Regulating Anions in the Solvation Sheath of Lithium Ions for Stable Lithium Metal Batteries

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Supporting Information

ABSTRACT: Safe lithium (Li) metal batteries have been plagued by dendrite growth due to a heterogeneous solid electrolyte interphases (SEI) on the Li metal anode. Modulating the solvation sheath of Li ions enhances the uniformity and stability of SEI significantly. However, anion regulation in the solvation sheath for constructing stable SEI is rarely touched. Herein, the solvation structure of original bis(flurotosulfonyl)imide (FSI−) anions in the solvation sheath is altered by introduction of other anions, promoting the complete decomposition of FSI− and forming a stable SEI on the Li metal anode. Moreover, both the oxidation stability window of the electrolyte and current collector protection were enhanced. Furthermore, the components and structure of the solvation sheath were disclosed by combining 17O nuclear magnetic resonance and molecular dynamics simulations. This work provides fresh insight into the interrelation among various anions on regulating the solvation sheath of Li ions and demonstrates guidance in rationally designing electrolytes for stable and safe Li metal batteries.

Lithium (Li) metal is the most attractive anode candidate for high-energy-density batteries for its high theoretical specific capacity (3860 mAh g−1) and low reduction potential (−3.04 V vs standard hydrogen electrode).1 Li metal batteries are being revived due to the increasing demand from portable electronics and electric vehicles. However, practical Li metal batteries are hindered by safety risks owing to dendrite growth.2−4 In principle, dendrite growth is induced by nonuniform Li plating through heterogeneous solid electrolyte interphases (SEI).5−7 Therefore, understanding the SEI formation process and constructing stable and uniform SEI are vital for promoting practical Li metal batteries.

The ingredients of SEI are derived from the reduction products between the electrolyte and highly reactive Li metal.8−10 Concretely, Li ions are solvated by solvents and anions, forming a solvation sheath in the electrolyte.11 Hence, the preferential decomposition products from solvents and anions in the solvation sheath compose the main components of SEL.12 Regulating the components and structure of the solvation sheath of Li ions provides an effective route to construct uniform and stable SEI.

Many strategies have been devoted to regulating the solvation sheath of Li ions from solvation components and structure. In terms of components, the types of solvents,13−17 anions,18,19 and even additives20,21 in the solvation sheath have significant effects on the uniformity of SEI. For instance, fluorinated carbonates or ethers can improve the uniformity of SEI by increasing the content of F-rich species.22,23 There is preferential conscription of solvents in the structure of the solvation sheath of Li ions. Cyclic carbonate solvents are solvated more easily in comparison to linear carbonate solvents, forming the inner solvation sheath.24 The solvation structure also changes evidently with the increased concentration of Li salts.25−27 On one hand, the anodic or cathodic stability window of the electrolyte can be enlarged with decreasing free solvents, such as the concept of aqueous Li ion batteries with ultrahigh concentrated electrolyte.28,29 On the other hand, partial anions can be recruited into the solvation sheath as the free solvents decrease, resulting in the...
decomposed anions as ingredients of SEI. Although the anions are indispensable, the anions in the solvation sheath and regulating anions for constructing stable SEI are rarely involved. If the interactions among different types of anions in the solvation sheath can be well understood, new adventures will be opened for regulating the solvation sheath of Li ions for stable and safe Li metal batteries.

In previous reports, LiNO₃ is proved to be effective in improving the performance of Li metal batteries. However, the effects of LiNO₃ are mainly obtained by investigating the physiochemical properties of SEI and the corresponding metallic Li plating behavior. Therefore, the solvation state of NO₃⁻ and the interactions between NO₃⁻ and other solvents or anions in the solvation sheath are significantly required.

