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High Li⁺ coordinated solvation sheaths enable high-quality Li metal anode

Shizhi Huang 🖻 Yu-Peng Huang Yijie Xia 🖻 Jingyi Ding	
Chengyuan Peng Lulu Wang Junrong Luo Xin-Xiang Zhang	I
Junrong Zheng Yi Qin Gao Jitao Chen	

Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing, the People's Republic of China

Correspondence

Yi Qin Gao and Jitao Chen, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, the People's Republic of China. Email: gaoyq@pku.edu.cn and chenjitao@pku.edu.cn

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Abstract

An advance Li-sphere possessing a definitely regular morphology in Li deposition enables a well-defined more robust structure and superior solid-electrolyte interphase (SEI) to achieve high-efficiency long-term cycles in Li metal anode. Here, a new sight of high Li⁺ cluster-like solvation sheaths coordinated in a localized high-concentration NO₃⁻ (LH-LiNO₃) electrolyte fully clarifies for depositing advanced Li spheres. Moreover, we elucidate a critical amorphouscrystalline phase transition in the nanostructure evolution of Li-sphere deposits during the nucleation and growth. Li-sphere anode exhibits ultrastable structural engineering for suppressing Li dendrite growths and rendering ultralong life of 4000 cycles in symmetrical cells at 2 mA cm⁻². The as-constructed Li spheres/3DCM|LiFePO₄ (LFP) full cell delivers a high capacity retention of 90.5% at 1 C after 1000 cycles, and a robust dendrite-free structure also stably exists in Li-sphere anode. Combined with high-loading LFP cathodes (6.6 and 10.9 mg cm⁻²), superb capacity retentions are up to 96.5% and 92.5% after 800 cycles at 1 C, respectively. Cluster-like solvation sheaths with high Li⁺ coordination exert significant influence on depositing a highquality Li-sphere anode.

K E Y W O R D S

advanced Li-sphere deposition, high-quality cycling stability, high Li⁺ coordinated solvation sheaths, localized high concentration NO₃⁻, ultra-stable structural engineering

1 | INTRODUCTION

Lithium (Li) metal, a next-generation high-energy-density anode material, will be of remarkable advances in developing the high-energy battery storage systems. It possesses

Shizhi Huang and Yu-Peng Huang contributed equally to this work.

an ultra-high theoretical specific capacity of 3860 mAh g⁻¹ and an ultra-low electrochemical potential of -3.04 V (vs. the standard hydrogen electrode).^{1–3} Indeed, the use of Li metal raises vital concerns on Li-dendrite growing hazards, vulnerable solid-electrolyte interphase (SEI), and uncontrollable volume expansion during Li plating/ stripping.^{2–4} Li dendrites can penetrate into the cell-separators

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and cause short circuits, posing fire and explosion hazards. SEI cracking/reformation inevitably occurs due to its fragile structure formed in conventional electrolytes and unlimited volume variation during the plating/ stripping of Li, which results in a continuous consumption of electrolyte and a low Coulomb efficiency (CE).² In addition, Li dendrites can be stripped into isolated Li that is inactive due to the loss of electrical contact, and leading to poor reversibility and bulk of capacity losses.^{5,6} These challenges severely restrict its commercialized application, and more favorable improvements are required to boost long-term cycling stability and high safety of Li-metal electrode. Recently, amounts of proven efforts, including three-dimensional (3D) host schemes,⁷⁻¹⁰ organic electrolyte optimizations,¹¹⁻¹⁴ solid/ quasi-solid electrolyte designs,^{15–17} SEI stabilized engineering,¹⁸⁻²⁴ lithiophilic seed constructions,²⁵⁻²⁷ and separator modifications,²⁸⁻³⁰ have been extensively demonstrated to inhibit the Li dendrite growths, establish a robust SEI and alleviate the Li volume expansion.

A definitely regular morphology (i.e., spherical, granular and columnar, etc.) with a well-defined stable structure and superior interface favors high efficiency and cycling stability of Li-metal anode.³¹⁻³³ Strategies aimed at tailoring the available deposition morphologies of Li metal have aroused wide ranging attention, such as adjusting deposited currents,³⁴ depositing on 3D hosts,¹⁰ modifying the interfacial kinetics,³⁵ applying stack pressure on Li deposition,³² and elevating deposited temperature.^{36,37} And among them, it has proved that an advanced Li-sphere deposition is one of the most effective structural engineering for suppressing the Li dendrite growths and obtaining stable interfaces.³⁴ There are at least four conclusive advantages in optimizing the deposition electrochemistry of Li-sphere anode. First, Li-sphere exhibits a ball-shaped morphology with continuous curved surfaces, which is smooth and without any designated dendritic-tip. Li dendrite formations will be suppressed and the safety hazards in Li-metal batteries can be greatly reduced. Second, in spherical structure, the specific surface area of per unit volume is minimum, which means fewer Li/electrolyte reactions for forming SEI on the fresh surface of Li spheres. Electrolyte consumption significantly decreases, higher CE and long-term plating/stripping will be attained. Third, among different structural composition, the most balanced symmetry is shown in Li-sphere and it could ideally accommodate to the volume changes. Fourth, the spherical Li deposits on the substrate can arrange in a regular pattern, which indicates a good spatial structure for fast transports of electrons and Li ions. Li-sphere construction provides a new prospect to improve the Li anode in structural viability, cyclic reversibility and

