Toward wide-temperature electrolyte for lithium–ion batteries

Long Chen¹ | Honglun Wu¹ | Xinping Ai² | Yuliang Cao² | Zhongxue Chen¹

¹Key Laboratory of Hydraulic Machinery Transients, Ministry of Education, School of Power and Mechanical Engineering, Wuhan University, Wuhan, China
²Hubei Key Laboratory of Electrochemical Power Sources, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China

Correspondence
Yuliang Cao, Hubei Key Laboratory of Electrochemical Power Sources, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China.
Email: ylcao@whu.edu.cn
Zhongxue Chen, Key Laboratory of Hydraulic Machinery Transients, Ministry of Education, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China.
Email: zxchen_pmc@whu.edu.cn

Funding information
National Key Research Program of China, Grant/Award Number: 2016YFB0901500; National Natural Science Foundation of China, Grant/Award Numbers: 21875171, 21972108, U20A20249; Key R&D Plan of Hubei Province, Grant/Award Number: 2020BA0A030; Hubei Natural Science Foundation, Grant/Award Number: 2020CFB771; Intergovernmental International Science and Technology Innovation Cooperation Project, Grant/Award Number: 2019YFE010186

Abstract
Lithium–ion battery (LIB) suffers from safety risks and narrow operational temperature range in despite the rapid drop in cost over the past decade. Subjected to the limited materials choices, it is not feasible to modify the cathode and anode to improve the battery’s wide-temperature performance, hence, optimizing the design of the electrolyte system has currently become the most feasible and economical way to broaden the operating temperature range of LIBs. Considering urgent demands for wide-temperature LIBs and achieved enormously excited results about wide-temperature electrolytes in recent years, a review about this topic and scope is timely and important at present. In this study, we first examine the physicochemical properties of current commercial electrolytes with emphasis on the variations of key parameters along with the temperature. After that, we give comprehensive overview of the employed strategies for separately improving the electrochemical performance of electrolytes toward low-temperature, high-temperature, and wide-temperature applications. Furthermore, recent progress of ionic liquids and solid-state electrolytes that are capable of working within wide temperature range is also summarized. We hope this review will provide deep understanding of the design principles of wide-temperature electrolyte, and inspire more endeavors to conquer the practicability issue of LIBs in extreme environments.

KEYWORDS
additives, lithium–ion battery, multicomponents, practicability, wide-temperature electrolyte
INTRODUCTION

With the continuous growth of energy demand, the consumptions of fossil fuels have accelerated rapidly, which has brought increasingly prominent environmental problems. To face the energy and environmental crisis, highly efficient, clean, safe, and renewable energy resources have been permanently explored, while the related research on the exploitation, storage, and utilization of these new energy resources have also become global hotspot. Since its invention in 1990, lithium–ion batteries (LIBs) have rapidly occupied the power supply market for electronic devices. With the further increase of energy density and the gradual decline of production costs, LIBs have almost monopolized the electric vehicle power battery market, and have extended their tentacles to gird-scale energy storage field. As the most advanced battery technology at present, LIBs possess plenty of advantages, such as high energy density, high output voltage, long cycle life, low self-discharge, no memory effect, and so forth, enabling it to maintain consistently strong competitiveness. Despite the rapid drop in cost over the past decade, LIB still suffers from safety risks and narrow operational temperature range.

Temperature is an important factor that affects the health and safe operation of LIBs (Figure 1). The operating temperatures of commercial LIBs are generally located in the range of −20 to 60°C, which can meet the needs of most portable electronic devices. Whereas for the power battery in electric vehicles, to accommodate the differences arise from regions and seasons, its operating temperature range is wider than that of portable devices. What is more, in the extreme application fields of the national defense and military industry, LIBs are expected to own charge and discharge capability at low temperature (−40°C), and can be stored stably at high temperature (storage at 70°C for 48 h, capacity retention >80%, soft-pack battery expansion rate <5%). In the aerospace field, the lower limit of the operating temperature of LIBs even needs to be extended to −50°C or lower. Although the battery thermal management system (BTMS) can help the battery maintain a suitable temperature during short-term operation to a certain extent, long-term storage or operation at these extremely high or extremely low temperatures will cause irreversible mechanical damage to the battery and even a safety hazard. In addition to the short-term effectiveness, BTMS also suffers from poor temperature measurement accuracy and additional space and weight, resulting in sluggish system response speed and reduced energy density of the battery system. Apparently, developing wide-range temperature tolerant LIBs is critically important to enhance battery stability, safety, and applicability.

To fundamentally understand the influence of temperature on the electrochemical performance of LIBs, it is necessary to discuss the relationship between electrochemical thermodynamics, electrochemical kinetics, and temperature. The working potential is an important parameter that directly reveals the battery’s wide-temperature performance, especially the low-temperature performance.

The influence of low temperature on battery polarization is mainly manifested in the following three aspects (Figure 2): first, the deterioration of electronic/ionic conductivity at low temperature will aggravate ohmic polarization; second, the slow diffusion kinetics of ions within the electrode leads to an increase in concentration polarization; finally, the high activation energy at low temperature causes high activation polarization. The above multiple effects together contribute to the increased impedance and polarization of the battery at low temperature, finally result in energy and power attenuations.

Different from the influence of low temperature, the primary problems of LIBs at high temperatures are the chemical decomposition of the electrolyte and the damage of the solid electrolyte interface (SEI)/cathode electrolyte interphase (CEI) layers. Lithium salts and solvents in the electrolyte will undergo chemical reactions at high temperatures, meanwhile, side reactions at the electrode/electrolyte interface will intensify, resulting in poor cycling performance or even safety issues.

Based on the above analysis of the factors affecting the wide-temperature performance of LIBs, it can be seen that the cathode, anode, and electrolyte must be modified.
fundamentally to improve the wide-temperature performance of the battery. However, the variety of commercially available electrode materials is limited, and their inherent properties at high or low temperatures are unlikely to alter. Therefore, it is not feasible to modify the cathode and anode to improve the battery’s wide-temperature performance. Electrolyte is called the “blood” of the battery and plays an important role in transferring Li+ and conducting internal circuits. The electrolyte is required to have a higher boiling point, a lower freezing point, a higher ionic conductivity, and good compatibility with the cathodes and anodes. The performance of the electrolyte is one of the key factors that determine whether a LIB can work under wide-temperature conditions. Therefore, optimizing the design of the electrolyte system has currently become the most feasible and economical way to broaden the operating temperature range of LIBs.

In this study, we first examine the physicochemical properties of current commercial electrolytes with emphasis on the variations of key parameters along with temperature, which we believe would provide essential knowledge for the design of wide-temperature electrolytes. In addition, wide-temperature electrolytes need to consider both high-temperature and low-temperature performance, whereas the vast majority of electrolytes do not have this versatility. Considering urgent demands for wide-temperature LIBs and achieved enormously excited results about wide-temperature electrolyte in recent years, a review about this topic and scope is timely and important at present.

In this study, we first examine the physicochemical properties of current commercial electrolytes with emphasis on the variations of key parameters along with temperature, which we believe would provide essential knowledge for the design of wide-temperature electrolytes. After that, we give a comprehensive overview of the employed strategies for separately improving the electrochemical performance of electrolytes toward low-temperature, high-temperature, and wide-temperature applications. Furthermore, recent progress of ionic liquids (ILs) and solid-state electrolytes that are capable
of working within wide temperature range is also summarized. We hope this review will provide deep understanding of the design principles of wide-temperature electrolyte, and inspire more endeavors to conquer the practicability issue of LIBs in extreme environments.

2 | LOW-TEMPERATURE ELECTROLYTE

The low-temperature performance of LIBs electrolytes is mainly limited by the following factors (Table 1):10–15 (1) Commercial electrolytes commonly contain EC components, but EC has a high freezing point (36.4°C), which will increase the viscosity of the electrolyte at low temperatures, or even partially solidify and deteriorate the ionic conductivity of the electrolyte. (2) The charge transfer resistance increases at low temperatures, which amplifies the electrode polarization during the charge and discharge processes. (3) The diffusion coefficient of Li⁺ within the bulk electrode decreases dramatically, resulted in enormously increased diffusion resistance.7 (4) Li⁺ ions are apt to deposit on the anode to form metallic lithium due to the large polarization at low temperatures. On the one hand, the electrolyte is continuously consumed, which makes the SEI film thicker. It has been demonstrated that the surface morphology of the anode transformed from a flat and smooth morphology to a microscopically rugged structure that comprises three distinct layers: a top dendritic layer, an intermediate porous layer, and a residual metallic lithium layer, which hinders the diffusion of

| Table 1 | Physical properties of solvents10–14 |
|---|---|---|---|---|---|
| Carbonates solvents | Boiling point | Freezing point | Dielectric constants | Viscosity (mPa s) | Flash point (°C) |
| EC | 248 | 36.4 | 89.78 | 1.90 | 160 |
| PC | 242 | −49 | 65.0 | 2.5 | 132 |
| DMC | 91 | 4.6 | 3.11 | 0.59 | 18 |
| DEC | 126 | −74.3 | 2.81 | 0.75 | 31 |
| EMC | 110 | −53 | 2.96 | 0.65 | 28 |
| EA | 77 | −84 | 6.02 | 0.45 | −4 |
| EB | 120 | −93 | - | 0.71 | 19 |
| EF | 54.3 | −79.6 | 7.16 | 0.358 | −13 |
| MA | 57 | −84 | 6.68 | 0.36 | −10 |
| MB | 102 | −84 | - | 0.6 | 11 |
| MF | 32 | −99 | 8.9 | 0.328 | −32 |
| DMS | 126 | −41 | 22.5 | 0.8732 | 30 |
| DES | 159 | - | 15.6 | 0.889 | 53 |
| PS | 187.5 | −14 | - | - | 67.2 |

Abbreviations: DEC, diethyl carbonate; DES, diethyl sulfite; DMC, dimethyl carbonate; DMS, dimethyl sulfite; EA, ethyl acetate; EB, ethyl butyrate; EC, ethylene carbonate; EF, ethyl propionate; EMC, ethyl methyl carbonate; MA, methyl acetate; MB, methyl butyrate; MF, methyl butyrate; PC, propylene carbonate; PS, propyl sulfite.
Li⁺. On the other hand, the precipitated metallic lithium may form lithium dendrites, which brings safety hazards.

Aiming at addressing the above issues, several strategies as follows have been proposed in previous works (Figure 3). (1) Optimization of solvent composition. Low freezing point and low viscosity cosolvents are used to reduce the melting point of EC-based electrolyte and improve low-temperature conductivity. (2) Optimization of lithium salts. Adding lithium salt with better low-temperature performance can also improve the low-temperature performance to a certain extent. (3) Low-temperature additives. Adding a more effective film-forming additive than EC can reduce the charge transfer resistance of the electrode/electrolyte interface and prevent the growth of lithium dendrites at low temperatures, which can improve the low-temperature cycling stability of LIBs.

