Inhibiting Dendrite Growth via Regulating the Electrified Interface for Fast-Charging Lithium Metal Anode

Xinyang Wang, Ming Chen, Siyuan Li, Chang Zhao, Weidong Zhang, Zeyu Shen, Yi He,† Guang Feng,† and Yingying Lu*  

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ABSTRACT: Extreme fast charging (XFC), with a recharging time of 15 min, is the key to the mainstream adoption of battery electric vehicles. Lithium metal, in the meantime, has re-emerged as the ultimate anode because of its ultrahigh specific capacity and low electrochemical potential. However, the low lithium-ion concentration near the lithium electrode surface can result in uncontrolled dendrite growth aggravated by high plating current densities. Here, we reveal the beneficial effects of an adaptively enhanced internal electric field in a constant voltage charging mode in XFC via a molecular understanding of the electrolyte–electrode interfaces. With the same charging time and capacity, the increased electric field stress in dozens of millivolts, compared with that in a constant current mode, can facilitate Li⁺ migrating toward the negatively charged lithium electrode, mitigating Li⁺ depletion at the interface and thereby suppressing dendrites. In addition, more NO₃⁻ ions are involved in the solvation sheath that is constructed on the lithium electrode surface, leading to the nitride-enriched solid electrolyte interphase and thus favoring lower barriers for Li⁺ transport. On the basis of these merits, the Li||Li₄Ti₅O₁₂ battery runs steadily for 550 cycles with charging current peaks up to 27 mA cm⁻², and the Li||S full cells exhibit extended life-spans charged within 12 min.

INTRODUCTION

Lithium metal, which owns the highest theoretical capacity (3860 mAh g⁻¹) and very low redox potential (−3.04 V vs standard hydrogen electrode, SHE), has been garnering great interest as the definitive anode choice for lithium-based batteries.⁴ Meanwhile, it is widely noted that charging rates which begin to compete with the refueling-time of internal combustion cars will eliminate so-called “range anxiety” and boost the mainstream adoption of electric vehicles. The U.S. Department of Energy has consequently identified extreme fast charging (XFC) as a critical challenge aiming to recharge 80% of the high energy density cell (>200 Wh kg⁻¹) within 15 min by 2023,⁵,⁶ signifying that an ultrahigh current of (>10 mA cm⁻²) is required for Li plating if lithium metal is used.⁴ Although there has been notable progress, Li metal is still plagued by low Coulombic efficiency (CE) and dendrite formation at high currents, leading to cycle-life decay and safety issues.⁵ Over the past years, tremendous efforts have been devoted into protecting Li via solid-state electrolyte deployments, concentrated electrolytes or additive modifications, interlayer protections, selective deposition, and so on.⁶–¹⁰ Among them, designing a lithiophilic three-dimensional (3D) current collector, which can homogenize Li-ion flux, has attracted much attention.¹¹ Although the current density can be generally increased to 10−20 mA cm⁻², the dendrite problem could occur once the amount of Li plating exceeds the capacity of designed collector structures. A 3D current collector, as a supporting material, also decreases the volumetric energy...
density and/or the weight energy density to some extent. The other targeted strategy is to regulate the composition of the electrolyte (i.e., solvent, Li salt, and additive) to regulate the properties of solid electrolyte interphase (SEI). For instance, 0.05 M LiPFO as an additive in LiTFSi-LiBOB dual-salt electrolytes,12 can significantly stabilize the fast-charge capability of Li with a current up to 1.75 mA cm−2. Nevertheless, higher current tolerance still calls for novel approaches, perhaps borrowed from other fields.13−15

When large currents are applied, the Li plating rate can be much faster than the transport rate so that a huge concentration gradient forms at the growth front of Li. In extreme cases, Li+ would be depleted at the anode surface and even drop to zero based on Chazalviel space charge model.16,17 Li deposits tend to propagate into the receding cation-available regions and form diffusion-limited apical-growing dendrites, which has been confirmed by both theoretical and experimental investigations.18−21 In addition, Li dendrites are strongly associated with the nonuniform SEI whose physicochemical features play a vital role in the nucleation and growth. The composition and morphology of SEI are controlled by the arrangement and chemical species of the solvation sheath at the interface.22−25 However, a thorough understanding of the electrified interfacial Li+ solvation structure26 and its derived SEI remains almost unknown. Developing an efficient approach to physically mitigating the ion concentration gradient while chemically optimizing the nanostructure of SEI is still a significant goal in pursuit of the practical use of the lithium anode.