electrochemical performance. Manke et al. have reported that the deposited currents were the underlying factors for ball-shaped Li deposition.³⁴ Accelerating the diffusion of Li⁺ through the SEI/Li interface and constructing 3D deposition skeleton to homogenize local charges can also achieve spherical Li deposition.^{35,38} Most commonly, when LiNO₃ was introduced into the electrolytes, spherical morphology of Li deposition was available.³⁵ It is because that LiNO₃ and its derived SEI have made a significant modification to promote the Li⁺ transports through the SEI/electrolyte interface, and the higher Li⁺ concentration beneath SEI is achieved. However, LiNO₃ is only slightly soluble in conventional electrolyte solvents, the spherical Li structures can only be maintained at low currents. These valuable studies on Li-sphere growths have been developed, but only a few additional host-material designs and property-influencing factors on the Li-sphere deposition have been explored. The fundamental electrodeposition chemistry of Li⁺, especially the correlative Li⁺ coordination solvated sheath in NO_3^- – added electrolyte to regulate the nucleation and growth of Li-sphere is still an enigma, but plays a decisive role in the electrodeposits of Li spheres. During the electroplating, there is a Li⁺ concentration gradient in the conventional electrolyte, in which the Li⁺ on the plating electrode surface will be quickly depleted, thereby breaking the electrical neutrality and resulting in a local space charge and further inducing the Li-dendrite deposition.²⁻⁵ Generally, the Li⁺ exists in solvated form in electrolyte, and the higher coordination number of Li⁺ at the solvated sheaths can increase the Li⁺ concentration on the surface of plated electrode and tailor the growth morphology of Li deposition.

Here, novel high Li⁺ solvation sheaths have been designed in a localized high-concentration NO₃⁻ electrolyte (LH-LiNO₃), in which the strong $Li^+ - NO_3^-$ coordination can form larger cluster-like solvation sheaths with high Li⁺ coordination number to increase the Li⁺ concentrations at the plating electrode surface. These unique NO_3^- – led high Li⁺ solvation sheaths are conducive to forming spherical structure during Li deposition, and it can inhibit the Li dendrites from the growing source. In LH-LiNO₃ electrolyte, the large cluster-like solvation sheaths also enable the SEI structure to be comprised of inorganic-rich components with fast Li⁺ kinetics, which can facilitate the Li⁺ diffusion through the SEI, and thus, high concentration of Li⁺ beneath the SEI is maintained and enough mass transports for Li-sphere growing is ensured. Well-proportioned Li nanospheres with a main size of \sim 21.8 nm are plated at a high current density of 2 mA cm^{-2} for 15 min, spherical structures of Li deposition are also remained even the deposited current densities are increased to 5 and 10 mA cm^{-2} . In MD simulated

consequences, this localized high-concentration $NO_2^$ makes an effect on forming the larger cluster-like coordination sheaths with Li⁺ coordination number up to 8 and 13. It fully clarifies the spherical growing mechanism by depositing Li under the cluster-like sheath structures with high Li⁺ coordination. An excellent plating/ stripping cycle of this advanced Li-sphere anode in symmetrical cell is up to 4000 times at 2 mA cm⁻², a 1000-time cycling stability at a higher current density (5 mA cm^{-2}) with high-loaded Li spheres (5 mAh cm^{-2}) is also achieved. Stable dendrite-free structures also maintain in Li spheres/3DCM|LiFePO4 (LFP) full cells with an advantageous capacity up to 147 mAh g^{-1} at 1 C in LH-LiNO₃ electrolyte; the prominent capacity retentions in high-loaded LFP cathodes of 6.6 and 10.9 mg cm⁻² retain 96.4% and 92.5% after 800 cycles at 1 C.

2 | RESULTS AND DISCUSSION

2.1 | Coordination solvation chemistry for the electrolytes

Fundamental nature mechanism of Li⁺ in the coordination solvation chemistry of the electrolyte is worthy of an indepth clarification on Li deposition. A three-dimensional carbonaceous host material (3DCM) with a 3D graphene structure and a high specific surface area (1238 $m^2 g^{-1}$) is determined as the Li plating matrixes, which can provide lithiophilic supporting hosts and reduce the local current density (Figure S1-S3).^{25,39-43} Owing to a certainly rapid reduction of Li⁺, Li is deposited at an appropriately high current density of 2 mA cm^{-2} , which certifies the kinetics and structure growths on Li deposits more convincing, and is more desirable for the practical application of Li metal anode. In Figure S4A, Li is deposited in LiNO3-free electrolyte (1 mole per liter (M) lithium bis (trifluoromethanesulfonyl) imide, namely LiTFSI, dissolved in 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) in a volume ratio of 1:1) at 2 mA cm^{-2} with a large nucleation overpotential of 220.1 mV. The plateau between the drop bottom and flat initial-segment in the deposition curve of voltage/time is recognized as the heterogeneous nucleation process involving charge transfers, mass transports, and energy conversions of thermodynamics during the nucleation and growth of Li deposition. Li nucleation at the initial stage in LiNO3-free electrolyte is sparsely distributed in a small size of 2-3.5 nm, and an amorphous structure without characteristic body-centered cubic (bcc) bright diffraction spots/rings in fast Fourier transformed (FFT) (Figure S4B-B2) is revealed. Subsequently, after a 15 min deposition, whisker-like structures grow and Li dendrites will form quickly (Figure S4C-F). Figure 1A

depicts a MD simulation in LiNO₃-free electrolyte, the maximal solvation sheath with a Li⁺ coordination number of 3 is revealed after a 30 ns equilibrating dynamic simulation (Figure S5). Li⁺-DME is confirmed as the dominant coordination pattern by a Li-O (DME) coordinated interaction in the solvation sheath. Low Li⁺ coordinated solvation sheaths in LiNO₃-free electrolyte show a low Li⁺ concentration on the electrode surface that can be rapidly depleted and lead to a local space charge, particularly in a high-current deposition, and easily resulting in the Li dendrite formation.^{9,44,45}

