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Electrolyte solvation structure as a stabilization mechanism for electrodes

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Abstract

Rechargeable batteries with high capacity, power and safety are urgently required for current and future technological demands. The solid electrolyte interphase (SEI) layer has a dominant impact on battery cyclability and the solvate is the key factor that determines the SEI layer. In this perspective, we first review the recent advances in understanding the influences of electrolyte composition on the solvation chemistry and SEI layer. The solvation structure of electrolytes seems to be the root cause of the stability of electrodes during cell cycling. We then discuss the strategy to manipulate the solvation chemistry by adjusting the compositions of the electrolytes, including the solvent, salt, concentration and additive. Finally, we concisely discuss the challenges in characterizing the structure of the solvates at the electrode|electrolyte interface. This review refreshes our current understanding of the key factors for stable electrode|electrolyte interfaces in the pursuit of high-performance battery systems.

Keywords: Electrolytes, solvation structure, electrode|electrolyte interface, mechanistic study

INTRODUCTION

Conventional lithium-ion batteries with graphite anodes have reached a bottleneck and their limited capacity cannot meet the urgent demand for high-power batteries with high energy and power density^[1]. To realize current-generation energy storage systems, developing electrodes with high specific capacity is imperative. Unfortunately, the large volumetric change and unstable interfacial characteristics of active materials lead to rapid capacity decay and insufficient cycling life^[2,3], which seriously hinder the practical



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application of electrodes for high-power rechargeable batteries.

Previous investigations have confirmed that the successful application of electrodes is largely dependent on the solid electrolyte interphase (SEI), which can mitigate the structural damage of electrodes and suppress the decomposition of electrolytes^[4-7], resulting in electrodes with high coulombic efficiency and long cycle life. Therefore, tremendous efforts have been made to construct stable SEI films on the electrode surface by electrolyte engineering. Many studies have concluded that the protective effects of the SEI layer are related to the inorganic components (MF and M_2CO_3 , $M = Li, Na$ or K) and it has been claimed that MF plays a critical role in improving the interfacial stability^[8-11].

However, recent emerging research has shown that the SEI layer is not the root cause for stabilizing electrodes. On the one hand, the electrode protected with the SEI cannot inhibit the capacity decay and electrolyte decomposition when electrolytes are not compatible with electrodes^[12]. On the other hand, the performance of electrodes is related to the solvation structure of the electrolyte (solvents bind the ions in the form of associative ion pairs), which determines the desolvation ability of the alkali metal. Moreover, the imperceptible changes of solvation structure can result in the difference of the forming potential and chemical composition of the SEI film because the interface electrolyte is the precursor of the SEI film. Therefore, the solvation structure of the electrolyte plays a more dominant role in stabilizing electrochemical performance than the SEI film^[13].

Herein, we summarize the latest advances regarding the fundamental interactions in the electrolyte and correlate electrolyte structure with electrode stability. Electrolyte structure is associated with the strength of the M^+ -solvent, M^+ -anion and M^+ -additive interactions in the electrolyte and the volume/shape of the solvent and anion. Thus, electrolyte structure can be tuned by varying the type of metal salt, solvent, salt concentration and additive. For each class, we provide examples to reveal how these factors regulate the electrolyte structure and improve the interfacial properties and cycle performance of the battery. Finally, we concisely discuss the major challenges of characterizing electrolyte structure and propose further research aspects in the relationship between electrode and interfacial electrolyte structure. We hope that this article can attract more attention to the solvation structure of electrolyte, and further explore the working mechanisms of electrolytes.

METAL SALT REGULATION

As the key component of an electrolyte, many salts have been reported for rechargeable batteries, such as hexafluorophosphate (MPF_6)^[14], bis(fluorosulfonyl)imide (MFSI)^[15,16] and trifluoromethanesulfonate (MCF_3SO_3) salts^[17]. The composition of metal salts plays a key role in the stability of batteries, especially the anions in salts that regulate the thermodynamic stability of the electrolyte. Generally, metal salts with poor thermodynamic stability are preferred as electrolyte salts because they can be easily reduced and render the formation of a stable SEI film on the electrode surface^[18,19]. For instance, the preferential reduction of Li difluorophosphate (LiDFP) or Li difluorobis(oxalato) phosphate leads to the formation of a dense and stable SEI layer, effectively suppressing Li dendrite growth and improving the cycle life of the Li-metal anode^[20,21].

