Feng, L. Zhang, C. Chen, J. Power Sources 2011, 196, 2109.

[265] Z. Liu, X. Kang, C. Li, N. Hua, T. Wumair, Y. Han, J. Solid State Electrochem. 2012, 16, 1917.

[266] Y. Qiao, J. Tu, X. Wang, C. Cu, J. Power Sources **2012**, 199, 287.

[267] F. Teng, Z. Hu, X. Ma, L. Zhang, C. Ding, Y. Yu, C. Chen, *Electrochim. Acta* **2013**, 91, 43.

[268] R. Qin, Y. Wei, T. Zhai, H. Li, J. Mater. Chem. A 2018, 6, 9737.

[269] L. Tai, Q. Zhao, L. Sun, L. Cong, X. Wu, J. Zhang, R. Wang, H. Xie, X. Chen, *New J. Chem.* 2015, 39, 9617.

[270] C. R. Sides, C. R. Martin, Adv. Mater. 2005, 17, 125.

[271] X. Zhao, L. Yin, Z. Yang, G. Chen, H. Yue, D. Zhang, Z. Sun, F. Li, *J. Mater. Chem. A* 2019, 7, 21774.

- [272] X. Dong, Y. Yang, B. Wang, Y. Cao, N. Wang, P. Li, Y. Wang, Y. Xia, Adv. Sci. 2020, 7, 2000196.
- [273] D. Howey, Y. Zheng, H. Perez, A. Foley, M. Pecht, X. Hu, Prog. Energy Combust. Sci. 2020, 77.
- [274] X. Wu, Z. Chen, Z. Wang, *Energies* **2017**, 10, 1121.
- [275] G. Zhang, S. Ge, T. Xu, X. Yang, H. Tian, C. Wang, *Electrochim. Acta* **2016**, 218, 149.
- [276] X. Yang, G. Zhang, C. Wang, J. Power Sources **2016**, 328, 203.
- [277] G. Zhang, H. Tian, S. Ge, D. Marple, F. C. Sun, C. Wang, J. Power Sources 2018, 376, 111.

[278] Z. Lei, Y. Zhang, X. Lei, Int. J. Heat Mass Transfer 2018, 121, 275.

[279] X. Yang, G. Zhang, S. Ge, C. Wang, Proc. Natl. Acad. Sci. U.S.A. 2018, 115, 7266.

[280] H. C. Song, S. Wang, X. Y. Song, J. Wang, K. Z. Jiang, S. H. Huang, M. Han, J. Xu, P. He, K. J.Chen, H. S. Zhou, *Energy Environ. Sci.* 2020, 13, 1205.



Nan Zhang is currently a Ph.D. candidate in the Department of Chemical and Biomolecular Engineering at the University of Maryland, College Park (UMD). He received his M.S. and B.S. in Materials Science and Engineering from Zhejiang University in 2018 and 2021, respectively. His research interests focus on advanced nonaqueous electrolytes and interphase study in high-energy secondary batteries, including lithium batteries and other energy storage devices.



Dr. Tao Deng is currently working as postdoctoral associate in the Department of Chemical and Biomolecular Engineering at the University of Maryland, College Park (UMD). He received his Bachelor and Master of Science degrees from Tianjin University and Rice University in 2014 and 2016, respectively. He obtained his PhD degree under the supervision of Prof. Chunsheng Wang from UMD in 2020. His research interests focus on advanced nonaqueous/solid-state electrolytes and interphase study in high-energy secondary batteries (lithium batteries, sodium batteries, potassium batteries, etc.) and other energy storage devices.



Shuoqing Zhang received his bachelor's degree and master's degree from Yanshan University and Tianjin University in 2017 and 2020, respectively. He is currently a Ph.D. candidate in the School of Materials Science and Engineering, Zhejiang University. His research interests lie in novel materials and novel electrolytes in energy storage and conversion devices, such as lithium-ion batteries and zinc-ion batteries.



Dr. Changhong Wang received his M.S. degree in Material Engineering from University of Science and Technology of China in 2014 supervised by Prof. Liwei Chen and Ph.D. degree in Mechanical and Material Engineering from University of Western Ontario, Canada in 2020 under the supervision of Prof. Xueliang (Andy) Sun. He has worked at the Singapore University of Technology and Design (SUTD) from 2014 to 2016 and focused on electronic synapses for neuromorphic computing. His current research interests include all-solid-state batteries, solid electrolytes, Li-S, pouch cells, and electronic synapses.



Prof. Lixin Chen received his Ph.D. in Materials Science and Engineering from Zhejiang University in 2000. He joined Zhejiang University as a lecturer in 1992 and became a professor in 2005. His research interest is energy storage materials, hydrogen energy technologies and secondary batteries.



Prof. Chunsheng Wang is Robert Franklin and Frances Riggs Wright Distinguished Chair Professor in the Department of Chemical & Biomolecular Engineering at UMD and a co-founder and UMD Director of the Centre for Research in Extreme Batteries (CREB), a joint battery research center between UMD and US Army Research Lab. His work has been cited more than 40000 times, with an H-index of 108. He has been recognized as a highly cited researcher by Clarivate since 2018. He was selected as the winner of the 2021 Battery Division Research Award by the Electrochemical Society.



Artic

Accepted A

Prof. Xiulin Fan received his bachelor's and PhD degrees from Zhejiang University in 2007 and 2012, respectively. From 2013 to 2017, he worked as a Postdoctoral Research Associate at the University of Maryland College Park (UMD), and then promoted as an Assistant Research Scientist in 2017 at UMD. Since August 2019, Dr. Xiulin Fan has been a professor at School of Materials Science and Engineering, Zhejiang University. His research interest is electrolytes and interphases in high-energy batteries. He has been recognized as a highly cited researcher by Clarivate since 2020.

This article provides a timely and critical review on fundamental mechanisms, recent advances and design strategies of electrolytes, electrodes and battery structures for low-temperature Li batteries.

N. Zhang, T. Deng, S. Zhang, C. Wang, L. Chen, C. Wang* and X. Fan*

Critical review on low-temperature Li-ion/metal batteries



Accepted Article