2.1 Low-temperature (co) solvent

The ideal low-temperature cosolvent ought to have the following properties: (1) Appropriate freezing point and boiling point, low vapor pressure, and remain liquid state within the battery operating temperature range; (2) Low viscosity and high dielectric constant (DN); (3) suitable electrochemical window, the oxidation potential should be higher than the potential of the cathode for delithiation, and the reduction potential should be lower than the potential of the anode for lithiation; (4) Improved low-temperature performance without compromising high-temperature performance. However, currently there is no single solvent that can simultaneously cover the above demands. The solvents that can be utilized in low-temperature electrolytes are mainly esters, including carbonates, carboxylates, and some sulfites.

Carbonate solvents include ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC), and so forth. So far, commercial LIBs still rely on carbonate-based electrolytes, which mainly include two types of carbonates: one is cyclic carbonate EC. It has high DN and high ionic conductivity, which helps to dissolve lithium salts and form a stable SEI film on the surface of the graphite anode, but the high freezing point of EC causes a significant increase in viscosity at low temperatures. The other type is chain carbonate, such as EMC, DEC, and so forth. Their structures are shown in Figure 4. They have a lower freezing point, which can help lessen the viscosity of the electrolyte and broaden the liquid range. However, chain carbonates generally have a low flash point, so they are easy to erupt at high temperatures, causing safety hazards.

Linear carboxylates include methyl acetate (MA), ethyl acetate (EA), methyl propionate (MP), methyl butyrate (MB), and so forth. The molecular structures are shown in Figure 5. Compared with carbonates with the same number of carbon atoms, the freezing point and boiling point of linear carboxylates are reduced by about 30%, and the viscosity is reduced by 50%. Therefore, it can be used as a low-temperature cosolvent to greatly reduce the freezing point and viscosity, thereby increasing the ionic conductivity of the electrolyte. However, lower carboxylic esters (with carbon atoms less than 4) usually have a higher vapor pressure and lower flash point than chain carbonates, thus causing safety risks at high temperature. Therefore, its proportion in the wide-temperature electrolyte must be strictly controlled. Sulfites include ethyl sulfite (ES), propyl sulfite (PS), dimethyl sulfite (DMS), diethyl sulfite (DES), and so forth. The molecular structures are shown in Figure 6. They possess a low melting point, low viscosity, high DN.
and satisfactory low-temperature property, and has been commonly used as additives until now.

Ding\textsuperscript{21} studied the phase diagrams of binary and ternary carbonate mixed solvents and found that the melting point of the mixed solvent is related to the solvent composition, the melting point of each component, and the relative content (Figure 7A,B). Hence, the freezing point of different electrolytes can be tuned by adjusting the composition and content of the solvent. In addition to the tunable freezing point, the multisolvent system owns a higher conductivity than the single-solvent system at low temperatures due to the disordered effect of Li\textsuperscript{+} coordination in various mixed solvents. Later, Smart et al. designed a ternary carbonate system composed of 1.0 M LiPF\textsubscript{6} and EC/DMC/DEC (1:1:1, by vol., the same below).\textsuperscript{10} By reducing the content of EC components, the electrolyte obtained a conductivity of 1 mS cm\textsuperscript{−1} at −40°C (Figure 7C), and the low-temperature performance at −20°C was better than that of the binary solvent system.

The ternary carbonate system can only exhibit a favorable electrochemical performance above −20°C, and the performance will greatly decay at lower temperatures. Therefore, some researchers have further proposed a quaternary carbonate system. Smart et al. reported a
quaternary system of 1.0 M LiPF$_6$ in EC/DMC/DEC/EMC (1:1:1:3) in 2003, which owned a conductivity of 1.32 mS cm$^{-1}$ at $-40^\circ$C, and 0.5 mS cm$^{-1}$ at $-60^\circ$C. Based on this electrolyte, a DD-sized 9 Ah battery consisting of LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode and MesoCarbon MicroBeads (MCMB) anode was assembled for further testing (Figure 7D). The capacity was about 35% of that at room temperature when discharged at C/10 at $-70^\circ$C. If being discharged at an extremely low current density of C/150, the capacity retention can even reach 69.9%, manifesting a preeminent low-temperature electrochemical performance. Shortly afterward, Xiao et al. applied the above electrolyte to a LiFePO$_4$/C battery and tested it at a current density of 1 C at $-40^\circ$C, the discharge capacity can still retain 51.3% of that at room temperature.

Appending a cosolvent with low viscosity, low freezing point, and good electrochemical stability to the electrolyte is another effective approach to improve the low-temperature performance of the carbonate electrolytes. Linear carboxylate can efficaciously lower the viscosity and enhance the conductivity at low temperatures, and more importantly, it helps to form a stable SEI film on the surface of the graphite anode. Herreyre et al. found that the conductivity of binary/ternary electrolytes containing EA and MB reached 7 mS cm$^{-1}$ at $-20^\circ$C, while the conductivity of conventional electrolyte was only 2 mS cm$^{-1}$, specifically, the discharge capacity of the electrode at $-40^\circ$C in 1.0 M LiPF$_6$-EC/DMC/EA (1:1:1) electrode was 81% of that at room temperature, and the capacity retention far exceeded that in EC/DMC/DEC system. In 2010, Smart and coworkers proposed an electrolyte system of 1.0 M LiPF$_6$ in EC/EMC/X (2:6:2) (X = MP, EP, MB, EB, PB, BB), which also exhibited excellent low-temperature performance, the discharge...
capacity of 7 Ah LiNi_{0.8}Co_{0.2}O_2-MCMB full battery at −60°C was 72.6% of that at room temperature, and was nearly twice the capacity in the more complex quaternary carbonate system. As a collaborator of Jet Propulsion Laboratory (JPL), A123 has developed a carbon-LiFePO_4 battery based on methyl butyrate electrolyte. When used at −40°C, the discharge capacity at a current density of 11 C exceeded 90% of the capacity at room temperature.

Previous researches have elucidated that fluorinated solvents can also improve the low-temperature performance of the electrolyte.\textsuperscript{23-26} The outermost electron orbit of fluorine has seven electrons, so it has the strongest electronegativity and weak polarity. Fluorine has the functions of lowering the freezing point of the solvent, reducing the energy levels of highest occupied molecular orbital and lowest unoccupied molecular orbital, and enhancing the antioxidant ability of the solvent (Table 2).\textsuperscript{4,14,27,28} Furthermore, F atoms have a strong attraction to H atoms, which can quench the chain reaction in the combustion process, and improve the flame-retardant performance and flashpoint of the solvent. However, fluorinated solvents possess a common disadvantage, that is, fluorine has a strong electron absorption effect, so it will reduce the DN value. DN is the electric permeability of a material expressed as a ratio with the electric permeability of a vacuum, which can be used to measure the ability of the insulator to store electric energy in an electrical field. The role of the DN of a solvent is associated with its capability to dissolve ionized solutes. Generally, cyclic solvent has higher DN value, naturally shows a higher conductivity and better ability to dissolve lithium salts. Yamaki et al. emphasized that the use of methyl fluoroacetate (MFA) or ethyl fluoroacetate (EFA) instead of MA or EA for LIBs can improve the compatibility with the aluminum current collector. None-theless, it has poor thermal stability and is prone to hydrolyze and generate HF to corrode the current collector and the cathode material. LiAsF_6 has high thermal stability and is hard to be hydrolyzed, but it is expensive and toxic. LiClO_4 exhibits a formidable oxidability and poses a high safety hazard. The main shortcoming of LiBF_4 is that the ionic association is too strong, resulting in low conductivity and poor rate performance at both room temperature and high temperature. Worse still, it cannot form a stable SEI film on the surface of graphite, although its low-temperature performance is better than LiPF_6.

2.2 Low-temperature lithium salts

Lithium salts include inorganic lithium salts and organic lithium salts. Among the inorganic lithium salts, LiPF_6 is currently the most widely used lithium salt, which has moderate cost, high conductivity and solubility, and decent compatibility with the aluminum current collector. Nonetheless, it has poor thermal stability and is prone to hydrolyze and generate HF to corrode the current collector and the cathode material. LiAsF_6 has high thermal stability and is hard to be hydrolyzed, but it is expensive and toxic. LiClO_4 exhibits a formidable oxidability and poses a high safety hazard. The main shortcoming of LiBF_4 is that the ionic association is too strong, resulting in low conductivity and poor rate performance at both room temperature and high temperature. Worse still, it cannot form a stable SEI film on the surface of graphite, although its low-temperature performance is better than LiPF_6.

LiBOB is a new type of lithium salt, in which the boron atom has a strong electron-withdrawing ability.\textsuperscript{35}

| Fluorinated esters | Boiling point (°C) | Freezing point (°C) | Flash point (°C) |
|-------------------|-------------------|--------------------|-----------------|
| FEC               | 249               | 18                 | 120             |
| MTFA              | 43.5              | −78                | 19              |
| ETFA              | 61                | −78                | −1              |
| TFEA              | 78                | ≤−80               | −7              |
| TFENB             | 113               | ≤−80               | 21              |
| TFENH             | 150               | −76.2              | 52              |

Abbreviations: ETFA, ethyl-2,2,2-trifluoroacetate; FEC, fluorinated ethylene carbonate; MTFA, methyl-2,2,2-trifluoroacetate; TFEA, 2,2,2-trifluoroethyl acetate; TFENB, 2,2,2-trifluoroethyl n-butyrate; TFENH, 2,2,2-trifluoroethyl n-caproate.
The connection with the oxygen atom in oxalate can disperse its charge and make it easy to dissociate. LiBOB has high thermal stability and good film-forming property but suffers from low solubility in linear carbonate. Researchers obtained a new lithium salt LiODFB by replacing the two F atoms in LiBF4 with oxalate, which combines the advantages of both LiBF4 and LiBOB, such as high solubility, unparalleled wide-temperature performance, and high rate performance. The other organic lithium salts include LiFSI, LiTFSI, and LiCF3SO3, all of which have excellent thermal stability, but LiTFSI and LiFSI will corrode aluminum foil, so they can only be used as additives rather than the main salt. Overall, the above organic lithium salts (LiBOB, LiODFB, LiFSI, LiTFSI) have the common issues: relatively high cost and low purity. Therefore, they are still far from commercial applications. The molecular structures of organic lithium salts mentioned above are shown in Figure 9.

Zhang et al. comparatively studied the low-temperature performance of the electrolyte when LiPF6 or LiBF4 was used as a lithium salt in propylene carbonate (PC)/EC/EMC (1:1:3), respectively (Figure 10A,B). Although the conductivity of the electrolyte containing LiBF4 is lower, the electrochemical impedance of the battery is reduced and the low-temperature discharge capacity is enhanced. The discharge capacity in the LiBF4-containing electrolyte at −30°C reached 86% of that at room temperature, while this value was only 72% for LiPF6-containing electrolyte. However, the film-forming ability of LiBF4 is so poor that the battery capacity decayed rapidly at room temperature. Accordingly, by mixing LiBF4 and LiPF6, Zhong40 developed an electrolyte consisting of 1.0 M LiPF6 in DMC/EMC (3:5, by mass) + 16% BA + 10% EC + 0.7 M LiPF6 + 0.3 M LiBF4, which owns a conductivity of 0.75 mS cm−1 at −40°C. The capacity of the NCM811/Li half-battery in the above electrolyte was 64% of that at room temperature, and the battery exhibited good cycling stability.