Variations of charging procedures have been investigated to shorten the charging time. The most notable primitive ones are the constant current (CC) charging and constant voltage (CV) charging modes.27−29 Both are widely recognized as nonideal for XFC in traditional Li-ion batteries because of the propensity for Li plating on graphite under lower lithiation potentials.30,31 Compared with graphite lithiation, the different impacts of CC and CV charging modes on the Li electrodeposition process have been barely studied. Fundamentally understanding the electrochemical effects of the elementary charging modes on Li depositions may give deep insights to design novel charging technology and push forward the postlithium era. In this work, we investigated the dramatic changes of Li deposition behavior under the CC and CV modes in XFC. We found that the adaptively enhanced internal electric field established in CV mode, which refers to dozens of millivolts, has dual beneficial functions (Figure 1). On the one hand, the extra field stress can promote Li+ moving to negatively charged Li electrode and mitigate the ion concentration gradient, thereby suppressing dendrites. On the other hand, the solvation sheath containing more NO3− ions that is constructed at the interface drastically contributes to the nitride-derived SEI nanostructures because of its high oxidizability, favoring a more stable cycling. Molecular dynamics (MD) simulations of electrical double layers at electrolyte-lithium electrode interfaces were conducted to demonstrate a deep understanding of electrified interfacial characteristics. On the basis of the merits revealed, the Lill Li4Ti5O12 batteries were found to achieve stable cycling performance for 550 cycles with a charging current up to 27 mA cm−2, and the LillS full cells exhibited extended stable life-spans and increased CE within a short charging time below 12 min.

### RESULTS AND DISCUSSION

#### Li Plating/Stripping Performance on Copper Foils via CC and CV Modes

As shown in Figure 2a, the performance of CC or CV mode was first studied by a LillCu cell, since it allows us to determine the CE which reflects the loss of Li during each cycle. In CV charging mode, the ethanol/water-washed Cu foil is polarized to negative potentials vs Li/Li+, so that Li+ can migrate onto the surface of Cu foil under the internal electric field. Negative overpotential at the Cu electrode side triggers the nucleation and growth of Li. A fixed amount of Li plating is available by controlling the processing capacity. Meanwhile, 1 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME, 1:1 v/v) with 2 wt % LiNO3 as an additive is adopted as the electrolyte because of its well-defined Li grown morphology.32 Specifically, the DOL/DME ether-based electrolyte is common for sulfur/Li metal batteries, and LiNO3 is one of the most successful additives, which is widely used to improve the passivation and surface chemistry of Li.33 The addition of LiNO3 is necessary as it plays the critical role for Li metal’s reversibility (Figure S1).

Throughout this study, we used a fixed plating capacity of 1 mAh cm−2 and a stripping current of 1 mA cm−2, which are the most common testing conditions in the literature.3 For the Li plating processes, we tested the constant currents of 1, 2, 6, 12, and 16.8 mA cm−2, and the corresponding applied constant polarization voltages are, respectively, 25, 50, 200, 250, and 300 mV to ensure the same deposition time (Figure S2). As shown in Figure S3, although the CE improvement in the general charging condition is less obvious, a polarization of 200 mV in CV mode can significantly increase the cycling performance to a stable CE of ~96.5% for 140 cycles (Figure 2b). In comparison, a relatively high plating current of 6 mA cm−2 only offers a CE of ~95% which quickly falls within 45 cycles. Extreme fast charging currents of 12 and 16.8 mA cm−2 (corresponding to charging time of 5 and 3.57 min, respectively) were further examined (Figure 2c,d). Such huge plating currents make an immediate sharp decline in CE because of the interfacial Li+ ion depletion zone caused by sluggish transport kinetics and the broken fragile SEI. Encouragingly, the 300 mV polarized cells can exhibit an extremely fast charging process within 4 min with a peak current up to ~27 mA cm−2. Their integrated current profiles also indicate stable cycling performance (Figure 2e and Figure S4).

Electrochemical impedance spectroscopy (EIS) was conducted for LillCu cells to explore the evolutions of the Li formation after plating via both CC and CV methods. The
Electrical equivalent circuit and the relative Nyquist plots of these cells are shown in Figure S5. Interfacial SEI resistance ($R_{\text{int}}$) and the bulk resistance ($R_b$) that characterizes the system ohmic impedance are shown in Figure 2f. As the charging time decreases, the $R_{\text{int}}$ values of cells via both CC and CV methods increase first and then decrease. The increase of $R_{\text{int}}$ reflects the continuous generation and accumulation of fragile SEI during quicker plating; the following unexpected decline of $R_{\text{int}}$ in the faster charging region is attributed to the self-heating-induced healing mechanism. The $R_{\text{int}}$ values in the decline trend based on CV methods are quite smaller than those via CC modes, demonstrating the generation of tougher SEI and the resulting faster electrochemical kinetics for Li plating. Since the current collector, packaging and electrolytes are all the same, $R_b$ here reflects the difference of electronic impedances of the deposited Li. The $R_b$ values in the CV modes with the polarization from 200 to 300 mV display a decaying trend, while the relative CC modes show the opposite. The gradual increase in $R_b$ via CC modes is attributed to the easier formation of a thick Li layer, which can break away from the electronic circuitry of an electrode. By contrast, tightly fused and flattened Li deposition from CV modes would eliminate the long and tortuous pathway, thus getting smaller $R_b$. The EIS data matches well with the CE results, and the detailed explanations will be discussed in later sections.

