Toward Low-Temperature Lithium Batteries: Advances and Prospects of Unconventional Electrolytes

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Lithium batteries have been widely used in various fields such as portable electronic devices, electric vehicles, and grid storages devices. However, the low temperature-tolerant performances (−70 to 0 °C) of lithium batteries are still mainly hampered by low ionic conductivity of bulk electrolyte and interfacial issues. In general, there are four threats in developing low-temperature lithium batteries when using traditional carbonate-based electrolytes: 1) low ionic conductivity of bulk electrolyte, 2) increased resistance of solid electrolyte interphase (SEI), 3) sluggish kinetics of charge transfer, 4) slow Li diffusion throughout bulk electrodes. Meanwhile, conventional electrolytes have been close to the upper limit of optimum low-temperature performance owing to their intrinsic molecular structural properties. As a result, it is urgent to design unconventional electrolytes with lower melting point and higher ionic conductivity. Herein, the recent key advances in regard to unconventional electrolytes including fluorinated ester, ethyl acetate, gamma-butyrolactone, liquefied gas, ether, plastic crystal, and aqueous electrolytes are overviewed. Solvation structure modification and SEI optimization of unconventional electrolytes for low-temperature lithium batteries are focused. Finally, aiming at the deficiencies in current understanding, the inherent limitations and envision the future prospects of low-temperature lithium batteries are explored.

1. Introduction

Since the commercial lithium-ion batteries emerged in 1991, we witnessed swift and violent progress in portable electronic devices (PEDs), electric vehicles (EVs), and grid storages devices due to their excellent characteristics such as high energy density, long cycle life, and low self-discharge phenomenon. In particular, exploiting advanced lithium batteries at low temperature (−70 to 0 °C) is crucial to boost their further application for cryogenic service. In general, there are four threats in developing low-temperature lithium batteries: 1) low ionic conductivity of bulk electrolyte, 2) increased resistance of solid electrolyte interface (SEI), 3) sluggish kinetics of charge transfer, 4) slow Li diffusion throughout bulk electrodes. Hence, advanced electrolytes simultaneously with low melting point and low viscosity are indispensable for developing rational low-temperature lithium batteries. So far, many efforts have been devoted to exploit unconventional carbonate-based electrolytes (low-melting point cyclic carbonate/low-viscosity linear carbonate) for low-temperature lithium batteries. Nowadays, the majority of carbonate-based electrolytes can further lower freezing point using the low-melting point of cyclic carbonate ester and then enhance the low-temperature electrochemical performance.

It seems that conventional electrolytes have been closing to the upper limit of optimum low-temperature performance due to their intrinsic molecular structural properties. As a result, it is urgent to elaborately design new types of unconventional electrolytes with lower melting point and higher ionic conductivity. In recent years, unconventional electrolytes (including fluorinated ester, ethyl acetate [EA], gamma-butyrolactone [GBL], liquefied gas, ether, plastic crystal and aqueous electrolytes) for low-temperature lithium batteries have undergone rapid progress. Figure 1 shows a brief chronology of the developed electrolytes for low-temperature lithium batteries. As the main component, unconventional electrolytes, on a scientific level, have almost replaced the role of carbonate-based electrolytes since 2014. Most of the developed unconventional electrolytes can drastically promote battery performance at low temperatures. As far as we all know, there are a few reviews previously reported about low-temperature unconventional electrolytes for...
lithium batteries. Herein, in this Review, we overview the recent key progress in regard to unconventional electrolytes – fluorinated ester, EA, GBL, liquefied gas, ether, plastic crystal, and aqueous electrolytes. We focus on solvation structure modification and SEI optimization of unconventional electrolytes for low-temperature lithium batteries. Finally, in light of the deficiencies in current understanding, we explore the inherent limitations and envision the future prospects of low-temperature lithium batteries.

2. Carbonate-Based Electrolyte

Up to now, a large amount of multiple carbonate-based electrolytes has been demonstrated to improve low-temperature performance. For example, the mixed electrolyte with low proportion of ethyl methyl carbonate (EMC) (4 vol%), pioneered by M.C. Smart, has been demonstrated in earlier studies to deliver over 80% of discharge specific capacity at room temperature.\(^6\) The working temperature range is mainly determined by the composition of electrolyte, which not only affects the \(\text{Li}^+\) ion transport through the bulk electrolyte but also determines the quality of the formed SEI. In particular, with the increase in the content of ethylene carbonate (EC) in solvent mixtures, the discharge capacities at different temperatures have obvious improvement.\(^7\) In addition, it is worthy noticing that the working temperature of lithium batteries using carbonate electrolytes can also be dramatically lowered by adding other special additives (i.e., EA). For example, the commonly used carbonate electrolyte (1 M LiPF\(_6\) in EC/dimethyl carbonate [DMC]/diethyl carbonate [DEC] [1/1/1, v/v/v]) often frozen at the low temperature of \(-40^\circ\text{C}\). Remarkably, LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) (NMC111)/graphite cell without EA cannot operate at \(-40^\circ\text{C}\) because of the freezing behavior of electrolyte. In sharp contrast, at \(-40^\circ\text{C}\), LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) (NMC111)/graphite full cell using this electrolyte with EA delivers the 59.33% capacity retention to that at room temperature, suggesting EA is an effective additive of low-temperature electrolytes.\(^8\) According to the temperature dependences of the limiting current densities, as temperature decreases, the gap between the polarizations at anode/electrolyte and cathode/electrolyte interfaces rapidly closes (Figure 2). Formulating electrolytes with solvents of low freezing points and high dielectric constants is a direct approach to extend the service-temperature range of lithium batteries. However, the SEI formed by the decomposition products of common electrolytes cannot satisfy the electrochemical properties at ultralow temperature. Many efforts have been done to optimize interphase property, including the adjustment about solvents, salts, additives, and so on. Our review discusses the improvements on the basic of solvent, which mostly possesses low freezing points and high dielectric constants is a direct approach to extend the service-temperature range of lithium batteries. However, the SEI formed by the decomposition products of common electrolytes cannot satisfy the electrochemical properties at ultralow temperature. Many efforts have been done to optimize interphase property, including the adjustment about solvents, salts, additives, and so on. Our review discusses the improvements on the basic of solvent, which mostly possesses low freezing points and high dielectric constants.

3. Sulfolane-Based Electrolyte

Hirata et al. reported that sulfolane (SL) with medium LiFSI concentration (1–1.5 mol dm\(^{-3}\)) (LiFSI/SL) could be promising alternatives for conventional LiPF\(_6\)/EC-based electrolytes.\(^9\) LiFSI/SL enables reversible lithium intercalation into graphite electrodes...
due to its excellent SEI without the use of EC or SEI-forming additives even at 1 or 1.5 mol dm\(^{-3}\) LiFSI concentrations. Lithium ions in LiFSI/SL are fully dissociated due to the higher dielectric constant of SL that of common solvents. The higher average discharge voltages of the cells containing LiFSI/SL electrolytes are due to the high ionic dissociation of lithium ions in SL at \(-20^\circ\)C. Moreover, the low-temperature performance of 1.5 mol dm\(^{-3}\) LiFSI/SL down to \(-100^\circ\)C is ascribed to the noncrystallinity of the electrolyte. In this way, it offers a strategy to form electrolyte for low-temperature lithium batteries with the composition which is difficult to crystallize or pack the solvated ions together. But, it still needs some measures to promote electrochemical performance at lower temperatures.

