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A new synergistic lithium ion solvation structure effect tailored by the mixed organic/inorganic lithium salts is introduced to mitigate the growth of lithium-dendrite. A uniform lithium plating, lower polarization and higher coulombic efficiency are confirmed by lithium plating/stripping. The effect of different solvation structure was analyzed by Raman spectrum and simulations. Then, a reliable lithium sulfur full battery with high performances over hundreds of cycles was configured.

Rechargeable lithium ion batteries (LIBs) has dominated the energy market from handheld electronic devices to electric vehicles (EV) since their commercialization in 1991, but the energy density less than 300 Wh kg\(^{-1}\) is incapable of satisfying the energy request, particularly in the field of EV. Thus, the next generation lithium batteries, including the lithium metal battery (e.g., Li-LiCoO\(_2\)), lithium-sulfur (Li-S), lithium-oxygen (Li-O\(_2\)) batteries, have attracted great attention. This is because the used lithium metal (Li) anode has an extremely high theoretical capacity (3860 mAh g\(^{-1}\)), lowest redox potential (-3.040 V vs. SHE) and mass density (0.534 g cm\(^{-3}\)), which can give rise to the higher energy densities. However, the commercialization of lithium batteries is restricted seriously by the problems of lithium-dendrite growth, low columbic efficiency (CE) and limited lifespan. Thus, the development of strategies to suppress Li-dendrite growth and improve the CE is urgently needed. Herein, we present a new synergistic lithium ion solvation structure effect tailored by the mixed organic/inorganic lithium salts to mitigate the lithium-dendrite growth, in which a uniform lithium plating, lower polarization and higher coulombic efficiency are demonstrated in Li plating/stripping process.

In the past two decades, much effort has been devoted to restrain the Li-dendrites growth. A series of nanostructures (e.g., nanoparticles, nanorods, and nanotubes, three-dimensional hierarchical ones) and/or functional materials (e.g., carbon coating, Au nanoparticles) were designed on current collectors for a uniform Li nucleation and plating. In addition, a physical protection layer, solid electrolyte interphase (SEI) and solid-state electrolytes were also used to suppress the Li dendrites due to the resultant uniform distribution of Li\(^+\) flux. Alternatively, the electrolyte modification with additives (e.g., LiNO\(_3\), LiF, LiNO\(_3\)) can also suppress the Li-dendrites growth because of the formed robust solid electrolyte interphase films. Herein, we report that the Li-dendrite can be mitigated successfully by tuning the Li\(^+\) solvation structure using a mixed organic/inorganic lithium salt (i.e., LiTFSI/LiNO\(_3\)), in which the necessary constituents of Li\(^+\) solvation structure was analyzed by Raman spectrum and simulations. As a result, the polarization and CE can be improved significantly. In addition, a reliable lithium sulfur full battery is configured based on our discovery, in which the amount of lithium anode is strictly controlled while a higher capacity retention, CE and long lifespan is demonstrated.

Synergistic effect for Li plating. The ether-based electrolytes of 1.0M and 2.5M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/1,2-Dimethoxyethane (DME) (v/v, 1:1) was studied, in which 0.4M LiNO\(_3\) was added and then abbreviated as 1.0M/0.4M and 2.5M/0.4M, respectively. We find that an obvious different lithium plating phenomena exist in this two type of electrolyte. The Li-dendrite is easy to be observed on the plated lithium when the 1.0M/0.4M electrolyte was used (Fig. 1a-d, Fig. S1), while a smooth lithium was always obtained when the lithium plating was carried out in the 2.5M/0.4M electrolyte (Fig. 1e-h). The comparative results confirm that a high concentration of LiTFSI is conducive for the uniform lithium plating and then mitigate the Li-dendrite
Li⁺ distribution and then Li deposition morphology on substrate. This result reconfirms the necessity of LiTFSI/LiNO₃ synergistic effect, which could change the lithium solvation structure and then responsible for the uniform lithium plating. Then, we can re-consider the reported case of high LiTFSI concatenation in DME, in which the LiTFSI concentration may be reduced based on our discovery. iii) the lithium solvation structure changed by the LiTFSI/LiNO₃ synergistic effect maybe the main reason for the uniform lithium plating, because the lithium-dendrite can be always observed on the plated lithium, on which the SEI effect should be very limited. This viewpoint would be discussed later.