After adding 1 wt% LiNO₃ into LiNO₃-free electrolyte (LiNO₃-1), shown in the MD simulated results in Figure S6, NO_3^- is more inclined to participate into the solvation sheaths and coordinates with Li⁺. More specifically, these intensifying results clearly indicate in Figure 1B and Figure S7, when 5 wt% LiNO₃ was added to saturation (S-LiNO₃). Moreover, it presents a clusterlike coordination solvation sheath with the high Li⁺ coordination number up to 13 (Figure S8). NO_3^- additive boosts more Li⁺ coordination involving into the solvation sheaths, which further illustrates the enhanced interaction between NO₃⁻ and Li⁺. NO₃⁻ coordination mechanism follows the Gutmann donor principle (Figure 1C) with higher Gutmann donor number (DN, 22) than DME (DN, 20) and DOL (DN, 18),⁴⁶⁻⁵⁰ and states a promising coordination mode with Li⁺ in solvation sheath structures. Deposited in LiNO₃-1 electrolyte, amorphous nuclei gradually increase and then follow the nano block Li growths after depositing for 15 min (Figure S9). More obviously, in S-LiNO₃ electrolyte, large cluster-like coordination solvation sheaths with high Li⁺ coordination number up to 13 can boost more Li⁺ into the solvation sheaths and make an ideal Li⁺ concentration for depositing particle morphologies of Li, which slides toward a growing trend of spherical structure (Figure S10). The Li dendrites are largely inhibited by the growth source from the optimization of solvation sheaths with high Li⁺ coordination.

Shown in our molecular dynamics (MD) simulation results (Figure 1A,B), we discover that $LiNO_3$ -based ether-electrolyte has an aggregated solvation sheath with high Li⁺ coordination up to 13, but it is not more than 3 in LiNO₃-free electrolyte. This newly discovered solvation chemistry of high Li⁺ coordinated solvation structure highlights a responsibility for tailoring the growth morphology of Li deposition in a new-sight. These $NO_3^$ added electrolytes are available for depositing Li with stable morphologies and their associated NO_3^- – led solvation sheaths of high Li⁺ coordination certainly play a crucial role in structural Li growths. But the amount of LiNO₃ added in the electrolyte is limited, to further enlarge on the above-mentioned prospective mechanism



FIGURE 1 Coordination solvation chemistry and kinetics of Li deposition. MD simulation of the solvated sheath structures in (A) LiNO₃-free and (B) S-LiNO₃ electrolyte, the simulated box is about $60 \times 60 \times 60 \text{ Å}^3$. (C) Gutmann donor numbers of Li⁺–DMSO, Li⁺–DME, Li⁺–DOL, Li⁺–NO₃⁻, and the principle of designing the localized high-concentration NO₃⁻ (LH-LiNO₃) electrolyte. (D) ATR-FTIR and (E) Raman spectrometry characterizations on designed electrolytes. Experimental kinetics evaluations of the electrolytes: (F) transference number of Li ions (t_{Li^+}) and (G) its combined electrochemical impedance spectroscopy (EIS) before and after polarization in LH-LiNO₃ electrolyte, (H) Tafel plots, (I,J) cyclic voltammograms of Li deposition/dissolution on the 3DCM plating matrixes.

of this unique NO_3^- – led solvation sheaths on affecting the growth morphology of Li deposition, a novel electrolyte of localized high-concentration $NO_3^-(LH - LiNO_3)$ is prepared for increasing the stronger Li⁺ – NO_3^- coordination interaction. In Gutmann donor principle, shown in Figure 1C, dimethyl sulfoxide (DMSO) has the highest DN of 30 toward Li⁺, it can obtain a high-concentration NO_3^- additive whose saturation concentration up to 4 M when LiNO₃ dissolved. This saturated 4 M LiNO₃/DMSO solution can serve as the high-concentration NO_3^- additive with cluster-like solvation sheaths (Figure S11), and followed by a maximum addition of 6 wt% into S-LiNO₃ solution to prepare the LH-LiNO₃ electrolyte. In LH-LiNO₃ electrolyte, LiNO₃ has already reached saturation in S-LiNO₃ solution at a low solubility close to 5 wt%. And then, a high concentration of saturated 4 M LiNO₃/DMSO is added and a localized high-concentration NO_3^- has been achieved at the molecular scale. The Li⁺ – NO_3^-

coordination interaction largely strengthens and is beneficial for the structure controllable growth of Li deposition. Large cluster-like coordination solvation sheaths with ultrahigh Li⁺ coordination appear in this high-concentration NO_3^- additive (Figure S11), which accounts for the formation of NO_3^- –led solvation sheaths with high Li⁺ coordination. Designed electrolytes of LiNO₃-free, LiNO₃-1, S-LiNO₃, and LH-LiNO₃ are successfully prepared and shown in Figure S12–S14.

Figure 1D,E shows the attenuated total reflection-Fourier-transform infrared spectroscopy (ATR-FTIR) and Raman spectrometry characterizations to confirm this designed LH-LiNO₃ electrolyte. C–O stretching vibrations in pure DME and DOL locate at about 1107 and 1083 cm^{-1} , respectively, and shift to lower wavenumber when LiTFSI dissolved.^{51,52} It indicates that DME and DOL molecules are coordinated with Li⁺ through Li-O (DME) and Li-O (DOL) interactions, the vibration energies of C-O in DME and DOL molecules are reduced and show a typical red shift. As the NO_3^- additive added, the competitive coordination between solvent molecules and NO₃ gradually unfolds. With the concentration of NO_3^- increasing, the C-O stretching vibration peaks of DME and DOL tend to return (the parallel line marked area), which verifies that the coordination interactions of Li-O (DME) and Li-O (DOL) are reduced. NO₃⁻ additives are able to participate in the solvation sheaths and enhance the $Li^+ - NO_3^-$ coordination interactions. NO_3^- acts as a highconcentration additive (Figures S11-S15), the coordination of NO_3^- and Li^+ largely strengthens and high Li^+ coordination solvated sheaths are formed in LH-LiNO3 electrolyte. Such an enhanced effect in NO₃⁻ coordination interactions is also obvious in Raman spectrometry characterizations. The symmetric N-O stretching vibration of NO_3^- at 1050 cm⁻¹ exhibits a distinct peak shift with the increase of NO_3^- , which corresponds to the reinforced Li⁺ – NO₃⁻ coordination.⁴⁶ Raman spectrometry characterizations are highly accorded with the ATR-FTIR spectrometry results.