In this contribution, 2.0 M lithium bis(fluorosulfonyl)imide (LiFSI) and 0.20 M lithium nitrate (LiNO₃) in dimethoxyethane (DME) were selected as a model system to probe the interactions among various anions. This system was denoted as LiFSI/LiNO₃ electrolyte. The effect of the LiNO₃ concentration was also investigated. In addition to LiNO₃, both lithium perchlorate (LiClO₄) and LiFSI were selected rationally to further prove the concept of anion regulation. In this work, it is demonstrated that the introduction of NO₃⁻ alters the solvation structure of FSI⁻ in the solvation sheath, thus promoting the decomposition of FSI⁻ and generating uniform SEI with an abundance of LiSOₓ, LiF, and LiNₓOᵧ.

Moreover, the key role of NO₃⁻ is also disclosed from the aspect of the fundamental solvation component and structure. Furthermore, the electrochemical stability window of the electrolyte is widened, and the aluminum (Al) current collector is well protected.

The adequate reduction behavior on an anode and oxidation stability toward a cathode are prerequisites for an electrolyte applied in practical batteries. Both the reduction and oxidation potentials are direct descriptors for screening electrolyte. When there is only FSI⁻ or NO₃⁻ in DME, the initial reduction potentials of FSI⁻ and NO₃⁻ are at 1.3 and 1.7 V, respectively (Figure 1a). When NO₃⁻ is mixed with FSI⁻ in DME, the reduction potential of NO₃⁻ remains constant. However, the reduction potential of FSI⁻ is overlapped. The invariability of the reduction potential of NO₃⁻ contributes to rendering its beneficial role for stable SEI.
The oxidation decomposition of LiFSI electrolyte begins at 3.3 V (Figure 1b). Even though the concentration of LiFSI increases to 4.0 M, the oxidation window is only within 3.7 V (Figure S1a). When 0.20 M NO$_3^-$ was added into LiFSI electrolyte, the oxidation tolerance of electrolyte was enlarged to 4.3 V. The enlarged oxidation window was also confirmed by a linear sweep voltammetry test using platinum foil as the working electrode (Figure S1b). The oxidation window of the electrolyte depends on the concentration of LiNO$_3$. With the increase of LiNO$_3$ concentration, the oxidation window widens from 4.1 to 4.3 V and then remains at 4.3 V (Figure S1c). Therefore, the oxidation stability window of the electrolyte is widened by introducing NO$_3^-$, rendering the feasibility of employing low concentration LiFSI electrolyte in rechargeable batteries without significantly decreasing the ionic conductivity (Table S1).

The LiFSI/LiNO$_3$ electrolyte was further evaluated in Li|LiFePO$_4$ batteries. The lifespan of a cell with LiFSI electrolyte is only 36 cycles (Figure 2a). However, 500 cycles with 80% capacity retention and stable Coulombic efficiency (CE) were achieved in a cell with LiFSI/LiNO$_3$ electrolyte. The LiNO$_3$ concentration had almost no effect on the cycling performance and CE of LiFePO$_4$ batteries at initial stages (Figure S2a). When $50 \mu$m Li metal was employed to check the performance of various electrolytes, the stability of the LiFSI/LiNO$_3$ electrolyte was also proved (Figure S2b). The stable cycling performance with a higher areal capacity of 2.0 mAh cm$^{-2}$ was still maintained in LiFSI/LiNO$_3$ electrolyte (Figure S3a–c). Excellent rate performance of batteries was also achieved in the LiFSI/LiNO$_3$ electrolyte (Figure S3d). Moreover, the introduction of NO$_3^-$ avoided oxidation decomposition of the electrolyte and corrosion of Al foils (Figure S4), which was a notorious issue when LiFSI is employed as the salt in an electrolyte. The overcharge capacity in LiFSI electrolyte after 40 cycles (Figure 2b) is mainly induced by the decomposition of electrolyte and corrosion of Al foils. According to previous reports, the lifespans of LiFePO$_4$ batteries using carbonate electrolyte at the same test conditions are only 172 cycles. Therefore, the Li anode is well protected in LiFSI/LiNO$_3$ electrolyte during long cycling tests.