4. Ester Electrolyte

In addition, previous researches have also made clear that the introduction of special molecules (including methyl formate [MF], methyl acetate [MA], EA, ethyl propionate [EP], and ethyl butyrate [EB]) into commonly used carbonate electrolytes can significantly promote battery performance at low temperature.\(^{10-73}\)

In general, low-temperature performance of lithium batteries can be improved via a judicious selection of special cosolvents. In 2002, Smart et al. introduced different esters into carbonate-based electrolytes (1.0 M LiPF\(_6\) + EC + DEC + DMC, 1:1:1, v/v/v).\(^{13}\) In addition, the author found that the electrolytes containing higher molecular weight esters exhibited higher ionic conductivity than that of electrolytes with lower molecular weight esters at \(-60^\circ\)C. The cell with 1.0 M LiPF\(_6\) EC + EMC + methyl propionate (MP, 20:60:20 v/v %) could deliver six times more than the capacity delivered by 1.0 M LiPF\(_6\) EC + EMC (20:80 v/v %) electrolyte.\(^{14}\) More impressively, they also verified that such hybrid electrolytes were favor to increase rate capability at low temperatures. About 7 Ah lithium ions cells with 1.0 M LiPF\(_6\) EC + EMC + MP (20:60:20 vol%) electrolyte were able to provide more than six times the amount of discharge capacity afforded by the baseline all-carbonate blended electrolyte at low temperatures of \(-50\) and \(-60^\circ\)C. Overall, the cells assembled by such blended electrolytes with low viscosity additive delivered a relatively better performance at low temperatures compared with that of all-carbonate blended electrolyte.\(^{14}\)

4.1. EA-Based Electrolytes

EA electrolyte has low freezing point (\(-84^\circ\)C) and ultrahigh ionic conductivity at low temperature. In 2014, Petiton et al. solved the failure of common carbonate-based electrolytes under high current density using EA and vinyl carbonate (VC) as electrolytes.\(^{15}\) The obtained electrolytes were capable of forming passivating layer at anode surface. As a result, this electrolyte delivered superior rate capability at low temperature. The Li[Ni\(_{0.8}Co_{0.1}Mn_{0.1}\)]O\(_2\) (NCM111)/graphite pouch cells with carbonate-based electrolytes failed when operating at 3 C at \(-14^\circ\)C. Meanwhile, the cells filled with EA-based electrolyte exhibited better rate performance at 4 C. The aforementioned results indicated that such hybrid electrolyte contribute to improving interfacial compatibility of lithium batteries.

In 2018, on the basis of EA with low freezing point, Xia and coworkers developed an organic electrode-based rechargeable battery that used EA-based electrolyte.\(^{16}\) Polytriphenylamine (PTPAn) and 1,4,8,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA) were used as cathode and anode materials, respectively. EA-based electrolyte was used first time in an organic electrodes-based rechargeable battery (Figure 3a). The mechanisms of the reversible absorption/desorption of anions in the cathode and the reversible enolization of (C=O) \(\rightarrow\) (C=O–Li\(_n\)) in the anode dramatically influence the operation of the battery. They found that 2 M LiTFSI/EA had a high ionic conductivity (0.2 mS cm\(^{-1}\)) under ultralow temperatures of \(-70^\circ\)C. More impressively, this battery system can deliver nearly 100% of the room temperature. When the temperature drops to \(-55^\circ\)C, the discharge specific capacity of 90 mAh g\(_{\text{PTPAn}}\)^{-1} is the equal of 91% of that at room temperature.\(^{16}\) Even at the extremely lower temperature of \(-70^\circ\)C, the organic electrodes-based rechargeable battery with EA-based electrolyte still could afford 70% of discharge capacity obtained at room temperature and 0.5 C. However, due to the sluggish solvation/desolvation of Li\(^{+}\), intercalation compounds-based LIBs still cannot work at \(-70^\circ\)C. Furthermore, there are few analyses about how the EA worked even by not explaining the differences of SEI structure–property relationship between EC-based and EC-free electrolytes. In addition, that is not helpful for tackling challenges without the deep exploration and theoretical basis.

Unfortunately, the 2 mol kg\(^{-1}\) EA-based electrolyte was obstructed by the narrow potential window (1.5–4.7 V, vs Li\(^{+}/\)Li) in the application of Li metal anode for high-energy-density battery. Hence, in 2019, they design the 5 mol kg\(^{-1}\) LiTFSI/EA/dichloromethane (DCM) electrolyte with electrochemically inert, which could effectively reduce the viscosity and improve ionic conductivity. They obtained the solvation structure in the electrolytes by analyzing the results of spectral characterization (Figure 3b–d). As shown in Figure 3b, the low concentration electrolyte formed the solvent-separated ion pairs (SSIPs) due to its high solvent-to-salt molar ratio. And when
increasing the concentration of lithium salts, of course, the quantity of Li$^+$-coordinated EA molecules increased.

Meanwhile, the association of cation–anion (Li$^+$–TFSI$^-$) was mounting on the formation of contact ion pairs (CIPs) and cation–anion aggregates (AGGs) (Figure 4a). As they analyzed that there is no change in the solvation structure of CIPs and AGGs after introducing “inert” DCM (Figure 4b). DCM neither dissolved salt nor altered the structures of original solvation, so that they designed a localized high-concentration electrolyte with cosolvation structure. But what is the reason that the solvation structure has not changed after the introduction of the “inert” DCM.

Molecular dynamics (MD) simulations and density functional theory (DFT) calculations further explore the functions of the electrolytes’ solvation structure. The Li$^+$ cation can interact with solvent or anion and the order of reactivity is TFSI$^-$ > EA > DCM, due to the binding energy was only −1.23 eV of Li$^+$·(DCM). The “inert” property attributes to the weak interaction with Li$^+$ of DCM. Classical MD simulations were used to analyze these electrolytes and these electrolytes compared with the pure solvent and the common carbonate ester-based electrolyte (LiTFSI/EC). According to the MD-simulated electrolyte structure (Figure 4a) and the coordination number (CN) analysis (Figure 4b), it is obviously demonstrated that there is the coordination for Li$^+$ with TFSI- and EA molecules in ionic solvation cluster. In diluent (0.15 M), the synergy between 4.5 O (EA) and 1.1 O (TFSI) can promote dissolution of Li. The total CN of the Li–O and the EC-based solvents are very close. The CN of Li–N (TFSI) is 0.7. Different from 0.15 M EC electrolyte (0.1), Li$^+$ is mainly dissolved by O (EC) and hardly coordinated with TFSI$^-$.

