Nonaqueous electrolytes play important roles in determining the performance of lithium-ion batteries. However, the high flammability, poor thermal stability, narrow electrochemical window, and slow electrode reaction kinetics seriously hinder the application of batteries. Compared with traditional electrolytes, high-concentration electrolytes (HCEs) have a higher ion transfer number, wider electrochemical window, higher thermal stability, lower volatility, good flame resistance, and passivation of Al current collector at high potential. The HCEs can effectively overcome the shortcomings of traditional electrolytes, and provide a new direction for the development of next-generation batteries. Therefore, it is very timely to write a perspective on HCEs for directing future research. Herein, the recent development of HCEs is described.

1. Introduction

With the rapid increase in energy demand and the appearance of increasingly serious global environmental problems, the development of high-energy-density storage devices, especially, lithium metal batteries (LMBs), is becoming even more urgent. Metallic Li is considered to be ideal anode due to the extremely low electrode potential (−3.045 V vs. standard hydrogen electrodes, SHEs) and ultrahigh specific capacity (1700 mAh g⁻¹). However, the uncontrollable growth of Li dendrites and low Coulombic efficiency (CE) in traditional electrolytes severely hinder their potential applications. Although electrolyte additives have made a significant contribution to the performance improvement of LMBs, they are still pure in high flammability, poor thermal stability, narrow electrochemical window, and slow electrode reaction kinetics, which seriously hinder the application of batteries.

High-concentration electrolytes (HCEs) (the concentration of lithium salt usually >3 M) show different physical and chemical properties from traditional electrolytes due to their unique solvation structure. In HCEs, the interaction between cations and anions is stronger, and there are almost no free solvent molecules, thereby reducing the decomposition of the solvent in solid electrolyte interphase (SEI), so the cycle stability and CE are higher. At the same time, the HCEs also have the advantages of higher electrochemical window, thermal stability, flame resistance, and passivation of the Al current collector at high potential, which can effectively improve the shortcomings of traditional electrolytes. However, the use of high salt concentration electrolyte also faces some challenges, such as high viscosity and high cost, so further research and development are needed. In this Perspective, we will introduce the development of HCEs, and discuss advantages and disadvantages for LMBs. Moreover, we also point out the future research direction in this field and expect that this Perspective will give some kindly guidance to related researchers in future.

2. Advantages of HCEs for LMBs

The electrolyte conductivity decreases as the electrolyte concentration increases in some degree, so 1 M is considered as the best electrolyte concentration. In this Perspective, we will introduce the development of HCEs, and discuss advantages and disadvantages for LMBs. Moreover, we also point out the future research direction in this field and expect that this Perspective will give some kindly guidance to related researchers in future.
thereby inhibiting the growth of Li dendrites and the side reaction between the electrolyte and Li metal, and the excellent cycle stability and rate performance of batteries will be achieved.[15,16,30]

To achieve high energy density, a high voltage window is usually required. However, under high potential, the LiPF₆ (1 M) electrolyte is unstable and will react with a trace of water to generate HF, and then dissolve transition metal ions and significantly corrode electrode materials.[31,32] LiN(SO₂CF₃)₂ (LiTFSA) salt, as a commonly used lithium salt of HCEs, is more stable. Under the high pressure of 5 V, the metal ions in the HCEs have almost no free solvent molecules that can be coordinated, and the constructed 3D network inhibits the diffusion of metal ions into the bulk electrolyte, effectively protecting Al and transition metals.[30] The HCEs overcome the problem that LiTFSA electrolyte cannot passivate the Al current collector, so that batteries can work under a higher electrochemical window and obtain a higher energy density.