Unlike LiBF4, LiBOB has a favorable film-forming ability. In PC-based solvents, LiBOB can form a stable SEI film on the surface of graphite, whereas in linear carbonates, LiBOB has very low solubility, so it is generally used as an additive. Zhang et al. combined LiBF4 with LiBOB to develop an electrolyte composed of LiBF4-LiBOB (9:1, by mol) and PC/EC/EMC (1:1:3). LiFePO4/C battery with this electrolyte demonstrated excellent low-temperature performance, and its capacity at −50°C reached 35.7% of that at room temperature when discharged at 1°C.

Mandal et al. revealed that the electrolyte consisting of 0.9 M LiTFSI and EC/DMC/EMC (15:37:48, by mass) has a remarkable conductivity of 2 mS cm−1 at −40°C, and the LiNi0.8Co0.2O2/Li half-battery with this electrolyte retained 30% of its normal capacity at −40°C (Figure 10C,D). However, the TFSI-anion could severely corrode the Al and Cu collectors. Adding LiPF6, LiODFB, and other similar lithium salts to LiTFSI-based electrolytes can form AlF3 protective layer, thus alleviating the corrosion. Zhang et al. proposed that employing 0.2 M LiTFSI as an additive
in 1 M LiPF$_6$-based electrolyte could greatly reduce the charge transfer resistance,$^{42}$ and improve the cycling stability and rate performance.

### 2.3 Low-temperature film-forming additives

Additives have the advantages of small dosage and rapid effect without increasing the cost of battery compared with the other technologies. Therefore, employing additives to improve the low-temperature performance of LIBs is an effective strategy, which has drawn tremendous research interests in past decades.$^{43}$ The additives are mostly film-forming additives, which hold the ability to reduce film resistance and optimize lithium salt deposition behavior. Common additives include carbonates, sulfites, lithium salts, sulfones, and so forth.

Among carbonate additives, vinylene carbonate (VC) was the first to be commercialized. It has been demonstrated that adding 1% VC to the electrolyte can enormously improve the initial Coulombic efficiency and discharge capacity of the graphite anode.$^{44}$ The investigation showed that VC is reduced to free radical anions during discharge, the polymers generated by these anions were beneficial to the formation of a favorable SEI film, thereby inhibiting the decomposition of the solvent on the anode surface and strengthening the interface stability.

Fluorinated ethylene carbonate (FEC) is another commercially available additive. Xu et al. utilized 2% (by vol.) FEC as a film-forming additive for carbonate-based electrolytes which contributed to the formation of a desirable SEI film on the surface of the MCMB anode,$^{45}$ thereby significantly reducing the interface impedance and improving the cycling stability.

The sulfites mainly include dimethyl sulfite (DMS), diethyl sulfite (DES), vinyl sulfate (DTD), and so forth. Their structure is similar to carbonate esters, which is beneficial to form a desirable SEI film, diminish the charge interface impedance and improve the low-temperature performance. Wrodning et al. added 5%
(by vol.) ES to the PC-based electrolyte,\(^{20}\) which can effectively suppress the co-intercalation of PC. This is because the reduction potential of ES is about 2 V (vs. Li/Li\(^+\)), hence ES can form a passivation film on the surface of the graphite before the PC co-intercalation, and ultimately improve the low-temperature performance of the electrolyte. Yao et al. added 0.01% ethylene sulfate (DTD) to the electrolyte of 1 M LiPF\(_6\) in EC/DMC/EMC (1:1:1) and revealed that the reversible capacity of the MCMB/Li half-battery increased from 300 to 350 mAh g\(^{-1}\) owing to the decrease in total impedance.\(^{46}\) the cycle performance was remarkably improved as well.

Lithium salt additives are mainly LiBOB, LiODFB, and other boron-containing lithium salts that are beneficial to anode passivation and film formation. Zhang et al. added 1%–5% of LiBOB to the LiBF\(_4\) electrolyte and found that LiBOB can significantly remedy the imperfection of LiBF\(_4\),\(^{47}\) thus greatly enhancing the cycling stability. Cao et al. added 0.05 M LiBOB and 5% FEC as additives to 2.2 M LiFSI-TEP electrolyte,\(^{48}\) which prominently inhibited the side-reaction of TEP solvent on the surface of the graphite and formed a stable SEI film.

Sulfone-based solvents show good electrochemical stability and high conductivity, but also have a high freezing point, so they are mainly used as additives. Wang et al.\(^{49}\) proposed that the addition of methyl vinyl sulfone (MVS) and ethyl vinyl sulfone (EVS) can improve the compatibility of PC solvents with graphite anodes. Zuo et al.\(^{50}\) added 1% of three kinds of sulfone organics to the electrolyte of 1 M LiPF\(_6\) in EC/PC/DEC/EMC, the battery with additives offered better low-temperature performance than the batteries without additives. Unfortunately, the author did not specify these three sulfone compounds.

Moller et al. proposed that N, N-dimethyltrifluoroacetamide (DTA) exhibits lower viscosity and outstanding film-forming ability on graphite anodes.\(^{51}\) Adding 10% DTA to the PC solvent can notably lower the freezing point of the electrolyte to below -40°C, showing promising commercial application potential.

Hamenu et al. developed a type of Li-SiO\(_2\) nanosalt, which can dramatically enhance the conductivity and discharge capacity at low temperatures after being added to 1.0 M LiPF\(_6\) in EC/PC/EMC/DEC (20:5:55:20, by vol) + 2 wt% VC electrolyte.\(^{52}\) Won et al. combined PDMS-A with Li-SiO\(_2\) nano-salts and fabricated LiCoO\(_2\)/graphite battery containing these two additives.\(^{53}\) The capacity retention at -20°C after 50 cycles was 63.4%, far superior to that (38.7%) for the battery without additives. These research expounded that the silicon-containing compound participated in the film-forming reaction during the first cycle, and formed an SEI film with inspiring stability and extremely low impedance, which availed to improve the low-temperature performance of LIBs.

### 2.4 ILs

ILs are salts comprising organic cations (imidazolium, ammonium, pyrrolidinium, etc.) associated with inorganic anions (Cl\(^-\), AlCl\(_4\)^-\), PF\(_6\)^-, BF\(_4\)^-, NT\(_2\)^-, DCA\(^-\), etc.) or organic anions (CH\(_3\)COO\(^-\), CH\(_3\)SO\(_3\)^-, N(CF\(_3\)SO\(_2\))\(_2\)^-, TFSI\(^-\), etc.), which are liquid around room temperature.

ILs have received increasing attention for battery application due to their unique physicochemical properties, such as wide electrochemical stability window (>5.5 V vs. Li\(^+/\)Li), large liquidus range, negligible vapor pressure, high thermal stability (>300°C), and non-flammability. It is significant to note that the characteristic properties of ILs can be tuned by varying the combination of anion and cation or grafting different functional groups.

Subjected to the high cost, ILs are rarely employed in low-temperature electrolytes. Nakagawa et al. combined 1-ethyl-3-methylimidazolium cation with low viscosity and high conductivity with BF\(_4\)^- anion that can form a low-resistance SEI film,\(^{54}\) to obtain an IL 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF\(_4\)), which integrates the merits of both EMI\(^+\) and BF\(_4^-\). The results indicated that adding 1% EMI-BF\(_4\) to the electrolyte of 1 M LiPF\(_6\) in EC/EMC (1:2, by mass) can greatly improve the low-temperature performance of the battery. Specifically, the discharge capacity of LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_2\)/Graphite full battery significantly increased from 303.7 to 878.7 mAh at -30°C, and the capacity retention after 150 cycles at -10°C increased from 78.2% to 89.4%.

The grafting of short-chain ether functional groups into the cationic structure of the ILs can effectively reduce the viscosity of the ILs and increase the ionic conductivity, thereby it can be used in low-temperature electrolytes.\(^{55}\) Chen et al. studied a binary system electrolyte (LiODFB-Pyr1,2o1TFSI/DMS) composed of ether-modified IL [PYR1,2o1][TFSI] and sulfite (DMS),\(^{56}\) which owns a conductivity of 0.46 mS cm\(^{-1}\) at -40°C. The Li/LiFeO\(_4\) battery with this electrolyte exhibited outstanding electrochemical performance in the temperature range of -40 to 60°C.

### 2.5 Solid-state electrolyte

Compared with liquid electrolytes, solid-state electrolytes possess the advantages of high safety, desirable thermal stability, and wide operating temperature window. All-solid-state batteries that use solid electrolytes to match lithium metal anodes with high-capacity cathode materials have become the current research hotspots. As a result of the intrinsically low conductivity of solid-state electrolytes, they are rarely used in low-temperature
LIBs, only a few specially modified composite solid-state electrolytes that exhibit satisfactory conductivity at low temperatures can be used. Below, ionic gel and gel polymer electrolytes will be introduced as examples.

Ionic gel is a composite material, the solid matrix of which is filled with IL. The solid framework is the key to the design of functional ionic gels, mainly including CNTs, SiO2, TiO2, and MOFs. Kitagawa et al. studied an electrolyte system composed of EMI-TFSI and microporous ZIF-8. The DSC results showed that the EMI-TFSI in the micropores will not undergo solidification phase transition at temperatures as low as −150°C, while the isolated EMI-TFSI body will solidify at −42°C. EMI-TFSI@ZIF-8 has relatively stable conductivity between −45 and 68°C, while the conductivity of isolated EMI-TFSI will drop sharply below −9°C.

Gel polymer electrolyte is a composite electrolyte composed of polymer, lithium salt, and low molecular organic solvent (plasticizer), which can effectively improve the conductivity of solid polymer electrolyte and promote the dissolution of lithium ions. Scrosati et al. reported a gel electrolyte with LiAsF6 as the lithium salt, EC and PC as the plasticizer, and polyethylene oxide as the matrix. The conductivity of this gel electrolyte can reach 0.1 mS cm−1 at −60°C, and it exhibited a wide electrochemical window as high as 4.8 V, as well as good interface compatibility. Xu et al. explored a polymer electrolyte PFSA-Na membrane for solid sodium–ion batteries (SSIBs). Its ion conductivity retained 4.88 × 10−2 mS cm−1 at −15°C. The SSIBs exhibited outstanding low-temperature performance, the discharge capacity at −35°C exceeded 50% of that at room temperature, and the Coulombic efficiency was close to 100%. Note that the synthetic process of this electrolyte was simple and facile, showing the potential for commercial applications.