**Characterization of Lithium Deposit Morphologies and SEI Components.** The surface morphology of deposited Li is a critical factor affecting the overall electrochemical performance and CE of battery systems. Figure 3a–j display scanning electron microscopy (SEM) images of the typical morphology of Li, which is deposited in ether-based electrolyte at 16.8 mA cm$^{-2}$ and 300 mV for different charging capacities from 0.2 to 1.0 mAh cm$^{-2}$ (Figure S6). Different from well-defined, nearly circular structures of typical Li grown in normal mild plating conditions, we identify distinct evolutions of flattened petal-like morphology via the CV mode compared with dendritic Li via CC during XFC. In the early stages of Li plating (0.2 mAh cm$^{-2}$), subtly different morphologies can be distinguished (Figure 3a,b) where Li particles are more uniform and bigger in size by CV mode. As the capacity increases to 0.4 mAh cm$^{-2}$ (Figure 3c,d), the Li deposition in CV mode gradually grows and results in a flat closely packed morphology. In contrast, the extremely high current of 16.8 mA cm$^{-2}$ gives rise to a combination of small rod-type deposits with incompact irregular shapes. Its inhomogeneous deposition in both size and location is due to the well-known interparticle diffusion coupling, reflecting the development of Li$^+$ depletion zones around Li clusters. More loosely aggregated porous Li with fragile SEI formed in CC modes will be continually corroded by the electrolyte and result in the fast growth of mossy Li islands (Figure 3e,g). The formation of concentration gradients caused by sluggish Li$^+$ transport kinetics finally leads to catastrophic dendrite propagation in an attempt to instigate charge neutrality (Figure 3i). Interestingly, we find that Li begins to grow in the void spaces initially generated during the early deposition stage, and then a lateral densified structure is formed by CV mode (Figure 3f). Figure 3h,j indicates the convergence of macroscopic Li deposits since the particle boundary is further eliminated. The smooth petal-like Li deposits with diameters up to 45 μm demonstrate a better Li reversibility (Figure 3j and Figure S7). The cross-sectional SEM images (Figure S8) show that the Li thickness is decreased from 40 to 10 μm, which is consistent with the densification process.

The influences of CC and CV methods were also tested in a carbonate-based electrolyte that is less compatible with a Li metal anode (Figure S9 and Figure S10). Consistent with the literature, it formed needle-like dendrites, which leads to a porous bulk structure with high tortuosity in a constant plating current of 5 mA cm$^{-2}$. Instead of a fibrous network, denser and nearly particle-like structures are observed, suggesting that the...
CV mode is superior both in ether- and ester-based electrolytes.

The chemical composition of the SEI film was probed by X-ray photoelectron spectroscopy (XPS) of electrodes after 20 cycles. The typical signals exhibit different chemistry in CC and CV modes. Both the formed SEI films have two peaks in the N 1s spectrum (Figure 3k) at 404.2 and 398.8 eV, corresponding to LiNO2 and Li3N, respectively. The ratio of N largely increased from 0.92% to 1.28%, revealing adequate reduction behavior of the salt or additive when using the CV method. It depicts that the nitride products of decomposed LiTFSI mainly consist of Li3N rather than oxynitride (Figure S11), perhaps by reason for its lack of N−O structures. Thus, the obviously increased signal of LiNO2 (Figure 3k,l) seems to be the facile reduction behavior of the additive LiNO3.

