Perspective

Electrolyte solvation structure as a stabilization mechanism for electrodes

Li Zhang, Yuhui Chen

School of Energy Science and Engineering, Nanjing Tech University, Nanjing 211816, Jiangsu, China.

Correspondence to: Prof. Yuhui Chen, State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing Tech University, 30 puzhu South Road, Jiangbei New District, Nanjing 211816, Jiangsu, China. E-mail: cheny@njtech.edu.cn

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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
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, 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 $M\text{CO}_3$, $M = \text{Li, Na or K}$) and it has been claimed that MF plays a critical role in improving the interfacial stability.

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. 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.

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 $M^+\text{-solvent}$, $M^+\text{-anion}$ and $M^+\text{-additive}$ 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 ($\text{MPF}_6$) salts, bis(fluorosulfonyl)imide (MFSI) salts and trifluoromethanesulfonate ($\text{MCF}_3\text{SO}_3$) salts. 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. For instance, the preferential reduction of Li difluorophosphate ($\text{LiDFP}$) 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.

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 $\text{ClO}_4^-$ anion has a small interaction with a $\text{Na}^+$ 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 $\text{ClO}_4^-$ anion around the electrode surface [Figure 1C]. As a result, the free moving $\text{ClO}_4^-$ anion leads to a low Coulombic efficiency and Na corrosion in the Na plating/striping process. When
NaCF$_3$SO$_3$ 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$^+$-CF$_3$SO$_3^-$ (-122.5 kcal/mol) causes the CF$_3$SO$_3^-$ anion to approach the electrode [Figure 1D] and induces serious side reactions. In contrast, the medium interaction of Na$^+$-PF$_6^-$ (-121.9 kcal/mol) not only reduces the degree of freedom of PF$_6^-$ but also results in PF$_6^-$ being far from the electrode [Figure 1E]. Thus, a remarkable cycle performance was achieved in NaPF$_6$-based electrolytes[22]. Similar results were observed in KFSI- and KPF$_6$-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.[24] 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 LiPF$_6$ 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
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
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]ₙ cluster changes to K⁺[EC]ₙ[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
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 $M$\textsuperscript{[31,32]}.

In addition to original additives, inorganic additives have also been researched, such as LiNO\textsubscript{3}, which has been used to change the solvation sheath of Li ions due to the large binding energy of NO\textsubscript{3} anions toward a Li\textsuperscript{+} ion\textsuperscript{[33]}. As expected, NO\textsubscript{3} anions preferentially coordinate with Li\textsuperscript{+} ions and instead of FSI anions in the solvated sheath when 0.20 M LiNO\textsubscript{3} was added into the 2.0 M LiFSI in the DME electrolyte. As a result, NO\textsubscript{3} alters the type of bonding of FSI anions to Li\textsuperscript{+} 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, Mg(NO\textsubscript{3})\textsubscript{2}, has been introduced\textsuperscript{[34]}. However, its behavior is entirely different from that of LiNO\textsubscript{3}. When Mg(NO\textsubscript{3})\textsubscript{2} is added, the stability of the electrolyte|electrode interface is significantly improved. Furthermore, the positive effect of the NO\textsubscript{3} ion in forming a stable SEI and Mg\textsuperscript{2+} ions decreasing the number of solvent molecules surrounding the Li\textsuperscript{+} because of the strong interaction of Mg\textsuperscript{2+}-solvent are beneficial for Li\textsuperscript{+} desolvation [Figure 4E]. Some portion of Mg\textsuperscript{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\textsuperscript{2+} and NO\textsubscript{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.\textsuperscript{[35]} and Xu et al.\textsuperscript{[36]} reported SnCl\textsubscript{2} and SnF\textsubscript{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\textsubscript{2} (SnF\textsubscript{3}) and Na metal. Fang et al.\textsuperscript{[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\textsubscript{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
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.