Aiming at low-temperature application, reasonable design of multicomponent mixed solvent system has been demonstrated as the most effective approach. Besides, the moderate cost and easy-to-magnify characteristics are expected to facilitate its industrial production. Introducing appropriate low-temperature film-forming additive are also recognized as a practical strategy due to the low cost and adjustable ability. It is anticipated that the combination of the above two strategies could attain electrolytes with excellent low-temperature performance.

The utilization of mixed lithium salts can also improve the low-temperature performance of the electrolyte but may bring some concerns such as reduced conductivity and increased cost. ILs and solid electrolytes could greatly enhance battery safety, whereas their performance is far inferior to the ester-based electrolytes subjected to the intrinsically low conductivity at low temperature.

3 | HIGH-TEMPERATURE ELECTROLYTE

Although the sluggish diffusion of Li+ at low temperatures leads to a sharp decline in electrochemical performance, the diffusion is a reversible process and is not harmful to the composition and structure of the battery. The electrochemical behavior of the battery at high temperature is completely different from that at low temperature. The lithium salt LiPF6 in the current electrolyte system is thermodynamically unstable at high temperatures (>60°C), and the following chemical reaction will take place:35

$$\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5.$$  (1)

The product PF5 is a strong Lewis acid, which is inclined to react with organic solvents with high DNs and trace moisture in electrolytes. Furthermore, PF5 will also react with the SEI film, and the generated HF, RCOF, POF3, and other substances will increase the interface impedance and corrode the current collector. The specific reactions are presented in Equations 2–5:15

$$\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF},$$  (2)
$$\text{RCO}_2\text{Li} + \text{PF}_5 \rightarrow \text{RCOF} + \text{LiF} + \text{POF}_3,$$  (3)
$$\text{Li}_2\text{CO}_3 + \text{PF}_5 \rightarrow \text{POF}_3 + 2\text{LiF} + \text{CO}_2,$$  (4)
$$\text{ROCO}_2\text{Li} + \text{PF}_5 \rightarrow \text{RF} + \text{LiF} + \text{CO}_2 + \text{POF}_3.$$  (5)

As can be seen, the side reactions that occur at high temperatures generate a large amount of LiF and increase the internal resistance. At the same time, the formation of gas products will increase the internal pressure, causing the battery to expand or even explode. Therefore, the current research on improving the high-temperature stability of LIBs mainly focuses on three aspects: (1) Develop lithium salts with excellent high-temperature performance that can replace LiPF6. (2) Seek lithium-salt stabilizers to inhibit the decomposition of LiPF6 at high temperatures. (3) Develop high-temperature film-forming additives to improve the high-temperature stability of SEI films (Figure 11).61

3.1 | High-temperature lithium salts

The advanced research of high-temperature salts mainly focuses on lithium–phosphate complexes and lithium borate complexes. These two types of lithium salts are centered on B or P atoms, so they exhibit strong electron-withdrawing ability, easily form large conjugated π-bonds, and dispersing the negative charge of the central ion to
make the anion more stable. At present, the most studied high-temperature lithium salts are LiBOB, LiODFB, LiTFSI, and other mixed coordination lithium salts.

Substituting larger anionic ligands for the F atoms in LiPF6 or LiBF4 can effectively improve the thermal stability of the lithium salt. Aurbach62 used −CF2CF3 as the substituent to obtain the lithium salt LiPF6(CF2CF3) (LiFAP), which has better thermal stability than LiPF6 (Figure 12A). The electrochemical property of Graphite/Li half batteries with 1 M LiPF6 + EC/DEC/DMC (2:1:2) and 0.5 M LiPF6 + 0.5 M LiFAP + EC/DEC/DMC (2:1:2) were comparatively studied, the results illustrated that the battery containing only LiPF6 cannot operate at 80°C at all, but the battery containing LiPF6 + LiFAP can still operate stably at 80°C (Figure 12B). Cui et al. synthesized LiBF2SO4 using SO42− as a substitute ligand,62 and tested the high-temperature performance of Li/LiFePO4 half battery with the electrolyte of 1 M LiBF2SO4 in PC/EC/EMC (3:3:4). It was found that LiBOB-containing electrolyte has lower conductivity than LiPF6−containing electrolyte, thereby the battery with LiBOB-based electrolyte delivered lower discharge capacity in the first few cycles. However, the high-temperature performance of LiBF2SO4-based electrolyte was significantly better than that of LiPF6-based electrolyte. The initial capacity of the battery in the two electrolytes was the same at 65°C, but the dissolution of Mn in LiPF6-based electrolyte resulted in a 19% decrease in battery capacity after five cycles. In contrast, the battery's capacity retention in LiBOB-based electrolyte was evidently higher. Note that LiBOB could form a unique SEI film, hence graphite could operate stably even in pure PC, which broadens the choice of electrolyte solvents.

As mentioned before, to overcome the low solubility of LiBOB in linear carbonates, Zhang et al. obtained lithium difluorooxalate borate (LiODFB) by replacing two F atoms in LiBF4 with oxalate in 2006.37 LiODFB has a higher solubility in linear carbonate solvents, additionally, it could form a stable SEI film on the graphite anode. Consequently, the Li/LiNi1−x−yMxNyO2 half battery with the electrolyte of 1 M LiODFB in PC/EC/EMC (3:3:4) exhibited high capacity retention of 90% after 200 cycles at 60°C. This was mainly because LiODFB undergoes a small amount of ligand exchange in the carbonates solvents at high temperatures, partially forming LiBOB, and thus achieves outstanding SEI film-forming properties, which can operate stably at high temperatures.36 Even if the content of LiBOB and LiODFB was decreased to the additive level, the electrolyte can still show excellent film-forming properties. Xu et al. assembled a LiNi0.8Co0.15Al0.05O2/graphite full battery with an electrolyte composed of 1.2 M LiPF6 in EC/EMC (3:7) + 1 wt% LiODFB.65 The battery delivered desirable capacity retention of 80% when stored at 55°C for 150 days. TEM and EIS measurements showed that the SEI film formed by the electrolyte with LiODFB additive was dense and had low impedance, which was beneficial to the improvement of high-temperature performance.
Both LiTFSI and LiFSI possess excellent thermal stability, but they are very corrosive to aluminum foil current collectors, so they are commonly mixed with other lithium salts. Wang et al. studied the effect of 1 M LiPF$_6$ + Li$_2$O/EC/EMC (1:1) electrolyte on the property of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$/graphite full battery and formulated that the presence of LiTFSI reduced the charge transfer resistance, self-discharge rate, and the amount of gas evolution under high-temperature storage, it could also improve the high-temperature and low-temperature performance. However, when the upper charge voltage exceeded 4.45 V, the content of Ni, Mn, and Co metal ions in the electrolyte increased, indicating that LiTFSI would aggravate the dissolution of transition metals. Feng et al. investigated the effect of the mixed-use of LiFSI and LiODFB with different molar ratios on the high-temperature performance of Li/LiFePO$_4$ batteries. The blank solvent was EC:EMC (3:7). The results illustrated that when the molar ratio of LiFSI to LiODFB was 4:1, the electrochemical performance was the best (Figure 12D). The discharge capacity retained as high as 149.63 mAh g$^{-1}$ after 100 cycles at 60°C, corresponding to an outstanding capacity retention of 91.3%, and the capacity at 5 C reached 42.5% of that at 0.5 C. By comparison, the retention for LiPF$_6$-containing battery was only 2.1%, and it could not be charged and discharged at high temperatures. SEM results proved that LiFePO$_4$ cycled in the blank electrolyte was covered by thick and uneven by-products, while in the mixed salt electrolyte system, a stable and dense SEI film was formed on the electrode surface, which inhibited the interface reaction between the electrode and the electrolyte. XPS revealed that the composition of the SEI film contains LiF, B-O, and B-F bonds, indicating that these two lithium salts
decomposed and participated in the film formation on the electrode surface, thereby significantly improving the cycling stability and rate capability at high temperatures.

### 3.2 Lithium salt stabilizing additives

Based on the previous analysis, we noticed that the deterioration of battery performance at high temperatures is mainly caused by the decomposition of the lithium salt LiPF$_6$ and its decomposition product PF$_5$. Generally, there are two strategies to improve the stability of LiPF$_6$-based electrolyte at high temperatures: inhibit the decomposition of LiPF$_6$ or weaken the reactivity of PF$_5$.

Inhibition of LiPF$_6$ decomposition is comparatively difficult because LiPF$_6$ itself has very poor thermal stability. Hiroi proposed that adding 0.05 wt% of LiF to the electrolyte with LiPF$_6$ as the solute could significantly reduce the gas production, because according to Le Chatelier’s principle, the addition of the product LiF promotes the reaction (Equation 1) equilibrium to shift to the left, thereby inhibiting the decomposition of LiPF$_6$.

Another strategy is to weaken the reactivity of PF$_5$. Studies have shown that PF$_5$ is electron-deficient, so a small amount of Lewis alkaline additives could significantly weaken the acidity and reactivity of PF$_5$. Ideally, if these compounds have a slight Lewis basicity, it can prevent the equilibrium of the reaction (Equation 1) from shifting to the decomposition direction.

Zhang et al. proposed a tris(2,2,2-trifluoroethyl) phosphate (TTFP), which formed a weak bond with PF$_5$, thereby stabilizing LiPF$_6$. The structure diagram of TTFP and the reaction mechanism were displayed in Figure 5A. Adding 15%–20% TTFP could make the electrolyte of 1 M LiPF$_6$ in PC/EC/EMC (1:1:1) flame resistant, and the Gr/Ni-rich battery with this electrolyte exhibited outstanding cycling performance at 60°C. Encouragingly, it could inhibit the co-intercalation of PC in graphite, thereby improving the Coulombic efficiency.

The lone pair electrons on the nitrogen atom are connected to electron-withdrawing groups such as $>$C = O or $>$P = O, which could be used as a weaker basic center to deactivate PF$_5$. Therefore, amide-based compounds could be utilized as stabilizers for LiPF$_6$, such as pyridine and hexamethylphosphoramide (HMPA).

Li$^{68}$ reported that 1 M LiPF$_6$-EC/DMC/DEC (1:1:1) containing 3 wt% pyridine displayed no discoloration when stored at 85°C for 1 month, and no decomposition products were detected by NMR. In contrast, the electrolyte without pyridine turned brown within 2 days. However, the addition of pyridine will cause a slight decrease in battery capacity. HMPA also owns the ability to stabilize lithium salts. Compared with the weak bond of pyridine-PF$_5$, the bond of HMPA-PF$_5$ was quite strong.

As a result, the electrolyte containing 3 wt% HMPA could be stored stably for 8800 h at 85°C without discoloration, and only trace decomposition products were detected by the composition analysis. Hexamethoxycyclotriphosphazene (HMOPA), which has a similar structure to HMPA, is another lithium salts stabilizer. The electrolyte with 3 wt% HMOPA could be stored at 85°C for 2000 h without discoloration, whereas the electrolyte turned brown after that. The analysis found that HMOPA has undergone a slow structural rearrangement at 85°C. The rearrangement product was ammonia substances, which were free of imino nitrogen atoms, thus exhibiting a relatively weak interaction with PF$_5$ and poor ability to stabilize the electrolyte. Besides, the ring-opening reaction between HMOPA and the cathode materials generates gel in the electrolyte, which further makes HMOPA far from practical application.