Synergistic effect on electrolyte properties. These two type of electrolytes have the similar stability in voltage-window (Fig. 2a), as confirmed by the linear sweep voltammetry (LSV). This result demonstrates that the solid electrolyte interphase formation (SEI) effect for the lithium plating could be limited because there is no obvious electrolyte decomposition. Then, we find that the 2.5M/0.4M electrolyte has the lower polarization (60mV) than that in the 1.0M/0.4M electrolyte (75mV) in the lithium plating/striping process using the Li|Li symmetry cell (Fig. 2b-c). In addition, this trend is more obvious upon cycling. This should be ascribed to the synergistic effect of LiTFSI/LiNO₃ at a relatively high concentration, where the unit and constituent of Li⁺ solvation structure is different from that in the lower concentration. This viewpoint is confirmed by the calculated lithium transfer number (i.e., Bruce-Vincent equation t⁺Li+=I⁺Ni(<ΔV=10 mV) was applied, I₀ is the steady-state current, R₀ and Rₛ are resistances before and after DC polarization).²⁵ (Fig. 2d-e). We find that the value of t⁺Li⁺ in the 2.5M/0.4M is 0.59, which is higher than 0.54 in the 1.0M/0.4M. This is because of the increased unit of Li⁺ solvation structure due to the increased LiTFSI concentration in the electrolyte. The advantage of 2.5M/0.4M electrolyte over that of 1.0M/0.4M is further confirmed by the improved coulombic efficiency using the Li|Cu cell. The average coulombic efficiency of 2M/0.4M electrolytes in initial 100 cycles is as high as 99%, which is higher than 98% in 1.0M/0.4M electrolyte (Fig. 2f). The result of lower

Fig. 1 Characterizations of plated Li and schematic lithium ion solvation structure and plating process. SEM of plated lithium in the (a–d) 1.0M/0.4M and (e–h) 2.5M/0.4M electrolyte for (a, e) 4 h, (b, f) 8 h, (c, g) 16 h and (d, h) 32 h, respectively. The scale label is 50 μm. Insets are the cross-sectional views, in which the scale label is 20 μm. Schematic illustration of lithium solvation structure and plating process in the (i–j) 1.0M/0.4M and (k, l) 2.5M/0.4M electrolyte.

growth. Note that the Li-dendrite become more obvious in the 1.0M/0.4M electrolyte when the plating time increases from 4 h to 32 h. Note that the plated lithium become thicker and thicker as increasing the plating time, then the lithium plating occurs between the electrolyte and lithium interfaces. Thus, we consider that the lithium plating maybe associated with the properties of electrolyte, while the Li⁺ solvation structure could be the main reason responsible for the different lithium plating behaviours. This is because the Li⁺ solvation structure is the basic unit of electrolyte, such as the Li⁺[DME]₄(DOL)₃.[LiTFSI]J₀.71(NO₃)J₀.28 and Li⁺[DME]₃.₆6(DOL)₂.₄7[TFSI]J₂.₈₆[NO₃]J₁.₁₄ for the 1.0M/0.4M and 2.5M/0.4M, respectively. Based on above analysis, we present the basic unit of Li⁺ solvation structure and propose the probable plating mechanism in different type of electrolyte (Fig. 1i–l), showing the different Li⁺ solvation structure effect for the lithium plating.