As shown in Figure 4b, the average CN and the ratio of free EA to Li$^+$ explained the reason why the electrochemical stability of the concentrated or localized concentrated electrolytes were improved. It was clearly seen that CN of Li–O (TFSI) and Li–N (TFSI) were significantly increased in concentrated 5 M electrolyte. The low-viscosity DCM molecules encased the smaller clusters which isolated from the AGGs, which are shown in Figure 4a. However, the structure of local solvation was hardly changed around Li$^+$. The mean-squared displacements (MSDs) of Li$^+$ cation in the electrolytes are shown in Figure 4c,d. Therewith, they calculated out the diffusion coefficient of Li$^+$. It is obvious that the diffusion coefficient of Li$^+$ in high concentration electrolyte (5 M) is almost ten times than that in dilute electrolyte (1 M) at 25 °C because of the appearance of AGGs and the deficiency of free EA. Then the diffusion coefficient (2.0 × 10$^{-6}$ cm$^2$·s$^{-1}$) at −70 °C was apparently improved by 17 times in cosolvent electrolyte at −70 °C (Figure 4b). As stated earlier, concentrated electrolyte with a cosolvent maintains a same
local solvent structure of the concentrated LiTFSI/EA. As a result, the concentrated EA-based electrolyte possessed high ionic conductivity of $0.6 \text{ mS cm}^{-1}$, low viscosity of $0.35 \text{ Pa s}$, and wide electrochemical window from 0 to 4.85 V. Therefore, this kind of novel electrolyte enables rechargeable lithium metal battery high specific energy of $178 \text{ Wh kg}^{-1}$ and power of $2877 \text{ W kg}^{-1}$ at $-70^\circ \text{C}$. The cosolvent electrolyte was designed using electrochemically "inert" diluent DCM for highly concentrated EA-based electrolyte, which inherited the merit of its expanded stable electrochemical window and circumvented its shortcoming of high viscosity. Benefit from this special solvation structure from concentrated electrolyte and the fast ionic conduction of diluent DCM, the structure and transport mechanisms of cosolvent electrolyte were confirmed, so that they offered a stimulating way of the application of rechargeable lithium metal battery at low temperatures. However, the low boiling point and high volatility of diluent DCM limited its further practical application at the elevated temperatures, which will be the focus of next step.

### 4.2. MP-Based Electrolyte

MP, a common carboxylate ester was chosen as the primary solvent for its sufficient dielectric constant and low melting point of $-87.5^\circ \text{C}$.[17] As the limitation of MP-based electrolyte is likely stems from poor reductive stability and irreversible Li plating, fluoroethylene carbonate (FEC) was added to stabilize negative electrode and positive electrode interfaces along with building a SEI. At $-40^\circ \text{C}$ with a 1 C discharge rate, the graphite||LiCoO$_2$ LIB was found to retain 72.4% of its room temperature capacity, which decreased to 63.2% at $-60^\circ \text{C}$ (Figure 5a). Despite the high-performing control, the graphite||graphite dual-ion batteries (DIBs) were found to far exceed the LIB capacity retention, retaining 93.1% and 84.4% of its room temperature capacity at $-40$ and $-60^\circ \text{C}$, respectively (Figure 5b). The low temperature improvement of the DIB mechanism was further investigated at $-60^\circ \text{C}$ under different discharge rates, which provided perhaps the most salient deviation of performance metrics (Figure 5c,d). At $-60^\circ \text{C}$ and a 0.1 C discharge rate, the graphite|| LiCoO$_2$ LIB and the graphite||graphite DIB displayed 78.1% and 87.3% capacity retentions, respectively. However, when the rate was increased to 10 C, the DIB still exhibited 61.7%, whereas the LIB was unable to provide any significant capacity (5.5%) under the same conditions.

### 4.3. GBL-Based Electrolyte

Lithium bis(oxalato)borate (LiBOB), a fluorine-free and environment-friendly salt, is a significant component of liquid electrolyte for lithium-ion batteries. It possesses superior thermal stability until $300^\circ \text{C}$ and can favor the formation of robust SEI on graphite anode and cathode electrolyte interphase (CEI) on high-voltage cathodes. It can effectively passivate aluminum current collector as well.[18] However, ionic conductivity of LiBOB/carbonate solvents is poor due to its small solubility in...
carbonate solvents. It has been reported that GBL was able to effectively dissolve LiBOB and thus improved ionic conductivity of electrolytes.\[^{18}\]

On account of its low melting point (43.5 °C), high flash point (98 °C), and high boiling point (204 °C), GBL-based electrolytes are very promising electrolytes of lithium batteries which operated in a wide range of temperatures. Nevertheless, irreversible capacity of lithium batteries using GBL/LiBOB is on a high level, which deteriorates cycle performance. To improve interfacial compatibility between GBL and lithium metal, therefore, Yang and coworkers introduced 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (F-EPE) as an additive of GBL-based electrolyte F-EPE possesses several diverting characteristics, such as low surface tension, low melting point, and high oxidation stability.\[^{18}\] It is common knowledge that the lower the surface tension is, the better the wettability is.\[^{19}\] As a result, such safe electrolyte enables LiCo\(_{1/3}\)Mn\(_{1/3}\)Ni\(_{1/3}\)O\(_2\)/graphite full cell excellent electrochemical performances (high discharge capacity of 74.2 mA h g\(^{-1}\) at −40 °C, Figure 6). This GBL/F-EPE system delivered comprehensive advantages of several parties, but it synchronously loses other distinct superiorities (low working temperature). GBL reduces the limitation of operating temperature. Meanwhile, F-EPE effects on the formation of SEI to improve the electrochemical performance at low temperature. However, the mechanism about how ester work in batteries to accelerate the ionic conduction kinetics. To be released from the control of carbonate-based electrolyte, there remain other electrolytes still for improving the low-temperature performance.

5. Ether Electrolytes

Apart from carbonate electrolytes, ether electrolytes are also attractive due to their superior compatibility with lithium metal. 1,3-Dioxolane (DOL) and dimethoxy ethane (DME), representative ethers, are suitable for the application at low temperature due to their relatively low freezing points of −95 and −58 °C, respectively.\[^{20}\] In fact, they are mainly utilized as solvents for high-energy lithium–sulfur (Li–S) batteries. Mikhaylik and Akridge demonstrated extraordinary Li–S low-temperature performance (retained capacity at −40 °C exceeded 80% of that at room temperature) based on DOL/DME (mass ratio of 86:14) at −40 °C.\[^{20}\] Up to now, many efforts have been devoted to fabricate Li–S cells using 1,3-dioxolane (DOL) and dimethoxy ethane (DME) and tetra(ethylene glycol) dimethyl ether (TEGDME) at room temperature. Although Li–S cell with TEGDME electrolyte delivered excellent battery performance at room temperature, low-temperature performance is poor. For example, the first discharge capacity of Li–S cell using TEGDME is only 357 mAh g\(^{-1}\) at −10 °C, which is much lower than that (1303 mAh g\(^{-1}\)) at 20 °C. To find out the optimum electrolyte based on TEGDME, Ryu et al. investigated the effect of

![Figure 5. Discharge profiles of a) graphite||LCO, and b) graphite||graphite full cells at different temperatures and 1 C rate. About −60 °C discharge profiles of c) graphite||LCO, and d) graphite||graphite full cells in 2 M LiPF\(_6\) in MP 10% FEC at different rates compared with room temperature (23 °C). Retention was based on the measured room temperature discharge capacity at 1 C. Reproduced with permission.\[^{17}\] Copyright 2019, John Wiley and Sons.](image-url)
MA and DOL on the discharge performance of TEGDME-based electrolyte.[21] Finally, the obtained optimum electrolyte-(5 vol%MA:47.5 vol%DOL:47.5 vol%TEGDME) based Li–S cell displayed high discharge specific capacity of 994 mAh g⁻¹ at −10 °C at first cycle.