### 3.3 High-temperature film-forming additives

The film-forming additives mostly have higher reduction potential. During the first discharge, they can decompose before the other solvent components of the electrolyte, and form a stable SEI film on the surface of the anode, therefore, suppressing the decomposition of the electrolyte at high temperatures. There are two main types of additives: inorganic additives and organic additives.

The research of inorganic film-forming additives mainly focuses on CO$_2$, dialkyl-pyrocarbonates, or other compounds that can directly or indirectly provide CO$_2$, as well as a series of phosphorus and nitrogen compounds. Aurbach$^{69}$ proposed that adding a small amount of CO$_2$ could form a stable Li$_2$CO$_3$ passivation layer on the surface of the anode, thereby effectively improving the cycling performance of LIBs. Wang et al. explored the influence of Li$_2$CO$_3$ as an additive on the high-temperature performance of Li/LiMn$_2$O$_4$ batteries.$^{70}$ and found that the addition of Li$_2$CO$_3$ helped to form a CEI film with excellent ionic conductivity on the surface of the LiMn$_2$O$_4$ electrode, thereby further enhancing the cycling performance at high temperatures (Figure 13A,B). Frustratingly, the solubility of Li$_2$CO$_3$ in organic solvents is very low, hence the improvement of battery performance is limited. Therefore, more research have focused on organic film-forming additives.

VC was first employed as a high-temperature film-forming additive. Aurbach’s research$^{73}$ pointed out that adding 5% VC to the electrolyte of 1 M LiFAP in EC/DEC/DMC (1:1:1) can distinctly improve the performance of
Graphite/Li half battery at high temperatures, showing almost no capacity attenuation after 100 cycles, while the control group without VC showed a nearly 50% capacity decline. Compared with VC, vinyl ethylene carbonate (VEC) contains one more electron-rich C=C bond, and the double bond is more reactive. Yang\(^74\) found that adding 2 vol% of VEC to 1 M LiPF\(_6\)-EC/DMC (3:7) could significantly improve the high-temperature performance of Li/LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\) battery, and the capacity retention at 50°C increased from 68.8% to 84.8%. The differential electrochemical mass spectrometry (DEMS) measurements revealed that the addition of VEC reduced the amount of CO\(_2\) released during the first discharge, and CO\(_2\) disappeared in the second cycle, indicating that with the participation of VEC, a stable SEI film was formed on the surface of the cathode and anode.

The structure of the sulfite additives is similar to EC, PC, and so. The central sulfur atom is more electronegative, consequently, the sulfite additive has stronger reducibility than carbonate. It can decompose on the graphite surface before other solvents to form a stable SEI film, and has negligible influence on the electrochemical performance of graphite. Kang et al. compared the effects of VC,\(^71\) succinonitrile (SN), and 1,3-propane sultone (PS) as additives on the performance of Li/LiNi\(_{0.4}\)Mn\(_{0.3}\)Co\(_{0.2}\)O\(_2\) batteries. The results show that all three additives could improve the high-temperature performance of the battery (Figure 13C). The capacity retention of the battery without additives after 50 cycles was only 78.2% at 60°C, while the retentions were 90.4%, 94.6%, and 98.9% for VC-, SN-, and PS-containing batteries, respectively.

At present, sulfonate additives such as 1,3-propane sulfone (1,3-PS), 1,4-butane sulfone (1,3-BS), and 1,3-propene sulfone (PES) have attracted much attention, and all of them have satisfactory film-forming properties. Zuo et al. found that adding 1 wt% 1,3-PS to 1 M LiPF\(_6\)-PC/EC/
EMC (1:1:3) could increase the first discharge capacity of the battery by 8%, and the discharge capacity increased by 8.9% after storage at 80°C for 4 h (Figure 13D). Xia et al. compared the effects of VC and PES additives on the performance of LiNi1/3Mn1/3Co1/3O2/Gr batteries, and found that batteries containing PES produced less gas than batteries containing VC, and exhibited better high-temperature performance, the capacity loss after 1000 cycles at 55°C was less than 20%.

3.4 Acid/water removal additives

LiPF₆ decomposes and hydrolyzes at high temperatures to produce HF. On the one hand, it will corrode the current collector. On the other hand, it can react with the components of the SEI film to form LiF, which increases the impedance of the SEI film. In addition, HF will react with cathode materials such as LiMn₂O₄ to cause the dissolution of high-valent metals and finally lead to capacity loss. Trace amounts of HF and H₂O in the electrolyte can be removed by additives, which mainly include organosilicon compounds and amines.

Aurbach et al. pointed out that adding a small amount of organosilicon compound to the LiPF₆-based electrolyte (the mixed solvent was EC/EMC, EC/DMC, or EC/DEC/DMC) could remove traces of HF and H₂O impurities in the electrolyte and avoid harming the electrode performance. He studied the effects of two high-temperature additives: organosilanes and alkylsilanes, on the performance of LiCoO₂/graphite battery at 60°C. In 1 M LiPF₆-EC/EMC (3:7) blank electrolyte, the capacity of the battery has decayed by more than 50% within a few cycles. Surprisingly, the addition of 0.5 wt% silicon additives remarkably improves the specific capacity and cycling stability. XPS analysis showed that Si-F-containing compounds appeared on the surface of LiCoO₂ after cycling, indicating that siloxane and alkoxysilane compounds could react with HF in the electrolyte to form an interface layer with lower impedance, thereby improving the high-temperature stability of the electrolyte.

Zuo studied the function of ethanolamine as an additive. Distilled water was added to the 1 M LiPF₆-EC/DME/EMC (1:1:1) electrolyte to elevate the moisture to 0.01%, and 0.1% ethanolamine was added to the control group simultaneously. These two groups of electrolytes were stored at 45°C for 24 h, after that the content of H₂O and HF in the electrolytes were tested. It can be observed that in the electrolyte without ethanolamine, LiPF₆ reacted with water at high temperatures and generated a large amount of acid. On the contrary, in the electrolyte containing ethanolamine, LiPF₆ reacted slowly with water, and the HF content was lower. As a result, the battery containing ethanolamine additive exhibited better cycling performance at high temperatures.

3.5 IL

In high-temperature LIBs, ILs with TFSI-type anions are widely studied. On the one hand, the IL formed by the TFSI anion has a large steric hindrance, and it is difficult for anions and cations to accumulate regularly. On the other hand, the fluorine on TFSI⁻ is strongly delocalized due to the negative charge, which weakens the interaction between anion and cation. Therefore, the IL formed by TFSI⁻ is not sensitive to water and has high thermal stability. The application of ILs composed of different cations and TFSI⁻ at high temperatures will be introduced as follows.

Imidazole-based ILs have high conductivity and low viscosity, which have become the research focus in recent years. The disadvantage is the narrow electrochemical window caused by the higher reduction potential than the Li⁺ insertion potential of carbon materials, therefore, they are not suitable for matching with carbon anodes. Srour et al. found that the thermal stability of 1 M LiTFSI in 1-methyl-3-hexylimidazole bis(trifluoromethanesulfonamide) imide ([C₁C₆IM][TFSI]) was as high as 300°C, and the ionic conductivity reached 7.423 mS cm⁻¹ at 60°C. The discharge capacity of the Li₄Ti₅O₁₂/LiFePO₄ battery with this electrolyte reached 130 mAh g⁻¹ and showed no capacity degradation after 50 cycles. The combination of imidazole ILs and organic solvents to form a multielement electrolyte can significantly improve electrochemical performance. Wang et al. designed an electrolyte composed of 0.3 M LiTFSI in 1,2-dimethyl-3-ethylimidazolide bis(trifluoromethylsulfonyl)imide([EMIM][TFSI])/DMC/VC (14:5:1) + 0.25 wt% LiODFB, the assembled Li/LiNi₁/₃Co₁/₃Mn₁/₃O₂ battery delivered a discharge capacity of 157.7 mAh g⁻¹ after 50 cycles at 80°C, suggesting an outstanding high-temperature performance.

Pyrrole-based ILs have relatively high viscosity and an electrochemical window higher than 5 V. Among them, ILs composed of PYR-based cations and TFSI⁻ or FSI⁻ anions have gained more attentions. Lewandowski et al. reported an electrolyte containing 0.5 mol/kg [PYR₁₃][FSI] and applied it to Li/LiFePO₄ batteries. The discharge capacity was about 153 mAh g⁻¹ at a current density of 0.5 C at 50°C, and there was still a discharge capacity over 110 mAh g⁻¹ even if the current density was boosted to 4 C. Similarly, Lombardo et al. mixed pyrrole-based ILs with organic solvents to form a multielement electrolyte. The results showed that the 1 M LiPF₆-EC/EMC (3:7) commercial electrolyte with...
[PYR$_{13}$][TFSI] presented good flame resistance, and the self-extinguishing time could be dramatically shortened by adding 30–50 wt% IL, while the conductivity was retained as well. The assembled Li$_4$Ti$_5$O$_12$/LiFePO$_4$ battery exhibited a discharge capacity of higher than 150 mAh g$^{-1}$ and a Coulombic efficiency close to 100%.

Piperidine-based ILs are similar to pyrrole-based ILs, which own good thermal stability, moderate ionic conductivity ($\approx$1.4 mS cm$^{-1}$) and a wide electrochemical window (>5.0 V vs. Li$^+/\text{Li}$), subjected to its high viscosity, it is often mixed with carbonate organic solvents. Li/ Si batteries with the electrolyte of 0.8 M LiTFSI in [PP$_{13}$][TFSI]/PC can work steadily for 100 cycles at 25°C without evident capacity degradation, while the reversible capacity at 100°C could be further increased by three to four times to 2230 mAh g$^{-1}$. Lewandoski et al. studied the compatibility of 0.4 M LiTFSI in [PP$_{13}$][TFSI] + 10 %VC with Li$_2$MnO$_4$ cathode.$^{81}$ The discharge capacity reached 125 mAh g$^{-1}$ in the first cycle at a current density of 0.1 C at room temperature, and there was almost no capacity degradation after 25 cycles, demonstrating good electrochemical compatibility. At the same time, this electrolyte offered a high flashpoint over 300°C and owned great non-flammability deservedly.

3.6 | Solid-state electrolyte

Consistent with the low-temperature applications discussed above, we also introduce the application of two composite solid-state electrolytes at high temperatures, ionic gel electrolyte, and gel polymer electrolyte.