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REFERENCES
1. Liu H, Cheng X, Chong Y, Yuan H, Huang J, Zhang Q. Advanced electrode processing of lithium Ion batteries: a review of powder technology in battery fabrication. Particuology 2021;57:56-71. DOI
2. Li M, Li W, Hu Y, et al. New insights into the high-performance black phosphorus anode for lithium-Ion batteries. Adv Mater 2021;33:e2101259. DOI PubMed
3. Ma Q, Zhao Z, Zhao Y, et al. A self-driven alloying/dealloying approach to nanostructuring micro-silicon for high-performance lithium-ion battery anodes. Energy Storage Materials 2021;34:768-77. DOI
4. Xu K. Li-ion battery electrolytes. Nat Energy 2021;6:763. DOI
5. Hu Z, Zhao L, Jiang T, et al. Trifluoropropylene carbonate-driven interface regulation enabling greatly enhanced lithium storage durability of silicon-based anodes. Adv Funct Mater 2019;29:1906548. DOI
6. Hou Z, Dong M, Xiong Y, Zhang X, Zhu Y, Qian Y. Formation of solid-electrolyte interfaces in aqueous electrolytes by altering cation - solvation shell structure. Adv Energy Mater 2020;10:1903665. DOI
7. Xing L, Zheng X, Schroeder M, et al. Deciphering the ethylene carbonate-propylene carbonate mystery in Li-Ion batteries. Acc Chem Res 2018;51:282-9. DOI PubMed
8. Aspern N, Röschenthaler GV, Winter M, Cekic-Laskovic I. Fluorine and lithium: ideal partners for high-performance rechargeable battery electrolytes. Angew Chem Int Ed Engl 2019;58:15978-6000. DOI PubMed
9. Zheng J, Yang Y, Fan X, et al. Extremely stable antimony-carbon composite anodes for potassium-Ion batteries. Energy Environ Sci 2019;12:615-23. DOI
10. Chen J, Fan X, Li Q, et al. Electrolyte design for LiF-rich solid-electrolyte interfaces to enable high-performance microsized alloy anodes for batteries. Nat Energy 2020;5:386-97. DOI
11. Shadike Z, Lee H, Borodin O, et al. Identification of LiH and nanocrystalline LiF in the solid-electrolyte interphase of lithium metal anodes. Nat Nanotechnol 2021;16:549-54. DOI PubMed
12. Zhang J, Cao Z, Zhou L, et al. Model-based design of stable electrolytes for potassium Ion batteries. ACS Energy Lett 2020;5:3124-31.
13. Ming J, Cao Z, Wahyudi W, et al. New insights on graphite anode stability in rechargeable batteries: Li Ion coordination structures prevail over solid electrolyte interphases. *ACS Energy Lett* 2018;3:335-40. DOI

14. Voropaeva DY, Novikova SA, Yaroslavtsev AB. Polymer electrolytes for metal-Ion batteries. *Russ Chem Rev* 2020;89:1132-55. DOI

15. Zheng J, G Q, Fan X, et al. High-fluorinated electrolytes for Li-S batteries. *Adv Energy Mater* 2019;9:1803774. DOI

16. Xie J, Li X, Lai H, et al. A robust solid electrolyte interphase layer augments the Ion storage capacity of bimetallic-sulfide-containing potassium-Ion batteries. *Angew Chem Int Ed Engl* 2019;58:14740-7. DOI PubMed

17. Tran N, Spindler BD, Yakovenko AA, et al. Effective electrochemical charge storage in the high-lithium compound Li$_8$ZrO$_6$. *ACS Appl Energy Mater* 2019;2:1274-87. DOI

18. Fan L, Ma R, Zhang Q, Jia X, Lu B. Graphite anode for a potassium-Ion battery with unprecedented performance. *Angew Chem Int Ed Engl* 2019;58:10500-5. DOI PubMed

19. Zhang W, Wu Z, Zhang J, et al. Unraveling the effect of salt chemistry on long-durability high-phosphorus-concentration anode for potassium-Ion batteries. *Nano Energy* 2018;53:967-74. DOI