Beyond this, electrolyte structures are directly altered by the type of anions [Figure 1A], where the location and arrangement of anions in the solvent sheath play a critical role in improving the electrochemical properties. For instance, the ClO_4^- anion has a small interaction with a Na^+ ion (-121.6 kcal/mol, Figure 1B) and possesses small volume in 1.0 M $NaClO_4$ in dimethoxyethane (DME) electrolyte, indicating a high degree of freedom of the ClO_4^- anion around the electrode surface [Figure 1C]. As a result, the free moving ClO_4^- anion leads to a low Coulombic efficiency and Na corrosion in the Na plating/stripping process. When

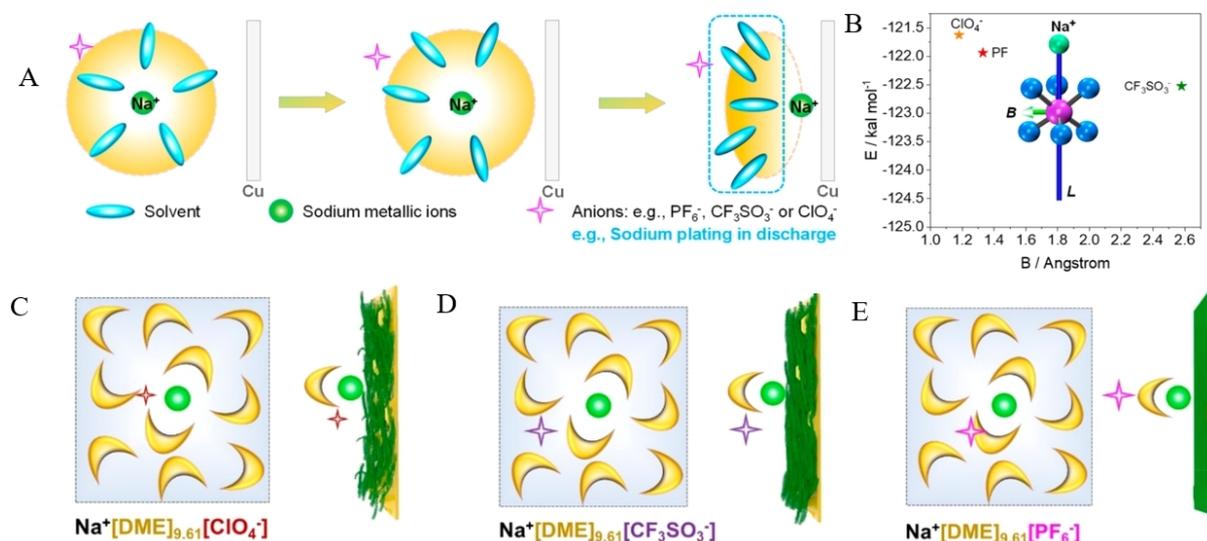


Figure 1. (A) Schematic illustration of the solvent structure during the desolvation process. (B) Calculated Na⁺-anion binding energy. Interfacial model of electrolytes with different metal salts: (C) NaClO₄; (D) NaCF₃SO₃; (E) NaPF₆. These figures are reproduced with permission from Zhou *et al.*^[22].

NaCF₃SO₃ is used as the Na salt, the Na⁺-anion interaction is significantly enhanced and the free anions are reduced, but the strong interaction of Na⁺-CF₃SO₃⁻ (-122.5 kcal/mol) causes the CF₃SO₃⁻ anion to approach the electrode [Figure 1D] and induces serious side reactions. In contrast, the medium interaction of Na⁺-PF₆⁻ (-121.9 kcal/mol) not only reduces the degree of freedom of PF₆⁻ but also results in PF₆⁻ being far from the electrode [Figure 1E]. Thus, a remarkable cycle performance was achieved in NaPF₆-based electrolytes^[22]. Similar results were observed in KFSI- and KPF₆-based electrolytes^[12,23], which further confirm the importance of metal salts in regulating electrode stability.