Experimental electrochemical kinetics of Li⁺ in designed electrolytes are evaluated in Figure 1F–J. Owning to the enhanced coordination interactions of NO₃⁻, the effective Li⁺ – NO₃⁻ coordination in deposited solvation sheaths can positively replace the solvation of solvents with Li⁺, and the restriction of Li⁺ migration by the solvated shells is reduced, the transference numbers of Li ions (t_{Li^+}) markedly increase with increasing NO₃⁻ additive (Figures S16–S18). In LH-LiNO₃ electrolyte, the t_{Li^+} is as high as 0.69, which is in favor of increasing the charge transfer efficiency (Figure 1F,G). In Tafel plots, exchange current densities (j_0) are calculated from the fitting linear regions (Figure S19). The j_0 value in LH-LiNO₃ electrolyte is 0.59, which is larger than the other

comparative electrolytes and depicts a fast charge-transfer kinetics. Cyclic voltammetry (CV) of Li deposition/ dissolution on the 3DCM plating matrixes further reveals the dynamic processes in these various electrolytes (Figure 1I). Obviously, NO_3^- added electrolytes can effectively improve the kinetics of deposition/dissolution, the LH-LiNO₃ electrolyte with a localized high-concentration NO_3^- shows a superior capability of Li⁺ in deposition/dissolution. The CV results of 12 cycles in LH-LiNO₃ electrolyte are solidly consistent and prove the stable and high reversibility of deposition/dissolution (Figure 1J).

2.2 | Cryo-TEM characterizations on Lisphere growths

To verify the regulating mechanism of this localized high-concentration NO₃⁻ on growth morphologies of Li deposition, here, cryogenic transmission electron microscopy (cryo-TEM) characterizations are used to reveal the nanostructure evolution of Li deposits in nucleation and growth process. Cryogenic condition ($\sim -176^{\circ}$ C) maintained by liquid nitrogen can availably minimize the structural damages of Li deposits by electron beam irradiation and make evolving nanostructures and SEI preferable.^{1,53} A 3DCM host is also determined as the Li plating matrix. As the Figure S20 shown, the deposition curve in LH-LiNO₃ electrolyte depicts a small overpotential of 16.1 mV when nucleates on the 3DCM plating matrixes at 2 mA cm⁻². It reveals the fast kinetics of Li⁺ in desolvation, mass transport and diffusion, and also indicates an excellent lithiophilicity on the 3DCM plating matrix. As exhibited in Figure 2A-D, the definite Li spheres of \sim 21.8 nm are uniformly distributed on the 3DCM plating matrix. A 0.24 nm spacing distance in the lattice fringes is assigned to the Li (110) lattice plane. Meanwhile, crystalline diffraction spot in FFT image is also consistent with the appearance of crystalline Li in Li (110) lattice plane.^{54,55} In this localized high-concentration NO_3^- electrolyte of cluster-like NO_3^- - led solvation sheaths, the Li deposit perfectly exhibits an ordered growth structure and a stable well-proportioned spherical shape. In Figure 2E, a clarified mechanism of the nucleation and growth in nanoscale evolutions is proposed to deepen the understanding of spherical Li deposition. As described by the classical heterogeneous nucleation theory, Li nuclei appear when the embryo's bulk energy overcomes the surface energy, and later, Li nuclei are able to grow when the embryo size exceeds the critical radius.⁵⁵ In Figure 2E1 and E11, abundant nucleated nanoclusters of amorphous structure are formed with the size of 2 nm. The addition of localized high-concentration NO_3^- may accelerate the heterogeneous nucleation of the



FIGURE 2 Structure characterizations on Li-sphere deposition. (A–C) Cryo-TEM characterizations and (D) size statistics of Li spheres that deposited on the 3DCM plating matrix for 15 min at 2 mA cm⁻² in LH-LiNO₃ electrolyte, (C) FFT pattern corresponds to the marked area in B. (E) Nanostructure evolutions in Li-sphere nucleation and growth: (E1–E31) cryo-TEM characterizations and their corresponding FFT patterns of Li-sphere nucleated and grown on the 3DCM plating matrix during a 15-min deposition at 2 mA cm⁻² in LH-LiNO₃ electrolyte. Inset, the FFT patterns correspond to E11, E21, and the marked area in E31, respectively. The growing evolutions of Li-sphere deposition curves of voltage/time in Figure S20. (F1–F11) Cryo-TEM characterizations of Li spheres grown on another plating matrix of Cu TEM grid at 2 mA cm⁻² for 30 min in LH-LiNO₃ electrolyte: inset, the high-resolution cryo-TEM image corresponds to F11.