The deposition morphology of cycled Li in LiFSI/LiNO$_3$ electrolyte is denser and more uniform than that in LiFSI electrolyte (Figures 2c,d and S5). Therefore, the polarization voltage of the LiFePO$_4$ cells with NO$_3^-$ is more stable (Figure S6). Interestingly, the morphology of cycled Li obtained in LiFePO$_4$ batteries at the same areal capacity is much different from that in LiFePO$_4$ cells (Figure S7) despite denser Li in LiFSI/LiNO$_3$ than that in LiFSI electrolyte. The Li plating/stripping in full batteries is more aggressive, in which transition metal ions can dissolve and migrate to the anode, impacting the formation of SEI and the following Li deposition.

The Li deposition behavior is mainly dictated by the uniformity of the SEI on the Li anode. Therefore, in-depth X-ray photoelectron spectroscopy (XPS) was conducted and demonstrated the completed decomposition of FSI$^-$ while introducing NO$_3^-$ (Figure 3). In S 2p spectra, two peaks of S$^-$ (162.1/163.3 eV, for 2p$^{3/2}$/2p$^{1/2}$, hereinafter) and $\cdot$SO$_2$$^-$/2p$^{3/2}/2p^{1/2}$ are derived from the original FSI$^-$. The appearance of species in a lower oxidation state suggests complete decomposition of FSI$^-$. While introducing NO$_3^-$, three new peaks assigned to Li$_2$S (159.8/161.0 eV), SO$_3$$^-$/2p$^{3/2}/2p^{1/2}$ (166.9/168.1 eV), and SO$_4$$^-$/2p$^{3/2}/2p^{1/2}$ (168.7/169.9 eV) emerge. The appearance of species in a lower oxidation state suggests complete decomposition of FSI$^-$.
Figure 4. (a) Natural abundance $^{17}$O NMR spectra of various electrolytes measured at 50°C. (b) Top panel: snapshots of the MD simulation boxes of LiFSI/LiNO$_3$ and LiFSI electrolyte. Colors for different atoms: H-white, Li-purple, C-gray, O-red, N-blue, F-green, and S-yellow. The unsolvated solvents are in light gray. Bottom panel: schematics of the solvation structure of Li ions in corresponding electrolyte. The magnified snapshots of (b) are shown in Figure S11. MD simulations of (c) Li–O, (d) Li–N, and (e) Li–F radial distribution functions, g(r).

N 1s spectra also confirms the incomplete decomposition. Both LiN$_2$O$_4$ (397.4 eV) and NO$_3^-$ (404.0 eV) are from the decomposition of LiNO$_3$ (Figure 3b). Moreover, the disappearance of S–F (686.4 eV, Figure 3c) in LiFSI/LiNO$_3$ electrolyte confirms the complete decomposition of FSI$^-$ in the presence of NO$_3^-$, which leads to more content of LiF (684.8 eV, Figure 3d) in LiFSI/LiNO$_3$ electrolyte (168.2 ppm, Figures 4a and S12). More FSI$^-$ is involved in solvation instead of more FSI$^-$ anions. The new peaks of O$_{FSI}$ (167.3 ppm) in 2.2 M LiFSI electrolyte shifts upfield by 0.9 ppm compared with that of 2.0 M LiFSI electrolyte (168.2 ppm, Figures 4a and S12). More FSI$^-$ anions participate in the solvation sheath in 2.2 M LiFSI due to decreased free solvents, leading to a decreased chemical shift. However, when 0.2 M NO$_3^-$ is added into 2.0 M LiFSI electrolyte, the peak of O$_{FSI}$ (168.0 ppm) only shifts upfield by 0.2 ppm. Under the same FSI$^-$/DME ratio in LiFSI/LiNO$_3$ electrolyte, a higher Li/FSI$^-$ ratio induces a smaller shift of the O$_{FSI}$ peak compared with LiFSI electrolyte, indicating that NO$_3^-$ is involved in solution instead of more FSI$^-$ anions.

