Application of High-Voltage Ether-Based Electrolytes in High-Voltage Lithium Metal Batteries

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Abstract: *The theoretical energy density of traditional lithium-ion batteries is close to its theoretical upper limit, and it is difficult to meet the endurance needs of future electric vehicles. In contrast, lithium metal negative electrode with its theoretical specific capacity of up to 3860 mAh/g, especially when matched with high voltage nickel-rich positive electrode (such as NCM), its energy density is expected to reach more than twice that of traditional graphite-based lithium-ion batteries, so it is considered to be one of the most potential candidates for the next generation of high energy density battery systems. However, the unstable solid electrolyte interface (SEI) between lithium metal and electrolyte seriously restricts its cycling performance. Lithium nitrate (LiNO3), as a commonly used additive for lithium metal negative electrode, plays an important role in lithium metal batteries. By forming anion-derived SEI layer rich in inorganic components such as Li3N, interface stability can be significantly improved, but its solubility in carbonate solvents is limited. Ether-based solvents have attracted much attention in LiNO3-based electrolyte because of their moderate DN value and good compatibility with lithium metal.*

Keywords: *High-pressure Ether-based electrolyte; Lithium Nitrate; Solvation Structure; Lithium Metal Battery*

Introduction

With the increasing demand for high-energy-density batteries, lithium metal batteries, lithium-sulfur batteries, and high-voltage cathode systems (such as lithium-rich manganese-based and nickel-based materials) have become research hotspots. Ether-based solvents are regarded as ideal electrolyte matrix materials due to their low viscosity, high ion mobility (>10 mS/cm), and excellent compatibility with lithium metal. However, the oxidation stability of traditional ether-based electrolytes is usually below 4.0 V (vs. Li^+/Li), making it difficult to meet the operational requirements of high-voltage cathodes (>4.3 V), which prompts researchers to seek breakthroughs from the perspective of regulating the electrolyte solvation structure.

The solvation structure of electrolytes, as a key factor determining their electrochemical performance, is essentially a dynamic coordination system formed through the coordination interactions between Li^+ ions, solvent molecules, and anions[1]. Its microscopic arrangement directly influences the ion transport kinetics, electrochemical stability, and electrode interfacial reactions of the electrolyte. From a spatial perspective, the solvation structure can be divided into two levels: the primary solvation sheath, consisting of solvent molecules or anions directly coordinated with Li^+ (with a coordination number typically ranging from 4 to 6); and the secondary solvation sheath, comprising solvent molecules arranged around the primary sheath through van der Waals forces or dipole interactions, which affects the energy barrier for ion migration.

Based on the coordination strength and spatial configuration between Li^+ and solvents or anions, solvation structures can be categorized into the following three types: solvent-separated ion pairs (SSIP), where Li^+ is fully surrounded by solvent molecules; contact ion pairs (CIP), formed by the coordination of an anion with a single lithium ion; and ion aggregates (AGG), structures where anions coordinate with two or more lithium ions[2, 3]. The proportional distribution of these three structures can be regulated by parameters such as lithium salt concentration, solvent donor number (DN), and anion acceptor number (AN), thereby determining the macroscopic properties of the electrolyte system[4, 5].