Among the ionic gel electrolytes, the SiO$_2$ matrix-based electrolyte which has high Young’s modulus, great thermal stability, high specific surface area, and outstanding ionic conductivity has been studied firstly. Chen et al. obtained SiO$_2$/[PYR$_{14}$][TFSI]/LiTFSI quasi-solid electrolyte by sol-gel method and assembled Li/LiFePO$_4$ battery with it.$^{82}$ The results indicated that the discharge capacity of the battery was 155.2 mAh g$^{-1}$ at a current density of 0.1 C at 55°C with no capacity decay after 30 cycles, showing good electrochemical performance. Functional modification of SiO$_2$ matrix can effectively reinforce the battery performance. Wu et al. stated that the grafting of SiO$_2$ particles with epoxy groups could significantly promote the dissociation of lithium salts and ILs,$^{83}$ and greatly improve ionic conductivity. The SCA/[Py$_{11}$][TFSI]/LiTFSI gel electrolyte was synthesized using this matrix and applied to Li/LiFePO$_4$ batteries. The discharge capacity reached 154.9 mAh g$^{-1}$ at a current density of 0.1 C at 30°C, and it was further increased to 168.6 mAh g$^{-1}$ at 90°C, which was close to the theoretical specific capacity.

The TiO$_2$ matrix is a porous oxide, which is capable of confining the IL well. Moreover, the ion transport channel of the TiO$_2$ group is three-dimensional and continuous, hence the ionic gel electrolyte based on this matrix owns favorable ionic conductivity. Chen et al. adopted the sol-gel method to achieve the controllable synthesis of a series of self-supporting ionic gels such as TiO$_2$/[PYR$_{13}$][TFSI]/LiTFSI.$^{84}$ The products have good thermal stability and safety. The Li/LiFePO$_4$ batteries employing this gel electrolyte retained 92% of its initial capacity after storage at 150°C for 10 h. The battery delivered a capacity of 150 mAh g$^{-1}$ after 300 cycles at room temperature, and still maintained a specific capacity close to 100 mAh g$^{-1}$ at a high current density of 2 C.

In addition to the abovementioned materials, several compounds with porous structure can also be employed as the matrix of ion gel electrolyte, such as clay, hexagonal boron nitride(h-BN), and so forth. Kalaga et al. proposed the Clay/PPMI/(1 M) LiTFSI solid-state electrolyte system,$^{85}$ which revealed good structural stability even at 355°C, and an electrochemical window of about 3 V. The Li/Li$_4$Ti$_5$O$_12$ battery with this electrolyte showed no capacity decay after 120 cycles at 120°C, and the Coulombic efficiency was close to 100%. Rodrigues et al. designed h-BN/[PP$_{13}$][TFSI]/LiTFSI composite electrolyte.$^{86}$ The assembled Li/Li$_4$Ti$_5$O$_12$ battery exhibited stable electrochemical performance at 150°C, with a discharge capacity close to 150 mAh g$^{-1}$ at C/2. On the contrary, the battery with commercial electrolyte were short-circuited at high temperatures.

Succinonitrile (SN) has a high lithium salt solubility, a high flashpoint up to 260°C, and low flammability, so it is commonly utilized as a high-safety polymer electrolyte. Guo et al. designed a LiOB-BN-PEO electrolyte with a temperature resistance of up to 170°C,$^{87}$ which is much higher than that of the traditional PEO electrolyte (100°C), and exhibited a conductivity of 1 mS cm$^{-1}$ at 150°C. Li et al. reported an electrolyte of SN-modified LiTFSI-PUA.$^{88}$ The assembled Li/LiCo$_2$O$_2$ battery offered a promising cycling performance at 55°C, and the discharge capacity was still higher than 100 mAh g$^{-1}$ at a current density of 2 C. More significantly, Li$_4$Ti$_5$O$_12$/LiCo$_2$O$_2$ full battery with this electrolyte could still light up the LED light after being folded at 180° for 100 times, demonstrating an inspiring safety and electrochemical performance.

Regarding high-temperature electrolyte, since LiPF$_6$ is unstable at high temperatures, it is important to choose suitable lithium salts. Employing organic lithium salts with better thermal stability could greatly improve the high-temperature performance, although they would bring increased cost and non-negligible corrosion to the current collectors. The combination of multicomponent
mixed solvent systems and necessarily functional high-temperature additives is a promising strategy to achieve high-temperature adaptable electrolyte.

ILs and solid electrolytes gain a moderate conductivity at high temperatures, which could greatly improve the electrochemical performance. In addition, battery safety is enhanced as well. However, the high cost and complex production process increase the difficulty of industrial applications.

4 | WIDE-TEMPERATURE ELECTROLYTE

As discussed above, different application fields put forward different demands on battery performance, while the limiting factors for battery performance in high and low-temperature environments are quite different. Unfortunately, a variety of low-temperature electrolytes have poor stability at high temperatures. On the contrary, the electrolytes capable of working at high temperatures often have low conductivity and inferior film-forming ability at low temperatures. It seems that developing “one stone two birds” electrolyte is really a tricky task, hence only a few works on carbonate-based or fluorine-based wide-temperature electrolytes have been reported so far.

4.1 | Carbonate-based wide-temperature electrolyte

Traditionally, ternary or quaternary mixed solvents in which the content of EC is lowered and the content of linear carbonate or carboxylate is raised are employed to improve the wide-temperature performance of the electrolyte. During 2009–2014, NASA’s JPL presided a 5-year wide-temperature LIB research project and developed three generations of wide-temperature electrolyte (Figure 14, Table 3). The composition of the SOA electrolyte developed by the university of southern california (USC)/JPL 15 years ago was 1.0 mol L⁻¹ LiPF₆/EC + DMC + DEC (1:1:1, by vol.), in which the EC content reached 33%, and the operating temperature range was −30 to 40°C. The first-generation of wide-temperature electrolyte was composed of 1.0 mol L⁻¹ LiPF₆/EC + DMC + DEC + EMC (1:1:1:3), the conductivity of this electrolyte reached 1 mS cm⁻¹ at −40; the second-generation electrolyte was optimized to increase the EMC content and lower the EC content, with a composition of 1.0 mol L⁻¹ LiPF₆/EC + EMC (1:4) or 1.2 mol L⁻¹ LiPF₆/EC + EMC (3:7). Adding carboxylic ester cosolvents into the second-generation electrolyte will produce the third-generation electrolyte, which could effectively reduce the freezing point and enhance the low-temperature conductivity. The operating temperature of the third-generation electrolyte ranged from −60 to 60°C, which is significantly higher than that of the older generation.

4.2 | Fluorine-based electrolyte

In contrast to the LiPF₆ with poor thermal stability, organic lithium salts with better thermal stability and good

![Figure 14](image-url) The effect of different solvent collocations on the conductivity at different temperatures. The lithium salt of the electrolytes are 1 mol L⁻¹ LiPF₆

| Table 3 | Development of USC/JPL electrolytes in recent years

| Electrolyte code | Composition of carbonate-based electrolytes | Operating temperature/°C | Source |
|------------------|------------------------------------------|--------------------------|--------|
| SOA              | 1.0 mol L⁻¹ LiPF₆/EC + DMC + DEC (1:1:1) | −30 to 40°C              | JPL/USC |
| Gen1             | 1.0 mol L⁻¹ LiPF₆/EC + DMC + DEC + EMC (1:1:1:3) | −50 to 40°C              | JPL/USC |
| Gen2             | (1) 1.0 mol L⁻¹ LiPF₆/EC + EMC (1:4)          | −60 to 50°C              | JPL/USC |
|                  | (2) 1.2 mol L⁻¹ LiPF₆/EC + EMC (3:7)          |                          |        |
| Gen3             | 1.0 mol L⁻¹ LiPF₆/EC + EMC (1:4) + carboxylic esters | −60 to 60°C | JPL/USC |
low-temperature performance, such as LiTFSI and LiFSI, are more suitable for wide-temperature electrolytes. Xia et al. proposed a new electrolyte system composed of 2 M LiTFSI-EA, which could offer a conductivity of 0.2 mS cm\(^{-1}\) at \(-70\) and work in an ultra-wide temperature range of \(-70\) to \(55^\circ\text{C}\). As LiTFSI has serious corrosion to Al foil, they chose organic PTPAn as the cathode and operated it in a relatively narrower voltage region, which caused a large loss in energy density. Wang’s group reported a type of perfluorinated electrolyte,\(^9\) dissolving LiFSI and other fluorine-containing lithium salts, FEC and methyl (2,2,2-trifluoroethyl) carbonate, into high fluorine non-polar solvents, such as methoxyperfluorobutane and tetrafluoro-1-(2,2,2-trifluoroethoxy) ethane. This type of electrolyte held the superior performance of fluorinated species, possessed a rather wide voltage window (\(=5.6\) V), and operated in a wide temperature range from \(-125\) to \(70^\circ\text{C}\). The LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\)/Li battery assembling with perfluorinated electrolyte offered a capacity of 172 mAh g\(^{-1}\) at room temperature, which was close to the capacity obtained in the conventional electrolyte. When the temperature dropped to \(-42^\circ\text{C}\), the traditional carbonate electrolyte was completely solidified and only an extremely low capacity of 13.3 mAh g\(^{-1}\) was released. By contrast, the specific capacity of the battery using perfluorinated electrolyte was as high as 160 mAh g\(^{-1}\), and the battery could still drive a fan at \(-95^\circ\text{C}\).

5 | CONCLUSION AND PERSPECTIVE

Broad temperature adaptability of LIBs has been a long-standing issue for many decades. In this regard, various attempts and considerable endeavors have thus been devoted to exploring wide-temperature electrolytes. Considering the different demands of application fields on the battery performance and the tough challenge to develop multifunctional electrolyte that can cover both high-temperature and low-temperature usage, most previous works focused on either high-temperature electrolyte or low-temperature electrolyte.\(^9\) In view of this, we separately discussed these two unfunctional electrolytes, with an emphasis on the rational design and modification strategy for the improvement of battery performance under extreme environment.

Regarding low-temperature electrolyte design, establishing the multicomponent mixed solvent system and employing low-temperature film-forming additive are currently the most promising approaches in terms of their superior electrochemical performance, lower cost, and ease of industrial production (Figure 15A). Besides, the utilization of mixed lithium salts can also improve the low-temperature performance of the electrolyte, but bring some problems such as reduced conductivity and increased cost. Suffering from the intrinsically lower conductivity, only a few specially designed ILs and gel polymer electrolytes can work at \(-30^\circ\text{C}\), the low-temperature performance of which is far inferior to that of ester-based electrolytes.

With respect to high-temperature electrolyte, employing organic lithium salts with better thermal stability together with high-temperature additives is currently the best strategy to address the issue (Figure 15B). Unlike in low-temperature batteries, solid-state electrolytes show strong competitiveness in high-temperature batteries due to their acceptable conductivity and better safety performance than conventional ester-based electrolytes, but the manufacturing cost need to be enormously reduced.