While both of these works approached electrolyte engineering from the lens of similar early approaches for other battery chemistries, further consideration is needed to understand the exact role of the soluble active material plays in mechanistically impeding low-temperature performance. But these systems still need to consider the exact role of soluble active material in hindering low-temperature battery performance.[22]

Recently, Lynden Archer’s group discovered that LiNO₃ possesses the ability of coordinating with and stranded DOL molecules in liquid-state electrolyte which arrested their crystallization completely. In addition, strong interactions between LiNO₃ and DOL distort bonds in DOL, couple motions of individual solvent molecules, and lower the thermodynamic activity of the electrolyte. As a result, such electrolyte exhibited ultrahigh ionic conductivity (1 mS cm⁻¹) at −50 °C. Operation of lithium batteries is challenging below −20 °C because of low ionic conductivity and sluggish diffusion in electrodes. McDowell and coworkers reported that FEC altered solvation structure (Figure 7) and formed thinner SEI (rich in inorganic species such as LiF, Li₂CO₃, and so on) in DOL/DME-based electrolyte at −60 °C.[23] Based on the morphological investigation, the size of electrodeposited Li particles in FEC-modified electrolytes is larger than that in pure ethers at low temperature. Hence, LiFePO₄/Li metal batteries exhibited high reversible capacity (75 mAh g⁻¹) at −40 °C. Whether these electrolytes can be used at high temperatures remains a challenge. In addition, it is generally known that ether-based electrolytes cannot support the high voltage property, which dramatically hinders the application of ether for lithium cells.

It has proved that the structure, chemistry, and transport characteristics of the SEI are vastly affected by temperature, which display different inorganic phases in the amorphous layer and smaller Li particles formed at low temperature.[24] Due to continuously changing surface area during deposition/stripping and the consumption of Li, the Li batteries displays inefficient cycling. And the low temperature leads to a lower reaction rates. As a result, a thinner SEI forms on the electrodes, which improves the Columbic efficiency. In contrast, it has demonstrated that the solvation structure of the electrolyte deeply affects the charge-transfer behavior at low temperature. [25] The performance was mainly influenced by the interfacial ion desolvation mechanics and the corresponding Li deposition morphologies. Finally, the LMBs are able to improve the Columbic efficiency with decreasing dendritic growth. According to this report, the 1 m LiFSI/diethyl ether (DEE) system applied into full cells with practical electrode loadings and promised to enable LMBs cycled at 23, −40, and −60 °C.

6. Fluorinated Electrolytes

Fluorinated ester, the derivative of carbonate electrolytes, is non-flammable. At the very beginning, FEC is often used as functional additive of SEI in liquid electrolyte. In 2019, Paillard and coworkers developed a novel electrolytes for graphite anode via the introduction of fluorosulfonyl isocyanate (FI).[26] Due to its high reduction potential (above 2.8 V vs Li⁺/Li), FI is reduced prior to carbonate components and then yields a conductive SEI layer. Therefore, this SEI could significantly lower interfacial resistance and accelerate the kinetics of ionic conduction. In addition, they comprehensively analyzed the morphology, structure, and composition of SEI and finally figured out that SEI consisted of a thick and protective inorganic inner layer (mainly LiF, Li₂SO₄, ROSO₂Li, Li₂S, Li₂SO₃ and low content of Li₂CO₃, Li₂O, and Li₂PF₆O₃) and a thin outer organic layer.

As stated earlier, it seems that the inner layer is more inorganic on account of FI just has one carbon atom. With the further consideration of the possible fragments which would produce upon reduction, O=F fraction along with F=SO₂=N=SO₂=F anion (FSI⁻) could contribute to the easier “mineralization” of SEI.[27] In addition, N=C=O fragment might participate in forming some insoluble organic polymer species to mechanically bind SEI layer during the process of electrochemical polymerization. These characteristics would endow these SEI favorable.
superiorities for ionic conduction. In particular, the formed SEI which possess a lower thickness of the organic layer after adding FI, demonstrating that it is beneficial for restraining diffusion limitations and taking part in the fast charge and discharge capability of the cell. However, Li-salt-based inorganic components cause the large amounts of inorganic composition inside SEI layer on account of more Li ions are consumed to form the SEI during the first cycle, which is the reason for the poor initial Coulombic efficiency in the graphite/Li cell with FI additive. Importantly, the addition of FI can prevent the crystallization of electrolyte at $-20^\circ$C. So that it would significantly improve low-temperature battery performances. Obviously, the cells utilized FI additive display higher capacities at different current rates than that with carbonate-based electrolytes at very low temperature. As a result, graphite/Li battery using 2 wt% FI exhibited outstanding rate capability (20 mAh g$^{-1}$ at 0.2 C) at $-20^\circ$C. The only fly in the ointment is that FI slightly decreases the initial Coulombic efficiency of graphite electrodes.

Furthermore, Wang and coworkers designed all-fluorinated electrolyte for low-temperature lithium batteries, which open up a very promising direction of low-temperature electrolyte.\cite{28} It is common sense that all-fluorinated electrolytes possess high ionic conductivity and wide electrochemical stability window, however, this electrolyte-based lithium cells still cannot operate when the temperatures is below $-30^\circ$C due to the high affinities between fluorinated solvents and Li ions. To resolve this problem, the author dissolves all-fluorinated electrolytes into highly fluorinated nonpolar solvents to obtain superelectrolyte (Figure 8).

This novel electrolyte can work at a wide operational temperature ($-95$ to $70^\circ$C) by reducing the affinities between solvents and lithium ions. On account of weak interaction between nonpolar all-fluorinated solvents molecules and Li ions which compared with that of Li ions and fluorinated carbonates, the solvation structures of the all-fluorinated electrolyte cannot be transformed by the Li ions in the designed electrolyte. The nonpolar solvents instead the highly polar molecules to break the strong interaction along with Li ions and then it can expand the liquid-phase range and increasing the transference number. Therefore, this novel superelectrolyte could maintain the electrochemical properties of all-fluorinated electrolyte even have a significantly improvement in physical properties. In addition, highly fluorinated nonpolar solvent with inherent stabilities of its electrochemical and chemical properties, suggested that the superelectrolytes will have an enhanced safety and electrochemical potential window. The change of solvation structure in this superelectrolytes is also expected to improve the electrochemical process.