1. High-Concentration Electrolytes and Localized High-Concentration Electrolytes

Traditional electrolytes for lithium-ion batteries and lithium metal batteries typically consist of 1M lithium salt (such as LiPF6) dissolved in organic solvents (e.g., EC/DEC/DMC, DOL/DME). The electrochemical window of conventional electrolytes is limited; carbonate-based solvents generally operate below 4.4 V, while ether-based solvents are typically stable below 3.8 V[6]. This characteristic severely restricts the development of high-energy-density battery systems. Recent studies have shown that constructing high-concentration electrolytes (HCE, salt concentration $\geqslant$ 3 mol/L) or introducing diluents into them to form localized high-concentration electrolytes (LHCE) can effectively broaden the electrochemical stability window of electrolytes[7, 8]. The core mechanism of the HCE system stems from the solvation structure reconstruction induced by high salt concentration. When the salt concentration reaches a critical threshold (3 – 5 M)[9, 10], the coordination between solvent molecules and Li^+ reaches a saturated state, and the concentration of free solvent molecules drops sharply to negligible levels, forming a solvation structure dominated by contact ion pairs (CIP) and aggregates (AGG)[11]. This results in a new type of electrolyte, which imparts unique characteristics to batteries, such as high rate capability, high energy density, stable operation, and high safety. Since free solvent molecules disappear in HCE, it can be regarded as a new type of ionic liquid. From the perspective of solvation structure, in HCE, most organic solvents coordinate with Li^+, and highly flammable free-state organic solvents are almost eliminated. Consequently, HCE is less flammable compared to conventional electrolytes. In conventional electrolytes, a significant portion of solvent molecules do not coordinate with anions or cations. Therefore, those free organic solvent molecules are more readily oxidized on the lithium metal anode, forming an SEI layer rich in organic components or decomposing at high potentials. In contrast, in high-concentration electrolyte systems, anions tend to tightly bind with Li^+, forming a large number of CIPs and AGGs[12]. Thus, the reduction in free solvent molecules decreases the likelihood of solvent decomposition at high potentials, significantly expanding the electrochemical window of the electrolyte. Furthermore, this promotes the formation of an SEI layer rich in inorganic components, enhancing its mechanical stability.

Although high-concentration electrolytes protect the lithium metal anode by forming an SEI layer rich in inorganic components and exhibit a wide electrochemical window, the extensive use of expensive lithium salts significantly increases the cost of HCE, making HCE commercially unviable. Moreover, the high concentration of lithium salts in the electrolyte also reduces the ionic conductivity of HCE and increases its viscosity. Therefore, designing new electrolyte systems with lower lithium salt concentrations is highly desirable.

The addition of fluorinated diluents to high-concentration electrolytes creates localized high-concentration electrolytes. Fluorinated diluents do not participate in the formation of the Li^+ solvation sheath, meaning they do not dissociate lithium salts. The incorporation of diluents effectively reduces the viscosity of the electrolyte, improves wettability, and preserves the anion-involved solvation structure[13]. Diluents are miscible with solvent molecules in the high-concentration electrolyte without causing salt dissociation or coordination with Li^+. As a result, localized high-concentration electrolytes can retain the inherent superior electrochemical performance of high-concentration electrolytes while overcoming the limitations of HCE. Commonly used diluents currently include fluoroethers and fluorobenzenes, among others. In addition to meeting the characteristic requirements of diluents mentioned above, these fluorinated reagents contain fluorine atoms with strong electron-withdrawing effects, which generally impart high oxidation stability.

2. Fluorinated Electrolytes

Fluorinated solvents are primarily formed by substituting hydrogen atoms in solvent molecules with fluorine atoms[15]. Due to the strong electronegativity of fluorine atoms, the tendency of lone pair electrons on oxygen atoms in solvent molecules to be lost is reduced[16], significantly lowering the lowest unoccupied molecular orbital (LUMO) energy level of the solvent molecules and enhancing their oxidation resistance[17]. The fluorine atoms in solvent molecules contribute to the formation of inorganic-rich SEI or CEI layers, such as those rich in LiF, on the cathode or lithium metal[18]. In contrast, non-fluorinated solvents tend to form organic-rich SEI and CEI layers on both the cathode and lithium metal anode. Additionally, when hydrogen atoms in solvents are replaced by fluorine atoms, the flammability of the organic solvents is also reduced. Therefore, electrolytes designed with fluorinated solvents have demonstrated significant improvements in the overall performance of lithium metal batteries in numerous experimental studies and practical applications.

Traditional ether solvents exhibit poor oxidation resistance. Fluorination of ethers not only improves their oxidation resistance but also modulates the solvation structure, leading to enhanced stability of the electrode-electrolyte interfaces (EEIs); both aspects can significantly improve the performance of lithium metal batteries[19]. Based on their polarity, fluorinated ethers are generally divided into two categories: non-polar fluorinated ethers and polar fluorinated ethers. Non-polar fluorinated ethers, due to their excellent oxidation resistance, low viscosity, and melting temperature, are commonly used in localized high-concentration electrolytes (LHCEs) as diluents for high-voltage lithium metal batteries, which can address the high viscosity issue caused by increased salt concentration. In addition to serving as diluents to modulate the Li^+ solvation structure, polar fluorinated ethers have garnered increasing attention in recent years, but the design of solvents that simultaneously enhance ionic conductivity and oxidation stability faces significant challenges. Designed by Ruan et al.[20], 1,2-bis(2-fluoroethoxy)ethane (FDEE) with a polar monofluoro functional group not only exhibits excellent oxidation stability under high voltage but also demonstrates outstanding cycling stability. The electrolyte using FDEE as the solvent forms a unique Li^+ solvation structure, thereby forming a robust SEI layer rich in inorganic components such as LiF. The results show that the Li||NMC811 battery, at a cutoff voltage as high as 4.7 V, after 150 cycles, still maintains a capacity retention rate of 93.4%.