Up to now, the existing wide-temperature electrolyte systems are still dominated by liquid electrolyte. Carbonate-based electrolyte consisting of multiple solvents and suitable cosolvents are able to work in the temperature range of \(-60\) to \(60^\circ\text{C}\). However, linear esters will decompose at higher temperatures (>\(60^\circ\text{C}\)), resulting in the flatulence of soft-pack batteries, which may lead to serious safety hazards. The perfluorinated electrolyte not only exhibit an ultra-wide working temperature range from \(-125\) to \(70^\circ\text{C}\), but also has an excellent flame-retardant ability due to the use of highly fluorinated solvents, therefore its safety is much higher than conventional carbonate-based electrolytes. However, only by further reducing the cost can this perfluorinated electrolyte move from laboratory research into industrial application.

Ester-based electrolyte is still the mainstream of current LIB electrolyte. Whether it is for high-temperature, low-temperature applications, or wide temperature applications, the modification of the electrolyte is still mainly concentrated in the following three aspects: multicomponent mixed solvent system, functional additives, and appropriate lithium salts.

Solvent plays a critically important role in electrolytes. The choice of solvents and their interactions directly determine the physical and chemical properties of the electrolytes, hence solvent regulation is the most effective approach to design functionalized electrolytes. However, suffering from complicated solvent chemistry, even a slight change in the composition would bring unpredictable results, thus rational design often requires extensive experimental validation.

Functional additives are indispensable for electrolytes. Generally, a rather low ratio of additives could greatly improve the performance of electrolytes. Except for film-forming additives, a certain proportion of overfilling additives and flame-retardant additives can enormously enhance battery safety.\(^9\) Regarding to lithium salts, even though LiPF\(_6\) is sensitive to water and...
unstable at high temperatures, it is still the best choice of lithium salts owing to its excellent electrochemical performance and relatively low cost. Organic lithium salts may be alternatives to LiPF₆ in the future, but only if it can be cheaply produced. Thus, the combination of solvent regulation and appropriate functional additives may be the best strategy in electrolyte design so far.

Developing electrolyte with high safety and wide operating temperature range is the future research focus of LIB. To promote the practical application of wide temperature electrolyte, several feasible research directions can be taken into careful consideration.

(1) Although LiPF₆ exhibits an excellent electrochemical performance at both room temperature and low temperature, it has poor thermal stability and is sensitive to moisture, thus causing poor high-temperature performance. In contrast, some organic lithium salts show exactly the opposite property. Therefore, the employment of organic-inorganic mixed coordination lithium salts may balance the high temperature and low-temperature performance of the electrolyte.

(2) EC is the key solvent for film-forming on the surface of anode, whereas its high melting point is detrimental to the low-temperature performance of the electrolyte. As the homologues, PC has similar electrochemical property with a lower freezing point of −49°C, which was once considered as an ideal solvent for wide-temperature electrolyte. However, the co-insertion of PC with Li⁺ into graphite anode leads to poor cycling performance. The dilemma of EC-based electrolytes has made researchers realize that the design of PC-based electrolytes compatible with graphite anodes should be an important research topic in the future.

(3) Theoretically, the higher the fluorine substitution ratio of the solvent molecule, the stronger the oxidation resistance and flame retardancy of the solvent. Carboxylic ester is the main cosolvent in the wide-temperature electrolyte system. Therefore, replacing the expensive fluorinated linear carbonate with carboxylic ester that has high fluorine substitution ratio can effectively reduce the cost, significantly improve the wide temperature performance and safety of the electrolyte.

(4) Phosphate ester solvents possess the characteristics of low viscosity, high DN, low cost, and nonflammability. However, phosphate ester is incompatible with graphite. At present, the research focus of phosphate ester electrolyte is still to improve its compatibility with the anode, and it has not yet been extended to the wide temperature application. The development of low concentration, wide operating temperature, and high safety phosphate ester electrolyte is an important research direction in the future.

ACKNOWLEDGMENTS
This study was financially supported by the National Natural Science Foundation of China (21875171, 21972108, U20A20249), the National Key Research Program of China (No. 2016YFB0901500), the Intergovernmental International Science and Technology Innovation Cooperation Project (2019YFE010186), the Hubei Natural Science Foundation (2020CFB771) and the Key R&D Plan of Hubei Province (2020BAA030).

CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.
REFERENCES

1. Koksbang R, Barker J, Shi H, Saidi MY. Cathode materials for lithium rocking chair batteries. Solid State Ionics. 1996;84:1-21.
2. Wang HM, Chen SS, Fu CL, et al. Recent advances in conversion-type electrode materials for post-lithium-ion batteries. ACS Mater Lett. 2021;3:956-977.
3. Dunn B, Kamath H, Tarascon JM. Electrical energy storage for the grid: a battery of choices. Science. 2011;334:928-935.
4. Lu J, Pan X, Fei G, et al. Correlation of thiamine metabolite levels with cognitive function in the non-demented elderly. J Power Sources. 2015;274:676-684.
5. Xu K. Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. Chem Rev. 2004;104:4303-4418.
6. Nian Q, Sun T, Liu S, Du H, Ren X, Tao Z. Issues and opportunities on low-temperature aqueous batteries. Chem Eng J. 2021;423:130253.
7. Zhang SS, Xu K, Jow TR. [Taking vulnerable plaque away, eradicating heart attack]. Electrochim Acta. 2004;49:1057-1061.
8. Nguyen CC, Lucht BL. Development of electrolytes for Si-graphite composite electrodes. J Electrochem Soc. 2018;165: A2154-A2161.
9. Huang S, Cheeong LZ, Wang D, Shen C. Thermal stability of solid electrolyte interphase of lithium-ion batteries. Appl Surf Sci. 2018;454:61-67.
10. Smart MC, Ratnakumar BV, Surampudi S. Electrolytes for low-temperature lithium batteries based on ternary mixtures of aliphatic carbonates. J Electrochem Soc. 1999;146:486-492.
11. Smart MC, Ratnakumar BV, Ryan-Mowrey VS, et al. Improved performance of lithium-ion cells with the use of fluorinated carbonate-based electrolytes. J Power Sources. 2003;119:359-367.
12. Smart MC, Ratnakumar BV, Whitcanack LD, et al. Improved low-temperature performance of lithium-ion cells with quaternary carbonate-based electrolytes. J Power Sources. 2003;119:349-358.
13. Smart MC, Ratnakumar BV, Surampudi S. Use of organic esters as cosolvents in electrolytes for lithium-ion batteries with improved low temperature performance. J Electrochem Soc. 2002;149:A361-A370.
14. Smart MC, Ratnakumar BV, Chin KB, Whitcanack LD. Lithium-ion electrolytes containing ester cosolvents for improved low temperature performance. J Electrochem Soc. 2010;157:A1361-A1374.
15. Zhang SS, Xu K, Jow TR. The low temperature performance of Li-ion batteries. J Power Sources. 2003;115:137-140.
16. López CM, Vaughhey JT, Dees DW. Insights into the role of interphasial morphology on the electrochemical performance of lithium electrodes. J Electrochem Soc. 2012;159:A873-A886.
17. López CM, Vaughhey JT, Dees DW. Morphological transitions on lithium metal anodes. J Electrochem Soc. 2009;156:A726-A729.
18. Herreyre S, Huchet O, Barusseau S, Perton F, Bodet JM, Biensan P. New Li-ion electrolytes for low temperature applications. J Power Sources. 2001;97:576-580.
19. Ein-Eli Y, Thomas SR, Chadha R,Blakey TJ, Koch VR. Li-ion battery electrolyte formulated for low-temperature applications. J Electrochem Soc. 1997;144:823-829.
20. Wrodnigg G, Besenhard J, Winter M. Cyclic and acyclic sulfites: new solvents and electrolyte additives for lithium ion batteries with graphitic anodes. J Power Sources. 2001;97:592-594.
21. Ding MS. Liquid-solid phase diagrams of ternary and quaternary organic carbonates. J Electrochem Soc. 2004;151:A731-A738.
22. Xiao LF, Cao YL, Ai XP, Yang HX. Optimization of EC-based multi-solvent electrolytes for low temperature applications of lithium-ion batteries. Electrochim Acta. 2004;49:4857-4863.
23. Nishikawa D, Nakajima T, Ohzawa Y, et al. Thermal and oxidation stability of organo-fluorine compound-mixed electrolyte solutions for lithium ion batteries. J Power Sources. 2013;243:573-580.
24. Sato K, Zhao L, Okada S, Yamaki J-i. LiPF6/methyl difluoroacetate electrolyte with vinylene carbonate additive for Li-ion batteries. J Power Sources. 2011;196:5617-5622.
25. Sato K, Yamazaki I, Okada S, Yamaki J-i. Mixed solvent electrolytes containing fluorinated carboxylic acid esters to improve the thermal stability of lithium metal anode cells. Solid State Ionics. 2002;148:463-466.
26. Zhang YS, Sevilla A, Wan LQ, Lemsichka IR, Vunjak-Novakovic G. Patterning pluripotency in embryonic stem cells. Energy Environ Sci. 2013;6:1806-1810.
27. Li S, Zhao W, Cui X, et al. An improved method for synthesis of lithium difluoro(oxalato)borate and effects of sulfonate on the electrochemical performances of lithium-ion batteries. Electrochim Acta. 2013;91:282-292.
28. Li SY, Li X, Liu J, Shang Z, Cui X. A low-temperature electrolyte for lithium-ion batteries. Ionics. 2015;21:901-907.
29. Yamaki J-i, Yamazaki I, Egashira M, Okada S. Thermal studies of fluorinated ester as a novel candidate for electrolyte solvent of lithium metal anode rechargeable cells. J Power Sources. 2001;102:288-293.
30. Lu W, Pu WJ, Xie K, Zheng CM. Evolution of vascular plants through redeployment of ancient developmental regulators. ACS Appl Energy Mater. 2020;3:733-742.
31. Liu Y, Xie K, Pan Y, et al. Impacts of lithium tetrafluoroborate and lithium difluoro(oxalate)borate as additives on the storage life of Li-ion battery at elevated temperature. Ionics. 2018;24:1617-1628.
32. Liu Y, Xie K, Pan Y, et al. LiPON as a protective layer on graphite anode to extend the storage life of Li-ion battery at elevated temperature. Ionics. 2018;24:723-734.
33. Lu W, Xie K, Pan Y, Chen ZX, Zheng CM. Effects of carbon chain length of trifluoroacetate co-solvents for lithium-ion battery electrolytes using at low temperature. J Fluorine Chem. 2013;156:136-143.
34. Lu W, Xie K, Chen ZX, Pan Y, Zheng CM. Preparation and characterization of trifluoroethyl aliphatic carboxylates as cosolvents for the carbonate-based electrolyte of lithium-ion batteries. J Fluorine Chem. 2014;161:110-119.
35. Xu K, Zhang SS, Jow TR, Xu W, Angell CA. LiBOB as salt for lithium-ion batteries: a possible solution for high temperature operation. Electrochem Solid-State Lett. 2002;5:A26-A29.
36. Scheldt B, Kroeckel UC, Schreiner C, Gores HJ, Winter M. Blends of lithium bis(oxalato)borate and lithium tetrafluoroborate: useful substitutes for lithium difluoro(oxalato)borate in electrolytes for lithium metal based secondary batteries. Electrochim Acta. 2013;107:26-32.
37. Zhang SS. An unique lithium salt for the improved electrolyte of Li-ion battery. Electrochim Commun. 2006;8:1423-1428.
38. Zhang SS, Xu K, Jow TR. A new approach toward improved low temperature performance of Li-ion battery. *Electrochem Commun.* 2002;4:928-932.