Safety is an important indicator of battery application. In HCEs, a nonvolatile and nonflammable solvent can be selected. And there is a strong interaction between solvent molecules and Li⁺, which can effectively reduce the inherent volatility of the electrolyte.[33] In addition, SEI generated by anions has good passivation ability and can inhibit side reactions at the interface.[15] Therefore, in terms of safety, HCEs have unique advantages and show excellent safety. In the work of Yamada and coworkers,[30] the Li||LNMO cells with HCEs showed better electrochemical performance than traditional electrolytes at 0.5 C and 40 °C, as shown in Figure 1a,b. When the current density is 2 C, the Li||LNMO cells with HCEs showed more stable cycle performance (Figure 1c). Moreover, the linear sweep voltammetry

![Figure 1](https://www.advancedsciencenews.com)

**Figure 1.** Charge–discharge curves of Li||LNMO cells at 0.5 °C a) commercial electrolyte and b) HCE; c) Cycling stability of Li||LNMO cells at 0.25 °C; d) LSV of an aluminum electrode in various concentrations of LiFSA/DMC electrolytes in a three-electrode cell; Flame tests of e) commercial electrolyte and f) HCE. Reproduced under a Creative Commons Attribution 4.0 International License.[30] Copyright 2016, The Authors. Published by Springer Nature.
Figure 2. Cycling stability of Li||LNMO cells at 1 and 3 M electrolyte at a) 2 C and b) 5 C; c) the amount of transition metal deposited on the different cycled lithium plates in 1 and 3 M electrolytes at 2 C; d) schematic illustrations of passivation films in 1 and 3 M electrolytes. Reproduced under a Creative Commons Attribution 4.0 International License.© 2020, The Authors. Published by Springer Nature.
(LSV) (Figure 1d) indicated that as the electrolyte concentration increased, the oxidation stability of the Al electrode increased, so the Al current collector can be effectively protected. In addition, it can be observed in the combustion test (Figure 1e,f) that HCEs exhibited more excellent thermal stability and flame retardant ability, and the safety performance is significantly improved.

In addition, HCEs also have the function of protecting the electrode materials and inhibiting the dissolution of transition metals in the electrolytes. In the work of Qiu et al., 3 m LiPF$_6$-ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) was used as the electrolyte, the Li sheet was used as the anode, and the cobalt-free Li$_{1.2}$Ni$_{0.15}$Fe$_{0.1}$Mn$_{0.55}$O$_2$ (LNFMO) as the cathode. As shown
in Figure 2a,b, the HCE can still remain stable after 500 cycles at current densities of 2 and 5 C. The discharge specific capacity was 150 and 125 mAh g⁻¹, and the capacity retention rate was 94% and 100% in the HCE, respectively. Moreover, the discharge specific capacity had obviously attenuated after 250 cycles in the traditional electrolyte. This demonstrates that the LMBs in the HCE not only have excellent cycle stability, but also exhibit excellent rate performance, which is beneficial to the rapid charge and discharge of the battery. In addition, it can be seen from the transition metal deposition graphs in different cycles (Figure 2c) that the transition metal deposition in the traditional electrolyte gradually increased with the increase in the number of cycles, whereas the transition metal deposition in the HCE only slightly increased, and further proved that the HCE suppressed the deposition of transition metals. Figure 2d shows a schematic diagram of cathode electrolyte interphase (CEI) formed in different electrolytes. In the traditional electrolyte, solvent molecules were decomposed to form organic-rich CEI, which exhibited fragile and nonuniform characteristics, so the electrode material cannot be protected, and a large amount of transition metal dissolved products were formed on the surface, resulting in poor cycle stability and rate performance, and low CE. Compared with the CEI formed by the decomposition of carbonates in commercial electrolytes, LiPF₆ prefers to be decomposed and participate in the formation of CEI in HCEs. The LiF-rich CEI exhibited strong, uniform, and dense characteristics, so it could protect electrode materials and inhibit the dissolution of transition metals, thus exhibiting excellent electrochemical performance.

3. Disadvantages and Improvement of HCEs

Although HCEs have many advantages, there are still some shortcomings that hinder their commercial development. High viscosity and high cost are currently the two main problems that restrict the practical applications of HCEs. Commercially, the batteries with traditional electrolytes require 24 h of wetting before use, whereas the batteries with HCEs have higher viscosity and therefore longer wetting times. When highly loaded electrode materials are used, the difficulty of wetting is bound to increase. In addition, the cost of the Li salt in the electrolyte is higher than other components, and the HCEs require more Li salt, which results in its cost significantly higher than that of traditional electrolytes. Therefore, these two problems must be solved first before commercial applications of HCEs.