Herein, serval phenomena and conclusion we can summarize: i) a relatively high LiTFSI concentration such as 2.5M is necessary, otherwise, a lithium dendrite can be observed even 0.4M LiNO₃ is introduced such as in 1.0M electrolyte. This result demonstrates the importance of synergistic effect of LiTFSI/LiNO₃, where the LiNO₃ effect need to be guaranteed by the relatively high LiTFSI concentration. This is a new viewpoint different from previous report.²³ i) the LiNO₃ in electrolyte is quite necessary, because the LiNO₃ can reduce the amount of LiTFSI significantly in electrolyte for a uniform lithium plating. We confirm that the lithium-dendrite is still observed even the LiTFSI concentration was increased from 1.0M, 2.5M to 5.0M if there is no LiNO₃ in electrolyte (Fig. S2). Note that the morphology of lithium was always plated in the form of smooth particles if the LiNO₃ was introduced into the electrolyte, otherwise the morphology of lithium was plated in the form of bulk particles without adding LiNO₃ (Fig. S3). The interaction between the Li⁺ and solvent and anions can affect the deposition morphology. Herein, the different number and frequency of anions (i.e., TFSI-/NO₃⁻) appeared in the first solvation shell are crucial to affect the Li⁺ de-solvation process,
polarization is consistent with that in the symmetric Li||Li cell. The decreased overpotential upon cycling should be ascribed to the plated/stripped lithium involved in the reaction, which become easier to be reacted again compared to that of pristine metallic lithium. Thus, we conclude that the increased unit and different constituents of Li+ solvation structure is the main reason responsible for the different lithium plating behaviours.

Synergistic effect for lithium ion solvation structure and simulations. The viewpoint of different constituent for the lithium ion solvation structure is confirmed by the Raman spectrum through the S-N-S bending modes of TFSI- in electrolyte (Fig. 3a-b).26 We find that most TFSI- exists in 1.0M/0.4M and 2.5M/0.4M electrolyte. (c-f) Structure of FI, LIP, IIP and AIP. Molecular dynamics simulations of lithium solvation structure and lithium plating in (g-h) 1.0M/0.4M and (i-j) 2.5M/0.4M electrolyte.

Applications in Li-S full batteries. The new concept of synergistic lithium solvation structure effect is further extended and applied in the Li-S fully battery, in which the plated lithium in different electrolytes was used directly. One great feature of our presented Li-S battery is the improved safety and good reliability, because the plated lithium is strictly controlled three times higher than the total capacity of sulphur cathode. We find that the Li-S full battery using the 2.5M/0.4M has a high capacity of 707 mAh g−1 and great capacity retention of 78.2% over 300 cycles at 0.25C. In contrast, the capacity retention of Li-S full battery in the 1.0M/0.4M electrolyte is only 45.7% after 300 cycles, even it has a high capacity in initial cycles (Fig. 4a-c). While the overpotential is slightly higher than usual and this should be ascribed to the intercalated carbon paper in the cell configuration.27 Benefiting from the uniqueness of synergistic Li+ solvation structure for lithium plating/stripping in 2.5M/0.4M electrolyte, the Li-S full battery demonstrates the higher capacity retention and Coulombic efficiency over 99.8%. These parameters are essential to guarantee the long lifespan for practical applications. In addition, the high coulombic efficiency over 99.8% is further confirmed in the rate test, where a high capacity of 882, 710, 523, 428, 369, and 313 mAh g−1 at the rate of 0.1, 0.25, 0.5, 1, 2.5, 3C was delivered (Fig. 4d).

In summary, a new synergistic lithium ion solvation structure effect tailored by the LiTFSI/LiNO3 is presented to mitigate the lithium-dendrite growth. We find that a more uniform lithium plating, lower polarization and higher coulombic efficiency are achieved in lithium plating/stripping process using the mixed LiTFSI/LiNO3 in which a relatively high concentration of LiTFSI is confirmed to be the necessity for the positive effect of LiNO3. The different solvation structure is proved to be the reason responsible for the different lithium plating behaviors by the Raman spectrum and simulations. In addition, a reliable lithium sulfur full battery with a high capacity retention (78.2%) and Coulombic efficiency (99.8%) over 300 cycles is introduced. We hope the presented
synergistic Li⁺ solvation structure effect could be widely considered in other rechargeable battery systems.

Conflicts of interest
There are no conflicts to declare.

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Notes and references


Lithium Dendrite-free Plating/Stripping: A New Synergistic Lithium Ion Solvation Structure Effect for Reliable Lithium Sulfur Full Battery

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A new synergistic Li$^+$ solvation structure effect is introduced to mitigate the lithium-dendrite and applied for safer Li-S full batteries.