39. Mandal BK, Padhi AK, Shi Z, Chakraborty S, Filler R. New low temperature electrolytes with thermal runaway inhibition for lithium-ion rechargeable batteries. *J Power Sources.* 2006;162:690-695.

40. Zhu C, Lv W, Chen J, et al. Butyl acrylate (BA) and ethylene carbonate (EC) electrolyte additives for low-temperature performance of lithium-ion batteries. *J Power Sources.* 2020;476:228697.

41. Zhang SS, Xu K, Jow TR. An improved electrolyte for the LiFePO₄ cathode working in a wide temperature range. *J Power Sources.* 2006;159:702-707.

42. Zhang L, Chai L, Zhang L, et al. Synergistic effect between lithium bis(fluorosulfonyl)imide (LiFSI) and lithium bis-oxalato borate (LiBOB) salts in LiPF₆-based electrolyte for high-performance Li-ion batteries. *Electrochem Acta.* 2014;127:39-44.

43. Kang B, Ceder G. Battery materials for ultrafast charging and discharging. *Nature.* 2009;458:190-193.

44. Matsuoka O, Hiwara A, Omi T, et al. Ultra-thin passivating film induced by vinylene carbonate on highly oriented pyrolytic graphite negative electrode in lithium-ion cell. *J Power Sources.* 2002;108:128-138.

45. Jie X, Wan-Hao Y, Yi-Wen Y, Zhou-Cheng W, Yong Y. Effect of fluoroethylene carbonate additive on the performance of lithium ion battery. *Acta Phys Chim Sin.* 2009;25:201-206.

46. Yao YW, Xu J, Yao WH, Wang ZC, Yang Y. Effect of ethylene sulfate as electrolyte additive on performance of Li-ion batteries. *Chin J Appl Chem.* 2010;27:823-828.

47. Zhang SS, Xu K, Jow TR. Enhanced performance of Li-ion cell with LiBF₄-PC based electrolyte by addition of small amount of LiBOB. *J Power Sources.* 2006;156:629-633.

48. Zeng D, Hu C, Li RL, et al. Polysaccharide extracts of Astragalus membranaceus and Atractylodes macrocephala promote intestinal epithelial cell migration by activating the polyamine-mediated K⁺ channel. *Nat Energy.* 2018;3:674-681.

49. Wagner R, Bros S, Kasnatscheew J, et al. Vinyl sulfones as SEI-forming additives in propylene carbonate based electrolytes for lithium-ion batteries. *Electrochem Commun.* 2014;40:80-83.

50. Zuo XX, Li WS, Liu JS, Xu MQ. Application of sulfoside additives in electrolyte for lithium-ion battery. *Chin Bat Ind.* 2006;11:97-99.

51. Möller KC, Hodal T, Appel WK, Winter M, Besenhard JO. Fluorinated organic solvents in electrolytes for lithium ion cells. *J Power Sources.* 2001;97:595-597.

52. Hamenu L, Lee HS, Latifatu M, et al. Lithium-silica nanosalt as a low-temperature electrolyte additive for lithium-ion batteries. *Curr Appl Phys.* 2016;16:611-617.

53. Won JH, Lee HS, Hamenu L, et al. Improvement of low-temperature performance by adopting polydimethylsiloxane-g-polyacrylate and lithium-modified silica nanosalt as electrolyte additives in lithium-ion batteries. *J Ind Eng Chem.* 2016;37:325-329.

54. Nakagawa H, Iuchi S, Kuvana K, Nukuda T, Aihara Y. Liquid and polymer gel electrolytes for lithium batteries composed of room-temperature molten salt doped by lithium salt. *J Electrochem Soc.* 2003;150:A695-A700.

55. Ferrari S, Quartarone E, Tomasi C, et al. Alkox substituted imidazolium-based ionic liquids as electrolytes for lithium batteries. *J Power Sources.* 2013;235:142-147.

56. Wu F, Zhu Q, Chen R, Chen N, Chen Y, Li L. Ring-chain synergy in ionic liquid electrolytes for lithium batteries. *Chem Sci.* 2015;6:7274-7283.

57. Fujie K, Yamada T, Ikeda R, Kitagawa H. Introduction of an ionic liquid into the micropores of a metal-organic framework and its anomalous phase behavior. *Angew Chem Int Ed.* 2014;53:11302-11305.

58. Fujie K, Otsubo K, Ikeda R, Yamada T, Kitagawa H. Low temperature ionic conductor: ionic liquid incorporated within a metal-organic framework. *Chem. Sci.* 2015;6:4306-4310.

59. Appetecchi GB, Croce F, Scrosati B. Kinetics and stability of the lithium electrode in poly(methylmethacrylate)-based gel electrolytes. *Electrochem Acta.* 1995;40:991-997.

60. Du G, Tao M, Li J, et al. Low-operating temperature, high-rate and durable solid-state sodium-ion battery based on polymer electrolyte and prussian blue cathode. *Adv Energy Mater.* 2020;10:1903351.

61. Ming J, Cao Z, Wu Y, et al. New insight on the role of electrolyte additives in rechargeable lithium ion batteries. *ACS Energy Lett.* 2019;4:2613-2622.

62. Aurbach D, Talyosy E, Markovsky B, et al. Design of electrolyte solutions for Li and Li-ion batteries: a review. *Electrochem Acta.* 2004;50:247-254.

63. Feng D, Chen S, Wang R, et al. Mixed lithium salts electrolyte improves the high-temperature performance of nickel-rich based lithium-ion batteries. *J Electrochem Soc.* 2020;167:110544.

64. Wang S, Qiu W, Li T, Yu B, Zhao H. Properties of lithium bis(oxalato)borate (LiBOB) as a lithium salt and cycle performance in LiMn₂O₄ half cell. *Int J Electrochem Sci.* 2006;1:250-257.

65. Xu Y, Feng D, Wang Y, Lin S, Xu L. Sodium tanshinone IIA sulfonate protects mice from ConA-induced hepatitis via inhibiting NF-kappaB and IFN-gamma/STAT1 pathways. *J Power Sources.* 2008;177:512-527.

66. Wang DY, Xiao A, Wells L, Dahn JR. Effect of mixtures of lithium hexafluoroarsenate (Li₃P₅O₆) and lithium bis(fluorosulfonyl)imide (LiFSI) as salts in Li[Ni₀.₅Mn₁.₅Co₁/₃]O₂/graphite pouch cells. *J Electrochem Soc.* 2014;162:A169-A175.

67. Zhang SS, Xu K, Jow TR. Tris(2,2,2-trifluoroethyl) phosphate as a co-solvent for nonflammable electrolytes in Li-ion batteries. *J Power Sources.* 2003;113:166-172.

68. Li W, Campion C, Lucht BL, Ravelb B, DiCarlo J, Abraham KM. Additives for stabilizing LiPF₄-based electrolytes against thermal decomposition. *J Electrochem Soc.* 2005;152:A1361-A1365.

69. Aurbach D, Ein-Eli Y, Chusid (Youngman) O, Carmeli Y, Babai M, Yamin H. The correlation between the surface chemistry and the performance of Li-ion intercalation anodes for rechargeable ‘rocking-chair’ type batteries. *J Electrochem Soc.* 1994;141:603-611.

70. Wang R, Li X, Wang Z, et al. Lithium carbonate as an electrolyte additive for enhancing the high-temperature performance of lithium manganese oxide spinel cathode. *J Alloys Compd.* 2015;618:349-356.

71. Kang KS, Choi S, Song J, et al. Effect of additives on electrochemical performance of lithium cobalt oxide at high temperature. *J Power Sources.* 2014;253:48-54.

72. Zuo XX, Xu M, Li W, Su D, Liu J. Electrochemical reduction of 1,3-propane sultone on graphite electrodes and its application in li-ion batteries. *Electrochem Solid-State Lett.* 2006;9:A196-A199.
80. Lombardo L, Brutti S, Navarra MA, Panero S, Reale P. Mixtures of organic liquid–alkylcarbonates as electrolytes for safe lithium-ion batteries. J Power Sources. 2003;12550-12556.

81. Lewandowski AP, Hollenkamp AF, Donne SW, Best AS. A review on new solutions, new measurements procedures and new materials for rechargeable Li batteries. J Power Sources. 2005;146:71-78.

82. Zuo XX, Su DG, Liu JS, Li WS. Study of ethanolamine as stabilizer of electrolyte. Battery. 2005:366-367.

83. Srour H, Chancellor L, Bolimowska E, et al. Ionic liquid-based electrolytes for lithium-ion batteries: review of performances of various electrode systems. J Appl Electrochem. 2016;46:149-155.

84. Lewandowski A, Aurbach D, Golomski K, Markovsky B, Gofer Y, Schmidt M, Heider U. On the use of vinylene carbonate (VC) as an additive to electrolyte solutions for Li-ion batteries. Electrochim Acta. 2002;47:1423-1439.

85. Li J, Yao W, Meng YS, Yang Y. Effects of vinyl ethylene carbonate additive on elevated-temperature performance of cathode material in lithium ion batteries. J Phys Chem C. 2008;112:12550-12556.

86. Xian J, Mai L, Aiken CP, Nelson KJ, Chen LP, Dahn JR. Comparative study on prop-1-ene-1,3-sultone and vinylene carbonate as electrolyte additives for Li(Ni0.5Mn0.5O2)/graphite pouch cells. J Electrochem Soc. 2014;161:A1634-A1641.

87. Long Chen received his B.E. in (2020) from the School of Power and Mechanical Engineering in Wuhan University. Now he is currently a graduate student under the supervision of Prof. Zhongxue Chen in Wuhan University. His research focuses on non-flammable and wide-temperature electrolytes for lithium-ion and sodium-ion batteries.

AUTHOR BIOGRAPHIES

88. Prof. Yuliang Cao received his Ph.D. (2003) from Wuhan University, and then he worked as a visiting scholar in Pacific Northwest National Laboratory from 2009 to 2011. He is now a professor at physical chemistry, Wuhan University. His research interests focus on developing advanced materials (e.g., alloys, transition metal oxides, phosphates, and novel electrolytes) for sodium–ion batteries and lithium–ion batteries.

How to cite this article: Chen L, Wu H, Ai X, Cao Y, Chen Z. Toward wide-temperature electrolyte for lithium–ion batteries. Battery Energy. 2022;1:20210006. doi:10.1002/bte.20210006