Zhao et al.[21] designed a novel fluorinated cyclic ether, 2-dimethoxy-4-(trifluoromethyl)-1, 3-dioxolane (DTDL), as a single solvent for high-voltage electrolytes. In the DTDL electrolyte composed of 2 M LiFSI, a solvation structure dominated by aggregate ion pairs (AGGs) was achieved, resulting in anion-derived SEI and CEI, which are essential for achieving excellent electrochemical performance in Li||NCM811 batteries.

Bao et al.[22] systematically investigated the influence of fluorine atom position and quantity on the physicochemical properties of fluorinated ethers and their corresponding electrochemical performance. They proposed a molecular design strategy for FDMB derived from DME. The Li^+ solvation sheath in FDMB-based electrolytes exhibits a higher anion/solvent ratio compared to DME-based electrolytes, resulting in an anion-derived SEI rather than a solvent-derived one. Consequently, Li||Cu cells using 1M LiFSI/FDMB electrolyte achieved rapid activation within 5 cycles (CE > 99%) with excellent cycling stability. When tested in Li||NCM532 cells at a cutoff voltage of 4.2 V, the capacity retention remained as high as 90% after 420 cycles, with an average Coulombic efficiency of 99.98%.

The application of fluorinated solvents in electrolytes is not limited to ethers; the fluorination of ester-based solvents also demonstrates unique advantages. Given the widespread use of carbonates (including cyclic carbonates and linear carbonates) in recent years, we first discuss fluorinated carbonate solvents for lithium metal batteries. Aurbach et al.[23] discovered that FEC-based electrolytes not only enhance the stability of lithium metal stripping/plating under high areal capacity but also significantly improve the electrochemical performance of high-voltage cathodes in lithium metal batteries due to the stable SEI derived from FEC.

Xiao et al.[24] utilized theoretical calculations to synthesize a solvent (2,2,2-trifluoroethyl) (BTC) with a low LUMO energy level. By combining LiPF6 and FEC, they developed a non-flammable electrolyte suitable for ultra-high-voltage lithium metal batteries operating across a wide temperature range. This non-flammable electrolyte significantly improved interfacial stability and lithium reversibility. Even at an ultra-high cutoff voltage of 4.7 V, the capacity retention remained at 95% after 160 cycles. Beyond the aforementioned fluorinated ether and ester solvents, other fluorinated solvents including fluoroamides (sulfonamides), fluorosilanes, fluorosulfones, fluorobenzenes, and fluoroalkanes have also been explored for high-performance lithium metal batteries. Through theoretical calculations, Xue et al.[25] found that the oxidation reaction energy between N,N-dimethyltrifluoromethylsulfonamide (DMCF3SA) and the LCO electrode surface is higher than that of EC, indicating superior oxidation stability of DMCF3SA. As a result, LCO||Li cells using 1 M LiFSI in DMCF3SA achieved capacity retention rates of 89% and 85% after 100 cycles at cutoff voltages of 4.55 V and 4.6 V, respectively. During cycling, the DMCF3SA-based electrolyte effectively suppressed grain boundary cracking, cathode corrosion, and significantly mitigated the increase in interfacial impedance and overpotential.

Conclusion

In summary, fluorinated solvents typically exhibit exceptional oxidation resistance, favorable wettability, and flame retardancy, which can fundamentally alter the intrinsic properties of electrolytes, thereby enhancing the electrochemical performance of lithium metal batteries. However, further research is still required on novel fluorinated solvents and their effects on the compatibility with lithium metal anodes and high-voltage cathodes, as well as the formation of stable EEIs, which is essential for the broader application of lithium metal batteries[26].

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