More impressively, Even when the temperature is down to $-85^\circ$C, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$/Li battery using this 1.28 m LiFSI-FEC/FEMC-D2 (here, D2 is tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane) can still deliver a relatively high discharge specific capacity (96 mAh g$^{-1}$), whereas the battery in 1 m LiPF$_6$-EC/DMC cannot provide any capacity below $-67^\circ$C. In addition, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$/Li battery using the obtained electrolyte (1.28 m LiFSI FEC/FEMC-D2) can still deliver 50% of its room-temperature capacity even at $-85^\circ$C, indicating this modified fluorinated electrolyte can provide extreme battery performance.\cite{29}

\textbf{Figure 7.} Solvation structure elucidated via $^{17}$O NMR experiments and MD simulations. a, b) $^{17}$O NMR spectra of FEC-modified ether electrolyte without (black) and with (red) the Li salts (LiTFSI and LiNO$_3$) at a) $27^\circ$C and b) $-40^\circ$C. The inset in (a) shows an FEC molecule with oxygen labeled. c–f) Radial distribution functions ($g(r)$, referenced to the bulk O density) of the LiTFSI/DOL/DME electrolyte at c) 25°C and d) $-40^\circ$C, and of the LiTFSI/DOL/DME/FEC electrolyte at d) 25°C and f) $-40^\circ$C. Reproduced with permission. Copyright 2020, American Chemical Society.
performance even the temperature is below the condensation point of CO$_2$ (−78 °C). This superior low-temperature battery performance was mainly attributed to the unique solvation structure of the superelectrolyte. However, this electrolyte goes for the cells at very low area capacity of 1.2 mAh cm$^{-2}$, which is much lower than that (5 mAh cm$^{-2}$) of commercialized lithium batteries at room temperature. As a result, the practical application of this electrolyte at low temperature still has a long way to go.

Promoting the discharge capacity of lithium batteries at ultra-low temperatures is crucial to the practical application of advanced electronics in extreme environments. Prof. Chen subsequently demonstrated all-fluorinated electrolyte (1 M LiPF$_6$ in methyl 3,3,3-trifluoropionate [MTFP]/FEC [9:1] solvent) to simultaneously provided high-voltage cathode and Li metal anode reversibility at low temperature.$^{[29]}$ It was found that this advanced electrolyte yielded a high ionic conductivity (0.75 mS cm$^{-1}$) at −60 °C. In addition, this MTFP/FEC electrolyte system produced highly fluorinated interphases and that is the reason why remarkable electrochemical stability comes in. Furthermore, this all-fluorinated electrolyte-based 4.5 V NMC811/Li battery provide long-term cycling stability (capacity retention of 80% after 250 cycles) at room temperature. In addition, this battery can provide 133 mAh g$^{-1}$ at −60 °C, far exceeding the commercial electrolyte (1 M LiPF$_6$ EC/DEC, 1:1). Nevertheless, the low rate of 0.1 C has not been surmounted, and even cannot reach the minimum working temperature of the previous study. In the meantime, they mentioned another

![Figure 8. Physical properties and simulated structure of the superelectrolytes. a) Conductivity of liquid and solid electrolytes. b) Temperature dependence of the magnetic moment of the four different electrolytes measured in a superconducting quantum interference magnetometer device in an applied field of 1 mT. The freezing points of the electrolytes (as indicated by the arrows) can be determined by the transition point. The cooling rate is 1 °C min$^{-1}$. c) cMD-simulated electrolyte structure for 1.28 M LiFSI-FEC/FEMC-D$_2$. About 125 LiFSI, 234 FEC, 280 FEMC, and 793 D$_2$ molecules were dissolved into a periodic box (65.1 x 65.1 x 65.1 Å$^3$). Li$^+$ ions and coordinated molecules (within 3 Å of Li$^+$ ions) are depicted by a ball-and-stick model, while the wireframes stand for the free solvents. Free D$_2$, FEC, and FEMC molecules are shown as cyan, blue, and red wireframes, respectively, whereas hydrogens are excluded in the LiFSIFEC/FEMC-D$_2$ electrolyte. d) The representative Li$^+$ solvation structure extracted from the cMD simulations. Reproduced with permission.$^{[28]}$ Copyright 2019, Springer Nature.](image)
unconventional electrolytes, which is also a significant member that can dramatically promote low-temperature performance, which we will talk about in next section.

Xia and coworkers developed a novel electrolyte by dissolving lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) into ethyl trifluoroacetate (ETFA) solvent. It has been verified that the ETFA has a weak ability to combine Li⁺ and the electron-withdrawing F atoms can reduce the affinity with Li⁺. The weak combination implies that the desolvation of Li⁺–ETFA molecules would be easier than typical carbonate electrolytes. The decreased binding energy of Li⁺–ETFA enables the rapid desolvation process in the SEI at low temperatures. Moreover, pure ETFA solvent has a low freezing point (−78 °C), which is much lower than those of most solvents used for LIBs. In addition, The ETFA electrolyte can tolerate a faster rate of 1 C at the low temperature and maintain a retention of about 50%, demonstrated that it can effectively accelerate the ionic conduction kinetics. F atoms consist in the electrolytes and contribute to the formation of SEI. Small molecules have been screened as a cosolvent to improve the low-temperature performance. Therefore, we can directionally constitute systems contained F atoms to lithium batteries at low temperature.

7. Liquefied Gas-Based Electrolytes

A number of reasonably polar small molecules often exist as gases at room temperature due to their low London dispersion forces. These types of polar gases may be liquefied at low temperatures or under moderate pressures. In addition, they were capable of solubilizing lithium salts and then formed liquefied gas-based electrolytes. Ionic conduction, redox phenomena, and other fundamental issues of liquefied gas-based electrolytes have been proceeded in very recent researches.

Liquefied gas solvents displayed the characteristics of improved electrostatic potential regions (bluest regions), which was highly related to the electrochemical reduction stability (tetrahydrofuran [THF] < fluoromethane [FM] < difluoromethane [DFM] < EC). THF owns a high electrochemical reduction stability and it concurrently implies that FM should have the same good reduction stability. Meanwhile, the lowest electrostatic potential regions of liquefied gas solvents (reddest regions), which was in the order of EC < THF < FM < DFM, was identically connected with the solubility of Li⁺ cation. There was a relatively small solubility of Li⁺ cation in EC or THF. It is shown that the solubility of Li⁺ cation in FM is much better than that in DFM.

Meng and coworkers selected six promising liquefied gas solvents from the polarized solvents which have the characteristics of excellent electrochemical stability. This promising liquefied gas solvents were compared with the conventional liquid solvents (Figure 9a). The growth of highest electrostatic potential regions is well identical to the high electrochemical reduction stability (Figure 9b). Equally, the growth of lowest electrostatic potential regions is connected with the relatively small Li⁺ cation in the solvent which was used.