CONCENTRATION REGULATION

Beyond the effect of anions in salt, the salt concentration also regulates the solvation structures of electrolytes^[24]. As the salt concentration increases, the number of free solvent molecules decreases, while the number of anions around M⁺ increases and anions are located closer to M⁺ [Figure 2A]. This interfacial situation results in an enhancement in cation-solvent stability and effectively suppresses solvent reduction or M⁺-solvent co-insertion. However, high concentration electrolytes (HCE) tend to bring high viscosity, low ionic conductivity and high costs. Considering these issues, a localized high concentration electrolyte (LHCE) has been designed. LHCEs possess the same solvation structure as HCEs but their ionic conductivity [Figure 2B] and viscosity are significantly improved, thereby achieving electrodes with fast charging performance^[25].

In addition, low concentration electrolytes (LCEs) have attracted extensive attention from researchers. LCEs not only present reduced costs and viscosity but also extend the operating temperature range of batteries. Zheng *et al.*^[26] designed dual-salt LCEs (0.1 M LiDFP and 0.4 M LiBOB/LiFSI/LiTFSI) for lithium-metal batteries. In dual-salt LCEs, a highly conductive and flexible SEI layer, originating from the reduction of LiDFP and LiBOB, inhibits the growth of Li dendrites and enhances the Coulombic efficiency from 83.8% in a conventional electrolyte using 1 M LiPF₆ to over 93% in LCEs. The improved electrochemical performance demonstrates the compatibility of LCEs toward Li-metal anodes. Li *et al.*^[27] developed an ultralow concentration electrolyte (0.3 M) for Na-ion full cells and achieved good storage sodium performance [Figure 2C]. This discovery refreshed our knowledge of the prevailing effect of salt concentration on the