Li spheres, more Li ions aggregate together in these NO_3^- – led solvation sheaths and maintain enough mass transports on the electrolyte/electrode interface. With the deposition time increasing, Li nuclei gradually grow, amorphous Li clusters of roughly 3.5 nm are evenly grown on the 3DCM plating matrix by a 5 min deposition (in Figure 2E2 and E21). Subsequently, when extended to 10 min, as shown in Figure 2E3, a small portion of larger spherical-Li particles in 9–12.5 nm sizes are obtained and begin to crystallize. The characteristic Li (110) lattice fringes of a 0.24 nm spacing distance between two adjacent lattice fringes appear in a partial region of the Li sphere (Figure 2E31). In the meanwhile, the inserted

FFT image corresponded to the marked area in Figure 2E31 evidences an amorphous phase reservation, which reveals an amorphous-crystalline phase transition in this nucleation and growth of spherical Li. These transition phases of amorphous structures in Li nuclei are metastable and have high bulk energy. A supersaturation of mass transports and decreasing trend in the bulk energy can facilitate the crystalline transformation in Li nucleation and growth.⁵⁵ An amorphous-crystalline nanostructure evolution during nucleation and growth uncovers a clarified mechanism for understanding the Lisphere deposition. Besides, in Figure 2F and Figure S21, larger Li spheres of ~163 nm are also deposited and

grown on another plating matrix of Cu TEM grid at 2 mA cm^{-2} in LH-LiNO₃ electrolyte. Structure viability in Li-sphere deposition is also effectively regulated on Cu TEM grid plating matrix.

2.3 | MD simulations and quantum chemistry calculations

Coordination solvation chemistry mechanism for regulating the advanced Li-sphere growths is explicitly unraveled in MD simulations and quantum chemistry calculations.^{56–61} A 30-ns simulation of Li⁺ coordination solvation in LH-LiNO₃ electrolyte is shown in Figure 3A, plenty of larger cluster-like coordination solvation sheaths with high Li⁺ coordination number (≥ 3) are clearly revealed in these time-evolving snapshots and gradually tend to be structurally stable during the equilibrating and stable simulation. Localized high-concentration NO₃⁻ in LH-LiNO₃ electrolyte promotes the clustering formation in Li⁺ coordinated solvation structure, which induces more Li⁺ to form high Li⁺ coordinated solvation sheaths through the aggregated NO_3^- coordination. Figure <u>3B,E</u> are the radial distribution function (g (r), solid lines) and coordination number (n (r), dashed lines) in the MD simulations of $LiNO_3$ -free, LiNO₃-1, S-LiNO₃, and LH-LiNO₃ electrolyte. In LiNO₃free electrolyte, Li-O(DME) and $\text{Li} - \text{N}(\text{TFSI}^{-})$ peaks at 1.7 and 1.8 Å are the main coordinated types in Li^+ coordinated solvation sheaths with low coordination number.^{11,19} However, in Figure 3C-E, it can be seen that the originally dominant Li-O(DME) bidentate ligands decrease with the addition of NO_3^- , new coordination structures of $\text{Li} - O(\text{NO}_3^-)$ and $\text{Li} - N(\text{NO}_3^-)$ appear at 1.7 and 3 Å. Participation of NO_3^- into the coordinated solvation sheaths further increases the coordination probability of Li⁺. The double step shape of the coordination number line in LH-LiNO₃ electrolyte indicates that after a single oxygen atom is coordinated to Li⁺, the remaining two oxygen atoms are also relatively stable in NO_3^- . This existence of localized high-concentration NO_3^- can make the solvation sheaths form larger stable Li-cluster structures with high Li⁺ coordination number reaching 8 and 13 (Li8-cluster and Li13-cluster, shown in Figure 3F,G). Evolution of coordination number in the maximum Li-cluster solvated sheaths of the above-mentioned electrolytes are analyzed in Figure 3H. We can find that the NO_3^- significantly improves the aggregation behavior with high Li⁺ coordination number. The S-LiNO₃ and LH-LiNO₃ can stabilize the coordination number up to 13 with similar Li⁺ concentration in these electrolyte systems.

To further explore the effect of NO_3^- , we take the 50 ns trajectories to count the coordination number distributions of these Li-cluster solvated sheaths after

equilibrium in each simulation system (Figure S22A). For the LiNO₃-free electrolyte system, the coordinated solvation sheaths rarely form the Li3-cluster with the Li⁺ coordination number of 3 (3.91%, shown in Figure S22B). When the NO_3^- increases, the maximum Li-cluster size increases abruptly, many cluster-like solvation sheaths with more than Li3-cluster aggregate (Figure S22C,D). LH-LiNO₃ electrolyte system with the localized high-concentration NO₃⁻ shows a group cluster propensity with Li8-cluster, and the coordination number of the largest cluster-like solvation sheath is as high as 13. The localized high-concentration NO₃⁻ can availably make the Licluster size distribution to be more concentrated, indicating an ideal cation concentration for growing Li spheres (Figure S22E). Aggregated NO_3^- can coordinate with multiple Li⁺ for more compact solvated sheaths owing to the stronger coordination ability of O atom (Figure S23), while the coordinated Li clusters of Li-O(DME) and $Li - N(TFSI^{-})$ are looser. NO_{3}^{-} is more rigid and smaller, which is more easily to insert into the solvated sheaths and stabilize the structure. Quantum chemistry calculation is used to explore the approximate similarities and differences in the reducing ability of solvated sheaths in Li3-cluster and Li8-cluster. In Figure 3I, the reduction potentials fluctuate greatly in three representative solvated sheaths of Li3-cluster structures that taken from MD simulation. The different coordination environments and configurations of Li⁺ significantly affect the reduction potential when the size of Li3-cluster is small. But when the coordination number of Li^+ is up to 8 in a compacted cluster, it seems that the reduction potential displays a smaller fluctuation than the Li3-cluster. It may be caused by the difference of conformational changes between oxidation and reduction state. For a smaller solvated sheath, when a Li⁺ gets an electron, the structure of the whole cluster needs to adjust to match the change during reduction process. Such adjustments can be achieved by changing the coordination ligand shape as Figure 3I shown. Obviously, a larger cluster solvated sheath tightly bonded by electrostatic action has a stronger ability to stabilize its shape to adapt to the change of electrons. As viewed in Figure 3J, the structure changes of Li8-cluster are indeed slighter than Li3-cluster. Larger Li-cluster sheaths with high Li⁺ coordination ensure stable solvation structures for spherical Li growing.