Due to the lower dielectric constant (≈10–15), liquefied gas solvents may reduce the ability of dissolving various salts. The characteristics of liquefied gas solvents (FM and DFM) are shown in Figure 9c. Because of their low viscosities, the ion mobility should be extremely high in the electrolytes. The values of relative dielectric, viscosity, and dielectric fluidity are shown in Figure 9c. The results suggested that the novel liquefied gas solvents did possess a superior dielectric-fluidity factor compared with common liquid solvents. It can be seen from the above data that if solvent possesses moderate dielectric constants individually, these solvents will hold relatively high electrolytic conductivities. In addition, these solvents kept up the outstanding viscosities and high electrolytic conductivity at extremely low temperatures. On the contrary, the common liquid solvents may be frozen at such low temperatures. Vapor pressure curves with liquid range of various conventional and liquefied gas solvents are shown in Figure 8d. The first point is the highest vapor pressures of FM and DFM at 25 °C, which are 3.8 and 1.8 MPa, respectively. Then the melting points of these solvents are below −100 °C. They also probe into other characteristics of these solvents with high expectations. There are physical characteristics of the liquid gas-based electrolyte shown in Table 1.

In 2017, Meng and coworkers dissolved tetrabutylammonium hexafluorophosphate (TBAPF₆) into liquefied polar gas to form liquefied gas electrolyte. It was found that DFM liquefied gas solvent has the characteristics of ultralow viscosity, high vapor pressure with the chemical reduction product LiF, which is a vital composition of SEI formed on the electrodes. Thin Li₂CO₃ layer formed by carbon dioxide reduction and the high mobility of lithium ions through the grain boundaries of highly ceramic surface may contribute to the drop of impedance through the negative SEI layer. In electrolytes, it is believed that a highly chemically uniform interface will contribute to get a more uniform distribution of current and suppress the continuous growth of lithium dendrites. Liquefied gas-based electrolyte can improve the stability of SEI layer on lithium metal, which was helpful to improve the electrochemical performance of lithium batteries at low temperatures. In contrast, FM-based electrolytes showed a high discharge capacity retention (98.3%) at −10 °C, whereas the normal liquid-based electrolytes showed only 86.2%. More impressively, LiCoO₂/Li battery used these liquefied gas electrolytes delivered a high Coulomb efficiency of 96% and a high-capacity retention rate of 60.6% at −60 °C.

Electrochemical performance of lithium metal batteries using liquefied gas-based, and ether-based electrolyte systems at various temperatures, is shown in Figure 10a. The cell used the carbonate ester- or ether-based electrolytes cannot work at lower temperatures of −40 °C. In addition, even the temperature returns to room temperature, the performance of the batteries that undergoes a cryogenic cycle is irreversible, as shown in Figure 10b. On the contrary, the liquefied gas-based electrolyte possessed the higher amount of coulombic efficiency (CE) (99.5%) at 20 °C and an average CE of 98.6% at −20 °C. Meanwhile, it is obvious that the liquefied gas electrolyte has a stable polarization. While the temperature returned back to 20 °C, the voltage profiles of the batteries using liquefied gas-based electrolytes were identical to that of the initial state, with CE slightly above 100%. Rate capabilities of lithium-metal batteries at various temperatures are also shown in Figure 10c. As shown that the highly stable lithium stripping/plating behavior and remarkable capacity retention of liquefied gas electrolyte have been confirmed even at the extremely low temperature.
of −60 °C at 5 mA cm⁻² (Figure 10c). Figure 10d shows that the value of polarization was linearly increased with the current below −40 °C, indicating that the ohmic resistance determined the impedance, but the diffusion cannot limit the electrolyte at such low temperatures. Furthermore, this electrolyte system cannot solve the low rate problem at −60 °C. That means the sluggish kinetics have not found a rational way to cope.

Subsequently, this group also modified the liquefied gas electrolyte by adding a fully coordinating cosolvent, THF. THF is thought to be fully coordinated with Li cations. Therefore, this hybrid electrolyte shows excellent electrochemical performance at high rate and wider temperature range. With the introduction of THF as the cosolvent, the DFM-based liquefied gas electrolyte can produce dense and uniform SEI lithium metal deposition and a stable lithium metal cycle without dendrites. The dendrite-free lithium metal anode significantly improves Coulombic efficiency during the long cycling. The Coulombic efficiency and the capacity are maintained with 99.6% and 5 mA cm⁻² at −60 °C. Due to the high dielectric-fluidity factor and exceptional electrolytic conductivity at low temperatures, the electrolyte support to grow out a low-impedance SEI, the cycle performance, and rate capability of Li-metal cycling were well maintained down to −60 °C.

Recently, on the basic of the previous work, they presented a FM-based liquefied gas electrolyte with acetonitrile cosolvent and high salt concentration. As a result, the FM-based liquefied gas electrolyte exhibited a unique solvation structure which observed in MD simulations. From the experimentally results, the cells with the FM-based liquefied gas electrolyte not only improved

![Figure 9. Physical and chemical properties of liquefied gas solvents. a) DFT calculated ionization potentials and electron affinities, b) electrostatic potential maps, c) relative dielectric, viscosity, dielectric fluidity values, and d) vapor pressure curves with liquid range of various conventional and liquefied gas solvents. Liquefied gas solvents: FM, DFM, fluoroethane (FE), 1,1-difluoroethane (1,1-DFE), 1,1,1,2-tetrafluoroethane (1,1,1,2-TFE), 2-fluoropropane (2-FP). Liquid solvents: acetonitrile (AN), propylene carbonate (PC), DCM, THF, DMC, DEC, EMC, EC, VC, FEC. Reproduced with permission[35] Copyright 2017, The American Association for the advancement of Science.]