To solve the above problems, an ideal diluent is proposed. First, the diluent has a low cost and can effectively reduce the viscosity of the electrolyte; second, the diluent does not change the local coordination environment and higher solubility of the HCEs, while ensuring that the electrochemical window is not shortened; finally, the diluent features high security. The 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTFE), tris(2,2,2-trifluoroethyl)orthoformate (TFEO), and bis(2,2,2-trifluoroethyl) ether (BTFE) have been introduced into HCEs as diluents, forming a new type of local high-concentration electrolytes (LHCEs), which satisfied the aforementioned conditions while maintaining the excellent characteristics of HCEs. Recently, Zhang et al. prepared 1.2 M LiFSI in DMC/BTFE (1:2 by mol) as the electrolyte. In the Li||Cu cells, the average CE of 1.2 M LiFSI/DMC was only 9% in the first 10 cycles, whereas the average CE of 5.5 M LiFSI/DMC was as high as 92.2%. After BTFE dilution, the average CE of 2.5 M LiFSI/DMC-BTFE increased to 99.5%, and the average CE of 1.2 M LiFSI/DMC-BTFE solution also increased to 99.3%, indicating that the electrochemical behavior was improved after dilution. As shown in Figure 3a, the capacity of the traditional electrolyte decays rapidly at the current density of 1 C, with a capacity retention rate of only 40% after 100 cycles. In the HCEs, although the battery performance was improved, its capacity retention rate was 76%. After being diluted by BTFE, it is shown in Figure 3a that the discharge capacity remained stable at 150 mAh g⁻¹ (capacity retention rate is 95%) after 300 cycles, and the average CE was 99.7%. When the 1.2 M LiFSI/DMC-BTFE battery was charged at a current density of 0.5 C and discharged at a current density of 2 C, the specific discharge capacity could still maintain at about 150 mAh g⁻¹ after 700 cycles, and the capacity retention rate was >80% (Figure 3c). Figure 3d shows that the solvation of Li⁺ is mainly carried out by DMC molecules, while the interaction between BTFE and other electrolyte components was weak. In addition, it is shown in Figure 3e that the free DMC molecules in 1.2 M LiFSI/DMC-BTFE were reduced and weakened the association between Li⁺ and FS⁻. It took a role in improving the ionic conductivity and dynamic performance of the electrolyte, and provided a new direction for the development and application of HCEs. Although LMBs have shown excellent performance in LHCEs, the interaction between diluent and solvent is still unclear and needs to be optimized, so further improvement and exploration are needed.

4. Summary and Perspectives

In this perspective, we summarize the unique advantages of HCEs including lower interface resistance of the anion-derived SEI layer which promotes uniform Li electroplating/stripping, high voltage window to achieve higher energy density, high level of battery safety with low volatility and good flame retardancy. Moreover, it protects the electrode material and inhibits the dissolution of the cathode transition metal. However, the disadvantages of high viscosity and high cost are obstacles to the development of potential applications of HCEs. Therefore, the research of HCEs still needs to continue to explore and optimize.

The LHCEs have successfully solved the shortcomings of high viscosity and high cost of HCEs. At the same time, the introduced diluents will not change the solvation structure of the Li salt in the electrolytes, inheriting the unique advantages of HCEs. To maintain high safety, screening and optimizing nonflammable and low volatility diluents will be a direction for future exploration. Moreover, the diversity of electrolyte components, the formation mechanism of the electrode and electrolyte interface, the corresponding in situ characterization test, both the perfection of theoretical calculation models and application expansion (other metal-ion batteries) need to continue to explore and optimize, thus to further promote the development of HCEs.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

batteries safety, high-concentration electrolytes, lithium dendrites, lithium metal batteries, metallic lithium anodes

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