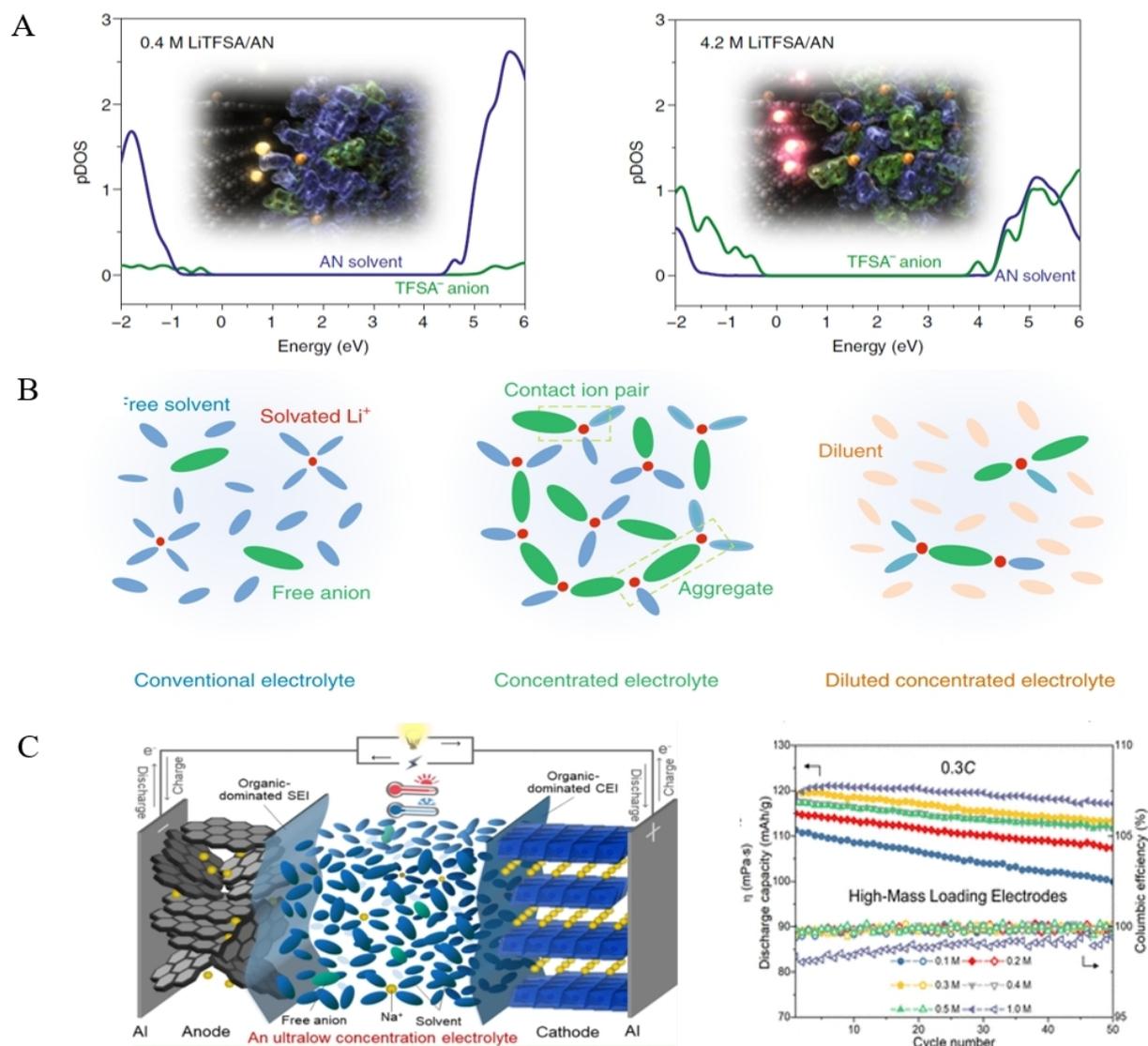


Figure 2. (A) Calculated electronic structures of electrolytes. (B) Schematics of solvation structures for dilute and concentrated electrolytes. (C) Schematic and cyclic capability of sodium-ion batteries at different electrolyte concentrations. These figures are reproduced with permission from Yamada *et al.*^[25] and Li *et al.*^[27].

electrolyte decomposition. However, the structure of the interfacial electrolyte in the LCE remains unclear and significant research regarding the electrolyte effect is still required.

SOLVENT REGULATION

To explore the critical factors that regulate electrode stability in the electrolyte, various electrolytes have been investigated^[28]. The binding energies in [Figure 3A](#) show that the solvent significantly affects the affinities toward Li⁺ ions in electrolytes, indicating that the solvation layer of electrolytes is closely correlated to the type of solvent^[29]. For example, compared to ester solvents, the ether solvent DME has the strongest solvating power towards Li⁺, which enhances the stability of the electrolyte. However, the strong interaction of Li⁺-DME inhibits Li⁺ desolvation and therefore destroys the structure of graphite when it is co-inserted. The interaction of Li⁺-diethyl carbonate (DEC) is significantly lower than that of Li⁺-DME, while its branched alkane chains weaken the interactions between the solvent molecules, resulting in a loose stack