| Group                  | Year   | Ingredients                        | Electrochemical window | Ionic conductivity [S cm⁻¹] | Cell constitutes | Rate capability |
|------------------------|--------|------------------------------------|-------------------------|-----------------------------|------------------|-----------------|
| Meng and coworkers[35] | 2017   | FM–carbon dioxide (19:1)/LiTFSI    | 6.83 V                  | 1.1                         | LiCoO₂/Li (3.5–4.1 V) | 0.1 C (−60 °C) (80.6 mAh g⁻¹) |
| Meng[38]               | 2019   | 0.5 M LiTFSI–0.5 M THF/ FM–carbon dioxide (19:1) | 4.2 V                  | 2.8                         | Li₄Ti₅O₁₂ (LTO)/LiNi₀.8Co₀.15Al₀.05O₂ (NCA) (1.3–2.7 V) | 5 mA cm⁻² (−60 °C) |
| Meng[39]               | 2021   | 1.2 M LiTFSI, 1 M AN in FM         | 4.5 V                  | 3.9                         | NCM/Li (4.5–3 V) |                |
ionic conductivity (9.0 mS cm\(^{-1}\) at 20 °C) but also promoted Li transference number (0.72). The point is that the cells possess an excellent conductivity (>4 mS cm\(^{-1}\)) over a wide temperature range, which is decided by FM’s critical point. Furthermore, liquefied gas electrolyte enables an excellent Li metal stability with high-average Coulombic efficiency and attributes to the dense Li deposition with an ideal Li-substrate contact even at -60 °C. Due to the FM-based liquefied gas electrolyte owns several superior electrolyte properties and enables to form the stable interface layers on both cathode and anode, Li metal anode and NMC/Li full cell (up to 4.5 V), both have significantly improving performance over a wide-temperature range from -60 to 55 °C.\(^{[40, 41]}\) From the analysis and consideration, they believe that the wider temperature range is mainly related to the increase in the amount of salt and cosolvent, which cause the operation temperature improves above FM’s critical point as the reduced volume change and increased the amount of FM in LiTFSI–AN–FM mixture. In addition, it is also expected to derate the internal pressure above the critical point by the higher concentration of cosolvent and salt. It is much different from the inert dilutes inside the localized high concentration electrolytes own slow transport kinetics caused by their relatively large size without taking part in the solvation shell. The FM–Li\(^+\) owns slightly solvating feature and the FM with small size in the liquefied gas electrolytes are considered to be supposed to the rapid ion transport and desolvation. Especially at low temperatures, the diffusion of free Li\(^+\) in the novel FM-based liquefied gas electrolyte is four times higher than average Li\(^+\) ion diffusion. Finally, high Li\(^+\) transference number (>0.94) can be estimated from MD simulations on account of the most charge transport occurs via the diffusion process of Li\(^+\)(AN)\(_2\)(FM)\(_n\) diffusion without free TFSI\(^-\) anions exist (<0.3% at all temperatures, unlike Li\(^+\)).

This type of low-temperature unconventional carbonate electrolyte is more likely to be an ideal model for theory research.

![Image of Figure 10](https://www.advancedsciencenews.com)
Unfortunately, the batteries using these electrolytes have to be protected by sophisticated protective structures due to high pressures of tens of bars. It provides a frustrating development approach. Meanwhile, liquid gas electrolytes might suffer from potential safety hazards, which is a big obstacle in large-scale practical application.

8. Plastic Crystal Electrolytes

Plastic crystal electrolytes have received much more considerable attention in recent years due to their high ionic conductivity and high electrochemical window.\(^{[42–44]}\) Succinonitrile (SN, \(\text{N}≡\text{C}–\text{CH}_2–\text{CH}_2–\text{C}≡\text{N}\)), a typical plastic crystal, is often used to prepare low-temperature plastic crystal electrolytes. In 2004, Armand and coworkers found that LiTFSI (5 mol%)/SN electrolyte delivered high ionic conductivity \((3 \times 10^{-3} \text{ Sc m}^{-1} \text{ at } 25^\circ\text{C})\).\(^{[43,45]}\) More importantly, the ionic conductivity of LiTFSI (5 mol%)/SN electrolyte still maintained \(4 \times 10^{-5} \text{ Sc m}^{-1} \text{ at } -20^\circ\text{C}\). These results fully validated that SN-based electrolytes can be used in low-temperature lithium batteries. Nevertheless, SN-based electrolytes might suffer from poor mechanical strength, which limits their application in solid-state lithium batteries.

To tackle this problem, in 2020, Wu and coworkers elaborately designed and fabricated a new kind of subzero SN-based polymer plastic crystal electrolytes (18 wt% poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), 30 wt% LiTFSI, 52 wt% SN) with high low-temperature ionic conductivity by tuning of lithium–salt–SN interaction.\(^{[46]}\) It was found that this solid polymer electrolyte exhibited excellent low-temperature ionic conductivity \((≈6 \times 10^{-4} \text{ Sc m}^{-1} \text{ at } 0^\circ\text{C})\) and satisfactory mechanical property. Meanwhile, LiCoO\(_2\)/LiTi\(_5\)O\(_{12}\) full cell with this electrolyte also delivered outstanding cycling stability (capacity retention of 80% after 100 cycles) and superior rate capability (73 mAh g\(^{-1}\) at current density of 150 mA g\(^{-1}\)) at \(-5^\circ\text{C}\) between 1.5 and 2.7 V. Although this SN-based solid polymer electrolyte is able to work at \(-5^\circ\text{C}\), it still needs to resolve the interfacial compatibility between SN and lithium metal in high-voltage lithium metal batteries.

It is well known that the serious reaction between SN and lithium metal will deteriorate electrochemical performance of lithium metal batteries. Hence, how to improve the interfacial compatibility between SN and lithium is crucial to develop high-voltage lithium metal batteries. In 2020, Cui’s group demonstrated a new kind of SN-based solid polymer electrolyte via an in situ polymerization of novel eutectic solvent including 1,3,5-trioxane (TXE) and SN initiated by lithium difluoro(oxalato) borate (LiDFOB).\(^{[47]}\) MD simulations and other characterization verified that there exists a uniform supermolecular structure in this solid-state polymer electrolyte (SPE) (Figure 11), which can significantly suppress the motion of SN and thus prevent the reaction between SN and Li metal. Meanwhile, this SPE is favorable to form robust polymer-based protective layer on LiCoO\(_2\) and Li, simultaneously. As a result, 4.3 V LiCoO\(_2\)/Li metal batteries delivered outstanding cycling stability (88% after 200 cycles) at room temperature. In particular, such 4.3 V LiCoO\(_2\)/Li metal battery can also operate at relatively low temperature of \(-10^\circ\text{C}\) (discharge specific capacity of 120.5 mAh g\(^{-1}\) at the first cycle and then gradually increase to 140.5 mAh g\(^{-1}\) after 35 cycles). However, ionic conduction mechanism of SN-based solid polymer electrolyte is unclear. In addition, the interfacial compatibility between SN and lithium metal in high-voltage lithium metal batteries.

Figure 11. a) MD simulation snapshots of LiDFOB, poly(formaldehyde) (POM), and SN mixture. b) Radial distribution functions \(g(r)\) of Li–SN, Li–POM, and POM–SN pairs calculated from MD simulation trajectories at 353 K. c) 1 H magic angle spinning (MAS) NMR of POM, SN, and POM–SN mixture. d) Comparison of PSL53 and SN–LiDFOB electrolyte. Reproduced with permission.\(^{[47]}\) Copyright 2020, John Wiley and Sons.
compatibility of SN with other negative electrode materials (graphite, silicon) remains a challenge.

9. Aqueous Electrolytes

Water-based lithium-ion batteries are attractive for next-generation energy storage system due to their high safety, low cost, environmental benign, and ultrafast kinetics process. Highly concentrated “water in salt” (WIS) electrolytes, a very promising electrolyte, exhibited wide electrochemical stability window and thus enhance energy density of lithium batteries. There is a common misconception that aqueous lithium batteries cannot operate below the freezing point of water. What is the result? It is worth studying by scientists.