2.4 | High-loaded Li spheres and SEI characterizations

Depositing at higher current densities of 5 and 10 mA cm⁻² has been further conducted on clarifying the growth effectiveness of Li spheres. In the deposition



FIGURE 3 MD simulations and quantum chemistry calculations of the solvated Li-cluster sheaths. The simulated box in the snapshot is about $60 \times 60 \times 60 \text{ Å}^3$. (A) Snapshots of a 30 ns MD simulation in LH-LiNO₃ electrolyte, radial distribution function (g (r), solid lines) and coordination numbers (n (r), dashed lines) in the MD simulations of (B) LiNO₃-free, (C) LiNO₃-1, (D) S-LiNO₃, and (E) LH-LiNO₃ electrolyte. The representative solvated sheaths of (F) Li8-cluster and (G) Li13-cluster in LH-LiNO₃ electrolyte, (H) coordination number (n (Li⁺)) of the maximum Li cluster as a function of MD simulation times in these above-mentioned electrolytes. Reduction potential calculations for the three representative solvated sheaths of (I) Li3-cluster and (J) Li8-cluster.

curve of plating at 5 mA cm⁻² in LH-LiNO₃ electrolyte (Figure S24), an acceptable nucleation overpotential of 41.2 mV is obtained. Even scaling up to 10 mA cm⁻², the

nucleation overpotential merely increases to 77.5 mV (Figure S25), which shows a larger binding energy and excellent dynamics for Li-sphere nucleating and growing

on the 3DCM plating matrix in LH-LiNO₃ electrolyte. Figure 4A,i display the Li deposits plated at 5 mA cm^{-2} for 10 min on the 3DCM plating matrix, the sphere-like morphologies at \sim 25.49 nm in size are maintained. When deposited at a higher current density of 10 mA cm⁻², parts of Li deposits are transformed into ellipsoid structure with a size of \sim 26.14 nm (Figure 4B,ii). Applying higher current densities can also keep the Li deposits in stably spherical or ellipsoidal structures. Furthermore, Li-sphere deposit evolutions of high-loaded capacities on the 3DCM plating matrix at 2 mA cm⁻² are exhibited in Figure 4C–F, iii-vi. Li-deposited host materials of 3DCM coated on a copper foil are \sim 148 µm and work as the capacity-limited electrodes after Li-sphere deposition. With 1 mAh cm^{-2} deposition, the spherical deposits are regularly dispersed on the 3DCM plating matrix (Figure 4D,iv) and gradually grow into Li spheres of 280-300 nm in size with the deposition capacity reaching to 2 mAh cm⁻² (Figure 4E,v). However, in LiNO₃-free electrolyte (Figure S26), a Li deposition of 2 mAh cm⁻² at low Li⁺ coordination solvent sheath grows into dendritic structure at 2 mA cm^{-2} . With the addition of NO_3^- , more Li ions participate in the solvation sheaths and significantly optimize the mass transfers of Li⁺ for depositing Li blocks and particles (Figures S27 and S28). Remarkably, even the deposition capacity is up to 5 mAh cm⁻² in this localized high-concentration NO₃⁻ electrolyte, the larger cluster-like coordination solvation sheaths with high Li⁺ coordination enable sphere-like Li growth in a size of \sim 280 nm (Figure 4F,vi). It exhibits high stability in spherical growing structure at highloaded Li deposition. These can construct the capacitylimited Li-sphere electrode with a well-defined stable structure to achieve high-efficiency cycling stability.

The structure-activity relationship between structure and interface in Li spheres was characterized on highresolution cryo-TEM in Figure 4G, abundant inorganicrich components are coupled on organic layers with constituting a multilayer-ordered SEI nanostructure. The internal multi-layers are the crystalline domains of inorganic components that completely cover on the surface of Li spheres and embed with each other to form a closeconnected inorganic-rich structure. These inorganic-rich crystalline domains in SEI are determined to be Li₂CO₃, Li₃N, Li₂O, and LiF by the lattice spacing measurements and FFT patterns (Figure S29-S31). And outsides, an amorphous polymer matrix appears and acts as a flexible protective film. Scanning from 0.01 to 3 V at 0.2 mV s^{-1} , the typical cyclic voltammetry (CV) has been used for validating this SEI forming mechanism on the Li-sphere/3DCM (Figure S32A). In the 1st scanned cycle, a distinct reduction peak of NO₃⁻ (LiNO₃) appears at \sim 1.65 V and belongs to the reduction of Li₃N, while the TFSI⁻ (LiTFSI) decomposes into LiF at ~ 1.2 V.^{11,12} The

unapparent reduction peak for solvents is below $\sim 0.75 \,\mathrm{V}$ and attributes to the organic component formation in SEI.¹² It is because that there are still a few organic solvent molecules can insert into the gaps between the inorganic components and decompose below ~ 0.75 V, which constructs a flexible layer of organics. Simultaneously, some decomposed products such as LiOH and CO₂ can further react with Li^+ or traces of H₂O to form the Li_2O , Li_2CO_3 , respectively.^{62–65} The inorganic components preferentially formed at high voltage can prevent further contacting the electrolyte, so the decomposition of organic solvent molecules is reduced and an advanced SEI that dominated by inorganic-rich phases is constructed. Upon being reduced at certain potentials, the produced SEI species can be arranged for the multi-layer nanostructure. More importantly, the above-mentioned peaks disappear in the next cycle, and it implies a stable and dense SEI.