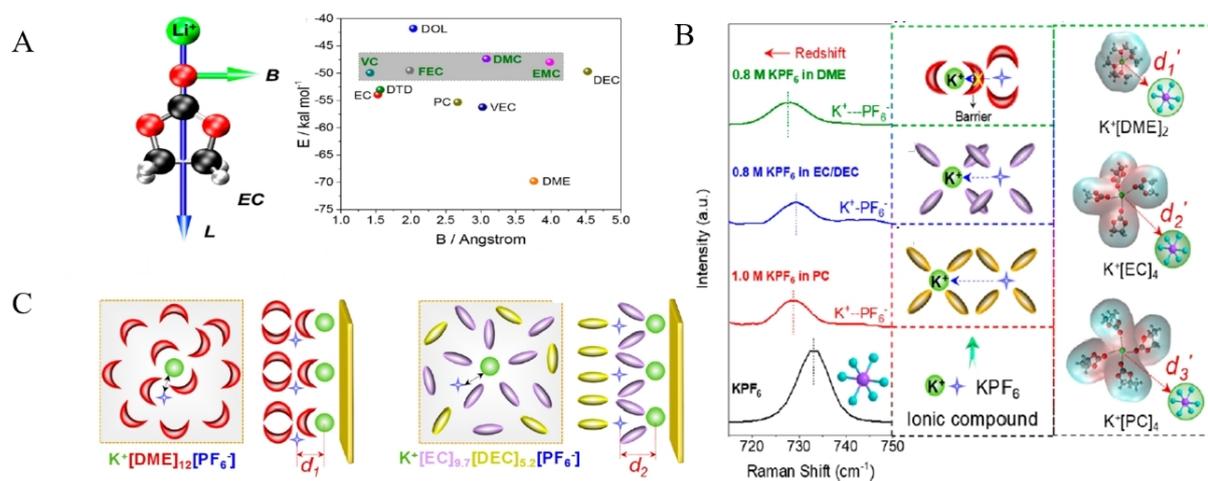


Figure 3. (A) Calculated binding energy of Li⁺-solvents. (B) Comparative Raman spectra and simulated cation solvation structures of electrolytes with different solvents. (C) Schematic illustration of solvation structure regulation by solvents. These figures are replicated with permission from Zhang et al.^[23] and Li et al.^[29].

form. Consequently, the graphite structure is destroyed because of Li⁺-DEC co-insertion. In contrast, Li⁺ can insert/extract from graphite in the dimethyl carbonate (DMC) electrolyte even though the interaction of Li-DME is almost the same as the force of Li⁺-DEC.

In addition, the type of solvent can influence the behavior of anions in the solvation layer. As shown in Figure 3B, solvated PF₆⁻ has a closer distance with the K⁺ ions in DME compared to PF₆⁻ in polycarbonate or EC/DEC, which may be related to the low dielectric constant of DME and the small symmetrical five-ring-structured K⁺[DME]₂. The close distance between the cation and solvent contributes to reducing the electronegativity change of the solvent and enhances the cation-solvent stability when the cation-solvent accepts one electron^[23]. According to the above analysis, it can be concluded that the characteristics of the solvent, such as functional groups (ester or ether group), volume/shape and dielectric constant, largely dominate the solvent structure of electrolytes.

In addition, the competitive coordination with M⁺ among solvents also impacts the solvation structure. For instance, when EC serves as a co-solvent, EC can replace the DEC in the solvation shell due to the stronger interaction of EC with K⁺ than DEC [Figure 3C], where the K⁺[DEC]_x cluster changes to K⁺[EC]_m[DEC]_n. Meanwhile, the peak position of P-F in PF₆⁻ anions undergoes a blue shift when EC replaces the branched and loose DEC [Figure 3B]. This result further verifies the effect of solvent on the distribution of anions in the solvent sheath. As a result, DEC can occupy the positions of free EC around the K⁺-EC solvation structure and weaken the strength of K⁺-EC due to the insertion of DEC into the K⁺-EC pair. Eventually, a highly reversible K plating is achieved^[12]. These may be the real reasons why the anode has good compatibility with the mixed solvents but not the individual solvents.

ADDITIVE REGULATION

Additives are foreign molecules introduced into the parent electrolyte in small doses. At present, additives are divided into organic and inorganic additives. Fluoroethylene carbonate and vinylene carbonate are two common original additives^[30]. Generally, these additives have lowest unoccupied molecular orbitals with lower energy than EC, DEC and DMC. In the process of the electrochemical reaction, they are reduced on the electrode surface prior to the solvent, thus affecting the composition and distribution of the SEI film. As

a result, the optimized SEI film inhibits the decomposition of the solvent and provides a favorable environment for the uniform deposition of metal ions. Apart from the above factors, additives can participate in the solvation structure to form M^+ -additions and are preferentially reactive with electrodes due to the weak interaction of M^+ -additions. Furthermore, the behavior of electrolyte decomposition is altered due to the decreasing population proportion of the solvent molecule and anion in the first solvation shell of M^+ ^[31,32].

In addition to original additives, inorganic additives have also been researched, such as LiNO_3 , which has been used to change the solvation sheath of Li ions due to the large binding energy of NO_3^- anions toward a Li^+ ion^[33]. As expected, NO_3^- anions preferentially coordinate with Li^+ ions and instead of FSI⁻ anions in the solvated sheath when 0.20 M LiNO_3 was added into the 2.0 M LiFSI in the DME electrolyte. As a result, NO_3^- alters the type of bonding of FSI⁻ anions to Li^+ ions and results in the polarization of FSI⁻, which promotes FSI to decompose completely and produces a LiF-rich stable interface [Figure 4A-D].