20. Liu S, Zhang Q, Wang X, Xu M, Li W, Lucht BL. LiFSI and LiDFBOP dual-salt electrolyte reinforces the solid electrolyte interphase on a lithium metal anode. *ACS Appl Mater Interfaces* 2020;12:33719-28. DOI PubMed

21. Shi P, Zhang L, Xiang H, Liang X, Sun Y, Xu W. Lithium difluorophosphate as a dendrite-suppressing additive for lithium metal batteries. *ACS Appl Mater Interfaces* 2018;10:22201-9. DOI PubMed

22. Zhou L, Cao Z, Zhang J, et al. Engineering sodium-Ion solvation structure to stabilize sodium anodes: universal strategy for fast-charging and safer sodium-Ion batteries. *Nanotechnology* 2020;32:47-54. DOI PubMed

23. Zhang J, Cao Z, Zhou L, et al. Model-based design of graphite-compatible electrolytes in potassium-ion batteries. *ACS Energy Lett* 2020;5:2651-61. DOI

24. Zheng J, Yan P, Mei D, et al. Highly stable operation of lithium metal batteries enabled by the formation of a transient high-concentration electrolyte layer. *Adv Energy Mater* 2016;6:1502151. DOI

25. Yamada Y, Wang J, Ko S, Watanabe E, Yamada A. Advances and issues in developing salt-concentrated battery electrolytes. *Nat Energy* 2019;4:269-80. DOI

26. Zheng H, Xiang H, Jiang F, et al. Lithium difluorophosphate - based dual - salt low concentration electrolytes for lithium metal batteries, *Adv Energy Mater* 2020;10:2001440. DOI

27. Li Y, Yang Y, Lu Y, et al. Ultralow-concentration electrolyte for Na-Ion batteries. *ACS Energy Lett* 2020;5:1156-8. DOI

28. Cheng XB, Zhang B, Zhao CZ, Wei F, Zhang JG, Zhang Q. A review of solid electrolyte interphases on lithium metal anode. *Adv Sci (Weinh)* 2016;3:1500213. DOI PubMed PMC

29. Li Q, Cao Z, Wahyudi W, et al. Unraveling the new role of an ethylene carbonate solvation shell in rechargeable metal-Ion batteries. *ACS Energy Lett* 2021;6:69-78. DOI

30. Hou T, Yang G, Rajput NN, et al. The influence of FEC on the solvation structure and reduction reaction of LiPF6/EC electrolytes and its implication for solid electrolyte interphase formation. *Nano Energy* 2019;64:103881. DOI

31. Bai P, Han X, He Y, et al. Solid electrolyte interphase manipulation towards highly stable hard carbon anodes for sodium-Ion batteries. *Energy Storage Materials* 2020;25:324-33. DOI

32. Zhang X, Chen X, Hou L, et al. Regulating anions in the solvation sheath of lithium Ions for stable lithium metal batteries. *ACS Energy Lett* 2019;4:411-6. DOI

33. Zhang J, Zhou L, Ming H, et al. Lithium dendrite-free plating/stripping: a new synergistic lithium Ion solvation structure effect for reliable lithium-sulfur full batteries. *Chem Commun (Camb)* 2019;55:5713-6. DOI PubMed

34. Lee SH, Hwang J, Ming J, et al. Toward the sustainable lithium metal batteries with a new electrolyte solvation chemistry. *Adv Energy Mater* 2020;10:2000567. DOI

35. Zheng X, Fu H, Hu C, et al. Toward a stable sodium metal anode in carbonate electrolyte: a compact, inorganic alloy interface. *J Phys Chem Lett* 2019;10:707-14. DOI PubMed

36. Xu Z, Yang J, Zhang T, et al. Stable na metal anode enabled by a reinforced multistructural SEI layer. *Adv Funct Mater* 2019;29:1901924. DOI

37. Fang W, Jiang H, Zheng Y, et al. A bilayer interface formed in high concentration electrolyte with SbF3 additive for long-cycle and high-rate sodium metal battery. *J Power Sources* 2020;455:227956. DOI