In-depth XPS characterizations to investigate the SEI compositions by Ar⁺ sputtering for 0, 2, 4, 8, and 10 min are measured in Figure 4H. In F 1s, the LiF peaks at 684.7 eV bring into line in the Ar⁺ sputtering tests from 2 to 10 min, while a C-F at 688 eV and weak LiF are on the outermost surface of SEI layer by a 0-min sputtering validation.^{11,66} The peak intensities of Li₂O at 528.2 eV in O 1s gradually increase with Ar^+ deepening.^{11,67-69} The distributions of Li₃N located at 398.4 eV are basically the same as LiF, its peak intensity on the outermost layer is lower, but with the Ar⁺ sputtering, it becomes higher and remains constant.^{11,12,33} Li_2CO_3 peaks in O 1s remain stable throughout the Ar⁺ sputtering process. These measured analyses of LiF, Li₂O, Li₂CO₃, and Li₃N accord with the cryo-TEM validations. LiF with a high interface energy can effectively adapt to the volume variation of Li spheres and increase the mechanical durability of SEI, the Li₂O, and Li₃N with excellent ionic conductivity are able to facilitate the Li⁺ diffusion to ensure the fast kinetics of deposition/stripping.^{19,20} Apparently, the produced SEI species are reduced at the certain potentials and arrange for a rigid-flexible nanostructure on the Li spheres, including rigid multilayer structures rich in LiF, Li₂O, Li₂CO₃, and Li₃N, and flexible layers of organics (schematized in Figure S32B). This advanced SEI is conducive to improving the structure durability, electrochemical reversibility, and long-term cycling stability.

2.5 | Electrochemical performance of Li-sphere anodes

Figure 5A shows the symmetrical cell performance at 2 mA cm^{-2} for 15 min. The working Li symmetrical electrodes (Li whiskers/3DCM, nano block Li/3DCM, Li nanoparticles/3DCM, and Li spheres/3DCM) are obtained



FIGURE 4 Li-sphere morphologies and SEI characterizations. (A,B) Cryo-TEM characterizations and (i,ii) size statistics of spherical Li deposits on the 3DCM plating matrix at higher current densities of (A,i) 5 and (B,ii) 10 mA cm⁻² in LH-LiNO₃ electrolyte for 10 and 5 min, respectively. (C,iii–F,vi) SEM structure characterizations of Li-sphere deposit evolutions on 0, 1, 2, 5 mAh cm⁻² at 2 mA cm⁻². (G) High-resolution cryo-TEM characterizations and (H) its corresponding in-depth XPS measurements of SEI formed on the Li-sphere deposits of 2 mAh cm⁻² at 2 mA cm⁻². Insert, corresponding the FFT pattern of (G), scale bar is 2 1/nm. Detailed nanostructures of inorganic-rich compositions in SEI are exhibited in Figure S29–S31.

by depositing Li on the 3DCM plating matrixes for 15 min at 2 mA cm⁻² in LiNO₃-free, LiNO₃-1, S-LiNO₃, and LH-LiNO₃ electrolyte, respectively. Li whisker/3DCM symmetrical cell in LiNO₃-free electrolyte exerts low stabilities with extreme polarization processes, which illustrates the poor electrochemical properties in a result of dendritic Li growths. Benefiting from the regular shapes, nano block Li/3DCM and Li nanoparticles/3DCM symmetrical cells can maintain the polarization voltage stable for a certain period. Advanced Li-sphere symmetrical cells,



FIGURE 5 Electrochemical performance measurements. (A) Symmetrical cell performance that plating/stripping at 2 mA cm⁻² for 15 min, the working Li symmetrical electrodes are obtained by depositing Li on the 3DCM plating matrixes for 15 min at 2 mA cm⁻² in LiNO₃-free, LiNO₃-1, S-LiNO₃, and LH-LiNO₃ electrolyte, respectively. (B) Coulombic efficiencies of Li plated on the 3DCM plating matrix at 2 mA cm⁻² for 15 min and stripped to 2 V in LiNO₃-free, LiNO₃-1, S-LiNO₃, and LH-LiNO₃ electrolyte, (C) the voltage-capacity profiles in LH-LiNO₃ electrolyte. (D) Long-term cycling properties of LiFePO₄ (LFP) full cells at 1 C, (E) charging/discharging profiles in LH-LiNO₃ electrolyte, the LFP-loading weight in the cathode is ~1.7 mg cm⁻². (F) Cycling properties in high-loaded LFP (6.6 and 10.9 mg cm⁻²) full cells. (G) Electrochemical performance comparisons between Li-sphere anodes and other Li metal anodes in LiFePO₄-based full cells.

an ultra-stable structural engineering for suppressing the Li dendrite growths, perform excellent 4000-time plating/ stripping cycles with small overpotential (\sim 26 mV). Even during the plating/stripping cycles of high-loaded Li-sphere electrodes (Figure S33–S35), low polarizations of \sim 26, 35, and 43 mV are presented at 2 mA cm⁻² for 2 mAh cm⁻², 5 mA cm⁻² for 2 mAh cm⁻², and 5 mA cm⁻² for 5 mAh cm⁻² in LH-LiNO₃ electrolyte, respectively, and stabilized for 1000 cycles. It evidently demonstrates that the spherical morphology in Li metal anode can