Recently, a new inorganic additive, $\text{Mg}(\text{NO}_3)_2$, has been introduced^[34]. However, its behavior is entirely different from that of LiNO_3 . When $\text{Mg}(\text{NO}_3)_2$ is added, the stability of the electrolyte|electrode interface is significantly improved. Furthermore, the positive effect of the NO_3^- ion in forming a stable SEI and Mg^{2+} ions decreasing the number of solvent molecules surrounding the Li^+ because of the strong interaction of Mg^{2+} -solvent are beneficial for Li^+ desolvation [Figure 4E]. Some portion of Mg^{2+} can also be reduced via a spontaneous chemical reaction to form a Li-Mg alloy on the Li-metal anode [Figure 4F]. As shown in Figure 4G, the synergistic effect between Mg^{2+} and NO_3^- endows Li|Li cells with dendrite-free Li plating and excellent cycling stability (1400 h).

Inspired by these works, metal fluorides and chlorides have also been used as additives to regulate the interfacial chemistry between the electrode and electrolyte. Zheng *et al.*^[35] and Xu *et al.*^[36] reported SnCl_2 and SnF_3 as electrolyte additives that can induce the formation of a protective Na-Sn alloy layer on a Na metal surface by the spontaneous reaction between SnCl_2 (SnF_3) and Na metal. Fang *et al.*^[37] revealed that a SEI bilayer with a Na-Sb alloy inner layer and a NaF-rich outer layer was formed in a HCE with SnF_3 additives. The bilayer structure realized uniform sodium deposition and effectively enhanced the cycling life of Na||Na symmetric cells. All these results prove that the inclusion of additives can pave the way for further applications of alkali-metal batteries.

SUMMARY AND OUTLOOK

In this article, we have reviewed the fundamental interactions in electrolytes from integrating solvent, salt and additive effects and discussed the stability mechanism of electrodes. The coordination between anions, solvents and additives with cations plays a key role in determining electrolyte solvation chemistry. More importantly, the electrolyte solvation structure has a profound influence on metal ion desolvation and interfacial chemistry. Even with the inspiring results reported above, our current understanding of the fundamental interactions in electrolytes is still at an early stage. Therefore, more endeavors are strongly required to focus on electrolyte solvation structure and further reveal the structure-function relationships, as described below.

Exploration of electrolyte solvation structure

In electrochemistry, the structure of interfacial electrolytes is extremely difficult to detect. In order to study the electrolyte structure at the interface, various experimental and theoretical simulation techniques have been carried out. However, there is still a lack of direct and effective evidence to describe the structure at the microscopic molecular level. Therefore, exploring accurate characterization techniques may provide a new