Ramanujapuram and Yushin studied the low-temperature performance of water-based electrolyte comprehensively to further understand the rate-limiting step of aqueous lithium battery at low temperatures.\[^{[48]}\] Interestingly, LiCoO\(_2\) in saturated LiCl-based aqueous electrolytes maintained 72% of their room-temperature capacity at 0.2 C even at \(-40^\circ\)C. In contrast, LiCoO\(_2\) cycled at 0.2 C did not show any capacity below \(-10^\circ\)C in organic electrolytes. It is shown that aqueous electrolytes offer lower charge transfer resistances and therefore can be charged and discharging at much higher rates at lower temperatures. In other words, charge transfer resistance is the rate-limiting step at low temperatures.

Likewise, Li and coworkers reported that advanced hybrid aqueous electrolyte with acetonitrile (AN) as cosolvent can minimize interfacial water at the negatively charged electrode surface, and then generate a thin and uniform interphase consisting of organic outer layer based on nitrile (CeN) and sulfamide (R=S=N=S) species and inner layer rich in LiF.\[^{[49-51]}\] As shown in Figure 12, the peak of CeN stretching vibration (2252 cm\(^{-1}\)) in AN molecular disappears in BSiS-A hybrid electrolytes and is replaced by two new peaks at 2263 and 2282 cm\(^{-1}\). The hybrid electrolyte displays high ionic conduction in a wide range of temperature due to the low freezing point (\(-48^\circ\)C) and low viscosity.

**Figure 12.** Raman spectra of WiSE and BSiS electrolytes compared with pure AN and water in a) 2230–2310 cm\(^{-1}\) (CeN stretching vibration of AN), b) 2800–3850 cm\(^{-1}\) (O–H stretching vibration of H\(_2\)O), and c) 720–780 cm\(^{-1}\) (S─N─S bending vibration of TFSI\(^{-}\)). d) Ionic conductivity of WiSE, BSiS, and “AN-in-salt” (AiSE, 12.8 mol LiTFSI in 1 kg AN) electrolytes at 25 °C. e) Ionic conductivity of BSiS-D\(_{0.28}\) and BSiS-A\(_{0.5}\) hybrid electrolytes in temperature range of \(-20\) to \(60\) °C. f) Photographs showing the states of WiSE, BSiS-D\(_{0.28}\), and BSiS-A\(_{0.5}\) electrolytes at 0 and \(-20\) °C. Reproduced with permission.\[^{[50]}\] Copyright 2019, John Wiley and Sons.
of AN\textsuperscript{[52–54]} In addition, LiMn\textsubscript{2}O\textsubscript{4}/Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} full cell using this electrolyte delivers excellent cycling stability and superior rate capability at both ambient and subambient temperatures. However, aqueous electrolytes still have the common problems of the high freezing point.

Proton batteries are emerging as a promising solution for energy storage. Ji's group reported a eutectic mixture electrolyte with a low melting point, the 9.5 M H\textsubscript{2}PO\textsubscript{4} electrolyte facilitates the low-T performance of aqueous proton battery (APB)\textsuperscript{[55]} At \(-78^\circ\text{C}\), the APB delivers a discharge capacity of \(28\text{ mAh g}^{-1}\) and a specific energy of 24 Wh kg\(^{-1}\) based on the active mass of both electrodes at the current rate of 25 mA g\(^{-1}\). The enhanced inertness of water at \(-78^\circ\text{C}\) can be understood from two aspects. First, water's dissociation constant (\(K_d\)) decreases, which reduces the activities of both H\(^{+}\) and OH\(^{-}\). Second, the HER and OER reaction rates (\(k\)) decline exponentially with temperatures considering the Arrhenius law (\(a = -k A e^\text{-ERT}\)). Thus, both thermodynamic and kinetic factors favor the phenomenal electrochemical inertness of water at \(-78^\circ\text{C}\). No capacity fading at low temperature demonstrated the reduction of water activity and thus offers a safe and reliable candidate for high-latitude applications.

10. Conclusions

Low-temperature lithium batteries have received tremendous attention from both academia and industry recently. Electrolyte, an indispensably fundamental component, plays a critical role in achieving high ionic conductivity and fast kinetics of charge transfer of lithium batteries at low temperatures (\(-70\) to \(0^\circ\text{C}\)). In the context of the limited low-temperature performance of conventional electrolytes due to their intrinsic molecular structural properties, many attempts have been devoted to exploit unconventional electrolytes (fluorinated ester, EA, GBL, liquefied gas, ether, plastic crystal, and aqueous electrolytes) with low melting point and low viscosity to fulfill the harsh requirement of low-temperature lithium batteries up to now. Herein, in this Review, we have elaborated fundamental knowledge (solvation structure modification and SEI optimization) of unconventional electrolytes of lithium batteries from various new perspectives. Although the emerging unconventional electrolytes possessing some distinct functions alleviated unique problems presented in low-temperature lithium batteries, there are still grand challenges and plenty of rooms for the rational investigation in low-temperature unconventional carbonate electrolytes. In addition, perspectives on future development and research opportunities of low-temperature unconventional electrolytes are also included.

Nowadays, the demand for wide-temperature range lithium-ion batteries has increased significantly. It is well known that aforementioned unconventional solvents (EA electrolytes, liquefied gas electrolytes, and ether electrolytes) often exhibited low melting point and low boiling point. However, some problems are still coexisting in a working low-temperature lithium battery. It is still challenging for exploring new kinds of unconventional electrolytes to meet the requirements of lithium batteries in a wide range of temperatures. Environmentally friendly and low-cost eutectic solvents-based electrolyte are very promising candidate due to relatively low melting point and superior thermal stability.

From the viewpoint of long-term development, many efforts (i.e., molecular simulation calculation) should be implemented to establish the structure–property relationship between solvent structure and low-temperature performance, which can offer new horizons and clear directions for the rational design of unconventional electrolytes.

Whether SEI and CEI are same at low temperature and room temperature. Obstacles lie ahead, current interfacial chemistry research (i.e., SEI layer) of low-temperature electrolytes are still limited by characterization condition. Hence, in-depth fundamental knowledge is required to understanding and recognizing for interfacial chemistry at low temperature. The development of in situ or operando technologies (freeze scanning electron microscope) is imperative. With a patulous understanding of this fundamental knowledge, the unconventional electrolytes are possible to be optimized and that also enhance battery performance at low temperatures.

According to our review, the small molecular structure is benefit to break through the limitation of low temperature. Based on the MD simulation, it has been found that the electrolytes have to exhibit unique solvation structures to accelerate the ionic conduction kinetics for low temperature batteries. Most decomposition products of lithium salts participate in the formation of SEI, including LiF, Li\textsubscript{2}O, Li\textsubscript{2}CO\textsubscript{3}, which is crispy during the process of charging and discharging. Combining with the reaction products of solvent, it forms stable SEI on the electrodes. The continuous decomposition of electrolytes results in the increased resistance of SEI. As a result, the electrolytes need to form stable SEI, but it also need to suppress the continuous decomposition.

Overall, in spite of great achievements in unconventional electrolytes for low-temperature lithium batteries, many challenges and opportunities need to be explored. Finding good low-temperature electrolytes remains a significant challenge.

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Conflict of Interest

The authors declare no conflict of interest.

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