enormously enhance the electrochemical cycling stability. Plated on the 3DCM plating matrix at 2 mA cm^{-2} for 15 min and stripped to 2 V, high Coulombic efficiency (CE) of Li spheres for the plating/stripping reversibility is up to 98.8% on average over 400 cycles (in Figure 5B,C). In LiNO₃-free electrolyte (in Figure 5B and Figure S36A), the CE of Li|3DCM quickly declines to 43.6% only after 100 cycles. In LiNO₃-1 and S-LiNO₃ electrolyte with the addition of NO₃⁻ (shown in Figure 5B and Figure S36B,C), the plating/stripping reversibility was improved and the CE maintained at around 90% after 200 cycles. Impressively, plated/ stripped at 1 mA cm⁻² for 1 mAh cm⁻² and 2 mA cm⁻² for 2 mAh cm⁻² (Figure S37), LH-LiNO₃ electrolyte enables high reversibility with the CEs up to 98.5% and 98.3% after 300 cycles. The cluster-like solvation sheaths of high Li⁺ coordination form an advanced spherical structure and an orderly multi-layer SEI comprising of inorganic-rich Li₂O and Li₃N components on Li spheres, which guarantees fast Li⁺ diffusion on the SEI/Li-sphere interface and ensures the fast kinetics of deposition/ stripping for high reversibility of Li plating/stripping.

More practical researches on the electrochemical performance of Li spheres were conducted on LiFePO₄-based full cells. Figure 5D demonstrates the long-term cycling properties of LiFePO₄ (LFP) full cells at 1 C with a limited Li capacity of 0.5 mAh cm^{-2} . These working anodes with limited Li deposition included Li whiskers/3DCM, nano block Li/3DCM, Li nanoparticles/3DCM, and Li spheres/3DCM are obtained by depositing Li on the 3DCM plating matrixes at 2 mA cm⁻² for 15 min in LiNO₃-free, LiNO₃-1, S-LiNO₃, and LH-LiNO₃ electrolyte, respectively. Rapidly slope-like capacity fall occurs in Li whiskers/3DCM|LFP full-cell, that is, drops to 24.7 mAh g^{-1} with sharp voltage declining in only 50 cycles (Figure S38), which owing to the dendritic growths arising from poorly electrical activity in Li whiskers. The nano block Li/3DCM and Li nanoparticles/3DCM anodes can retain 73.7% and 86.2% of their initial capacities after 500 cycles in LFP full cells, which benefits from the stable and regular structure growths (Figure S39). As for Li spheres, an excellent Li spheres/3DCM|LFP full cell has been constructed and stably performs high-quality cycling stability with a high-capacity retention of 90.5% after 1000 cycles at 1 C (Figure 5D,E). After the 1000th charging, cycling structures of Li spheres also stably preserve and grow into the granular nanostructures based on the LiFePO₄ charging. The Li nanoparticles with a size of 85 nm in the charged state are well-preserved on the 3DCM plating matrix without Li dendrite formation (Figure S40). More gratifyingly, when the high-load LFP cathodes of 6.6 and 10.9 mg cm⁻² are matched with capacity-limited Li-sphere anodes of 2 and 5 mAh cm⁻² (N/P = 2.8, 3.7, 1 C = 170 mA g⁻¹), respectively, the Li spheres/3DCM|LFP full cells exhibit

advantageous initial capacities up to 147.6 and 149.2 mAh g⁻¹, and the corresponding capacity retentions are 96.5% and 92.5% after 800 cycles at 1 C (Figure 5F and Figure S41). Additionally, whether in the charged state at 50th or after 800 cycles in these capacity-limited Li-sphere anodes, the stable structures still maintain and display strong adaptability to restrain Li dendrite growths for the applications in Li-metal batteries (Figure S42–S45). Shown in Figure 5G and Table S1, when compared to other Li-metal anodes in LiFePO₄-based full cells, this advanced Li-sphere anode possesses significant advantages over the current research works.

3 | CONCLUSION

In this work, we present that high Li⁺ solvation sheaths coordinated in a localized high-concentration NO_3^- can regulate the efficient spherical growths in Li deposition. The addition of localized high-concentration NO_3^- in the LH-LiNO₃ electrolyte can perfectly increase the Li⁺ coordination up to 8 and 13 in larger cluster-like NO_3^- – led solvation sheaths, which enables advanced Li-sphere growths at high current densities of 2, 5, and 10 mA cm $^{-2}$. Meanwhile, an amorphous-crystalline phase transition in the critical nanostructure evolution of Li-sphere deposition during nucleation and growth process is elucidated in details by cryo-TEM. An orderly multi-layer SEI on the Li spheres is rich in Li₂O and Li₃N components with superb ionic conductivity, which facilitates Li⁺ diffusion for high reversibility. Multiple rigid-layer of inorganic-rich components and a flexible layer of organics on the Li spheres successfully constitute a rigidflexible nanostructure and effectively elevate the structure durability, electrochemical reversibility and longterm cycling stability. Ultra-stable 4000-time plating/ stripping cycles in symmetrical cells at 2 mA cm^{-2} and a high Coulombic efficiency up to 98.8% on average over 400 cycles are achieved in this advanced Li-sphere anode. Dendrite-free Li stably grows and maintains in asconstructed Li spheres/3DCM|LFP full cells, and a highquality long-term cycling stability with a high capacity retention of 90.5% is obtained after 1000 cycles at 1 C. When matched the high-load LFP cathodes (6.6 and 10.9 $mg cm^{-2}$) with capacity-limited Li-sphere anodes of 2 and 5 $mAh cm^{-2}$, respectively, high initial capacities of 147.6 and 149.2 mAg⁻¹ are exhibited in Li spheres/3DCM|LFP full cells at 1 C. Remarkably, the capacity retentions retain 96.5% and 92.5% after 800 cycles, respectively. High Li⁺ coordination in a cluster-like solvation sheath enables advanced Li-sphere deposition and attains promising results in high-performance Li-metal batteries.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

ORCID

Shizhi Huang https://orcid.org/0000-0002-0068-476X *Yijie Xia* https://orcid.org/0000-0002-7931-4015

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SUPPORTING INFORMATION

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