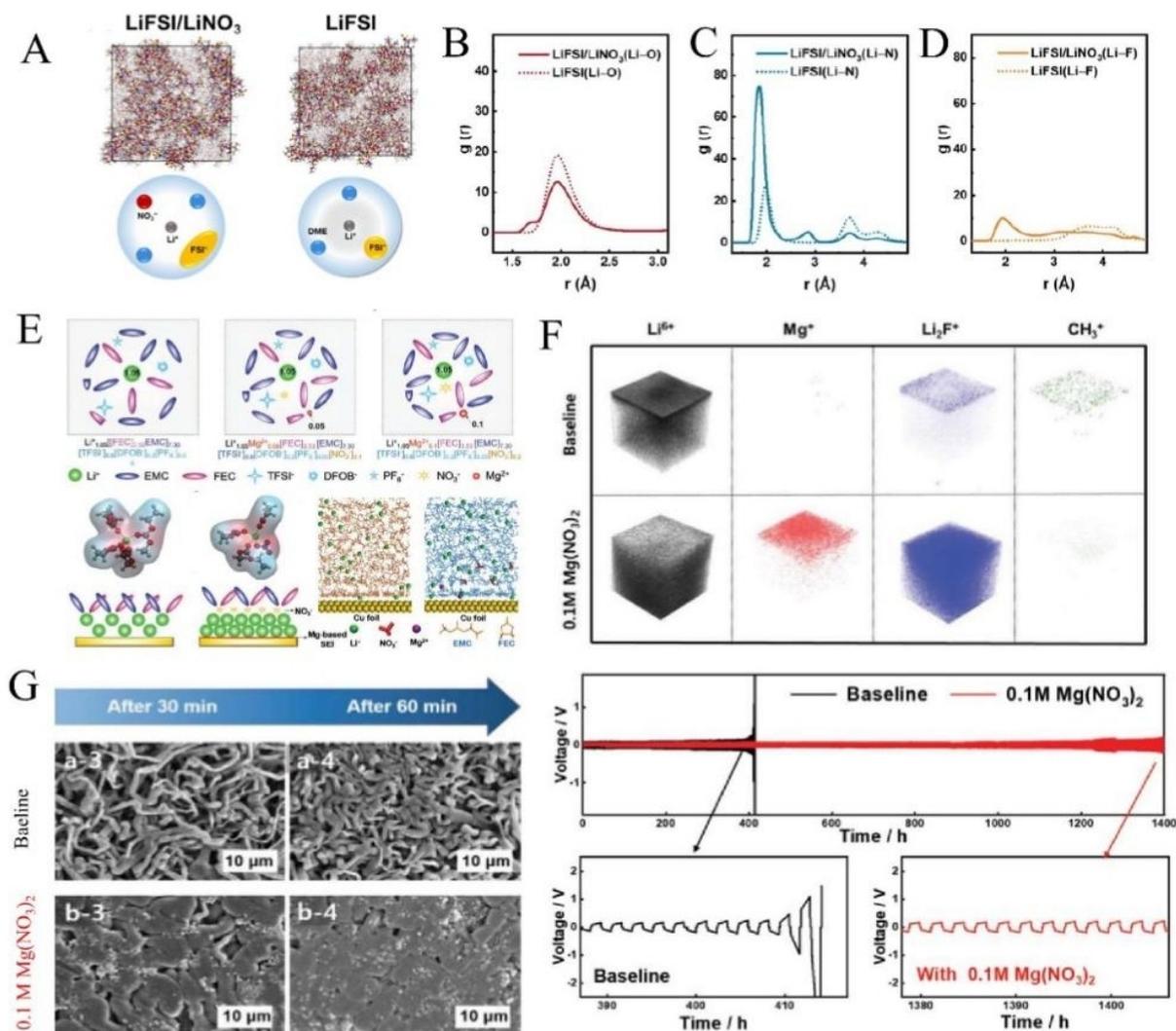


Figure 4. (A) Molecular dynamics simulations of LiFSI/LiNO₃ and LiFSI electrolytes. Radial distribution functions of (B) Li-O, (C) Li-N and (D) Li-F. (E) Schematic of interactions between cations and solvents. (F) Time-of-flight secondary ion mass spectrometry three-dimensional image of electrode surface. (G) Scanning electron microscopy images of deposited Li on Li-metal anode and electrochemical properties of symmetric Li|Li cells in the baseline electrolyte and the electrolyte with Mg(NO₃)₂ additive. These figures are reproduced with permission from Zhang et al.^[33] and Lee et al.^[34].

research paradigm to demonstrate electrolyte structure. Surface-enhanced Raman scattering, which can identify the bonding, adsorption configuration and orientation of molecules on solid/liquid surfaces, may be a promising technique for electrolyte structure analysis. Furthermore, electrospray ionization mass spectrometry can also be used to measure the solvation structure of electrolytes. Moreover, high-accuracy models should be constructed to investigate the cation-solvent, cation-anion and anion-solvent interactions in the electrolyte.

Exploration of electrode effect

The electrolyte structure on electrode surfaces is very different from that in the bulk electrolyte due to the ionic adsorption on electrodes and this difference increases when accompanied by the electrochemical reaction. Beyond the adsorption properties, the microstructure, activity and species of the electrode also impact the electrode|electrolyte interface by altering the electrolyte structure around the electrode.

However, recent reports of how electrode materials regulate the electrolyte distribution are rare. Therefore, a deep understanding of electrode|electrolyte interactions will provide new insights into the interfacial reaction.

DECLARATIONS

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Authors' contributions

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Conflicts of interest

Both authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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