According to the radial distribution functions generated from a 2.0 ns MD simulations in the canonical ensemble (NVT) at 298 K, the solvation structure of FSI$^-$ anions highly depends on the presence of NO$_3^-$ (Figure 4b–e). The new peaks of Li–O (1.7 Å, Figure 4c) and Li–N (2.9 Å, Figure 4d) prove the participation of NO$_3^-$ in the solvation sheath in LiFSI/LiNO$_3$ electrolyte. The increase of Li–N at around 2.0 Å and the decrease of Li–O at around 2.0 Å indicate that more FSI$^-$ interacts with Li ions through the Li–N bond rather than the Li–O bond in LiFSI/LiNO$_3$ electrolyte. Especially, the emerging Li–F peak at around 2.0 Å exhibits that the F atom
in FSI− can interact with Li ions directly. Therefore, the introduction of NO3− regulates the interactions between Li ions and FSI− and results in polarization of FSI−. Polarized FSI− is activated and thus decomposes completely (Figure S13), which combines with NO3− to generate favorable SEI with an abundance of Li2SOx, LiF, and Li2NO3.

On the basis of the above insights and understandings, LiFSI/LiClO4 electrolyte was designed. When 0.20 M LiClO4 was added into LiFSI electrolyte, the oxidation stable window of the electrolyte was widened to 4.4 V (Figure S14a). When it was applied to working batteries, LiFSI/LiClO4 electrolyte exhibited a stable and long cycling life compared to LiFSI electrolyte (Figure S14b,c). When 0.20 M ClO4− was added into 2.0 M LiFSI electrolyte, the peaks of ODMES shifted upfield by 1.4 ppm (Figure S15a), which is larger than that induced by the addition of 0.20 M LiNO3 (1.1 ppm). Accordingly, the oxidation window of LiFSI/LiClO4 is larger than that of LiFSI/LiNO3 (Figure S15b). Therefore, the addition of ClO4− further enhances the ion−dipole interaction between Li ions and DME solvents compared with the addition of NO3−. The peak of OFSI (167.0 ppm) in LiFSI/LiClO4 electrolyte shifts upfield by 1.2 ppm compared with 2.0 M LiFSI electrolyte (Figure S15a). The decreased chemical shift of OFSI is induced by participation of ClO4− in the solvation sheath, which is similar to the results of NO3−. However, the decreased chemical shift of OFSI in LiFSI/LiClO4 and LiFSI/LiNO3 is 1.2 and 0.2 ppm, respectively, illustrating that the effect of different anions on the polarization of FSI− is distinctive. The successful design of LiFSI/LiClO4 electrolyte confirms the generality of the interactions among anions and the effectiveness of regulating anions in the solvation sheath for electrolyte innovation.

In conclusion, stable Li metal full batteries and stable CEVs were achieved by a new and general strategy, regulating the anions in the solvation sheath. The effect of anion regulation on the components and structure of the solvation sheath was jointly disclosed by 17O NMR spectra and MD simulations. The solvation structure of FSI− is mediated and polarized by other anions, such as NO3−, which induces complete decomposition of FSI−. Therefore, a uniform and less resistive SEI is achieved with an abundance of Li2SOx, LiF, and Li2NO3. Moreover, the oxidation stability window is widened to 4.3 V, and corrosion of the Al current collector is avoided. The generality of the above understanding and strategy is also veriﬁed by the design of LiFSI/LiClO4 electrolyte. This work affords profound insight into understanding the interactions among various anions on regulating the solvation sheath of Li ions in electrolytes for rechargeable batteries, which can be extended into other battery chemistry, such as sodium batteries. This work also inspires new adventures in designing electrolytes by simple anion regulation in the solvation sheath for high-energy-density and safe Li batteries and other types of batteries.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b02376.

Experimental procedures, MD simulation details, linear sweep voltammetry curves, battery cycling performance, electrochemical performance, magnified morphologies of Li, voltage−time curves of LiLi cells, XPS spectra of the SEI, atomic concentrations, Tafel plots, natural abundance spectra, chemical structure of FSI−, conductivity data, and water content data (PDF).

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**Notes**

The authors declare no competing financial interest.

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