To further analyze the SEI composition in detail, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was conducted with a sputtering area of 100 μm × 100 μm. Depth profiles obtained in CC and CV modes for oxynitride secondary ions are shown in Figure S12a. It demonstrates that the signal intensity for NO2− species is significantly higher in the CV charging mode, which can be also visually distinguished from the relative 3D reconstruction of the ToF-SIMS data (Figure S12b,c). The existence of more abundant nitrogen products via CV can effectively enhance the ionic conductivity as well as the mechanical strength of the SEI film (Figure S13), which enables homogeneous Li+ flux and suppresses dendrites.22,41

Molecular Insights into Nanostructures of the Electrified Interface. The remarkable benefit from CV methods for stable Li deposits and SEI derivations during XFC can be attributed to the synergistic effects of the increased number of lithium ions and optimized Li+ solvation sheath near the lithium electrode surface. The charging voltages in CV mode are compared with that in the corresponding CC ways (Figure S14). It is clearly shown that higher polarizations averaged as dozens of millivolts are available in the CV charging procedures. Traditionally, the polarizations include overpotentials in the electrode, at the interface and in the nonaqueous electrolyte. It is difficult to deconvolute each source of polarizations with respect to their complicated temporal-spatial traits.32,58 However, in view of the same average deposition velocities in the electrode, it is

Figure 3. Electrodeposition morphology and interfacial chemistry of cycled Li. (a–j) SEM images of the different stages of Li metal growth on a Li metal surface: Li depositions charged at 16.8 mA cm−2 from 0.2 to 1.0 mA cm−2 (a,c,e,g,i) and Li depositions charged at 300 mV from 0.2 to 1.0 mA cm−2 (b,d,f,h,j). (k,l) Comparisons of the chemical components in SEI after CC or CV methods: XPS spectra of N 1s (k) and XPS spectra of O 1s (l).
reasonably believed that the enhanced internal electric field, referring to the increased polarizations in CV mode, could significantly overcome mass transport resistances and construct beneficial electrified configurations in the electrolyte.

Constant-potential molecular dynamics (MD) simulations, depicted in Figure 4a, were conducted to investigate ion distributions and fine solvation nanostructures around Li⁺ in the 1.0 M LiTFSI-2%LiNO₃-DOL/DME electrolyte. Once lithium deposition initiates on the copper current collector (Figure 2a), the working electrode which we focus on becomes the lithium metal. In this regard, two lithium metal facets here were adopted for lithium electrodes, and were applied with a series of working voltages to investigate the evolutionary trend of interfacial nanostructures with the internal electric field raised (for details, see Experimental Section and Table S1). Ion number density profiles of Li⁺ (uppermost), TFSI⁻ (middle) and NO₃⁻ (bottom), under polarizations of 0, 50, and 100 mV (with respect to the positive electrode), and the corresponding number of Li⁺ (c) in the innermost layer. (d–f) Solvation structures in the interface: Li⁺-NO₃⁻ coordination (d) in the interfacial region and schematic illustrations of solvation sheath (e,f) in electrified interfaces; the atoms are denoted as the same with (a).
surface, as the innermost layers are most-strongly associated with the following reduction behavior.26,42 The height of the primary sharp peak for Li+ gradually increases with the increased polarization, suggesting a growth in the number of cations near the Li electrode. Figure 4 c unambiguously demonstrates a near doubling in the number of Li+ from 0 to 100 mV in the innermost layer (ie. within 0−2.7 Å). It manifests that an enhanced internal electric field in CV mode can substantially facilitate Li+ migrating toward the negatively charged Li electrode for stable Li deposits during XFC.

With respect to anions, surprisingly, TFSI− and NO3− ions with negative charges do not move in the opposite direction in the electric field but also accumulate near the Li electrode with increased negative applied potentials (Figure 4 b). The abnormal phenomenon originates from the strong cohesive cation−anion association (ca. −278.28 kJ/mol for Li+−NO3− and ca. −196.15 kJ/mol for Li+−TFSI−, Table S2) where enriched Li+ can effectively attract more anions.26 The anion distributions under negative polarization can be well understood by the potential of mean force (PMF) profiles43 (see Figure S15), representing the free-energy variation as a function of distance to the electrode surface. The well-defined negative minima of PMF curves for NO3− and TFSI− (Figure 4 b) were observed under the polarization from 0 to 100 mV, indicating that NO3− and TFSI− ions can accumulate near the Li electrode under negative polarization. Meanwhile, the free energy relative to the bulk state of NO3− decreases from 0 to 100 mV, suggesting that NO3− ions can accumulate in the innermost layer and increase by a factor of about four at the impressed voltage of 100 mV (Figure S16 and Figure 4 b); however, the free energy of TFSI− remains stable, resulting in a slightly changed of TFSI− within the inner layer. In fact, both types of anions will start to be excluded in electrostatic interactions while the impressed voltage gets quite large (e.g., 1000 mV, see Figure S17). The calculated data demonstrate the unique lithiophilic performance of NO3−, which agrees with previous work for its charge properties and smaller steric effects.42 In the wildly strengthened internal electric field, the intensive distribution of NO3− ions near the Li electrode surface will facilitate the formation of a more uniform and homogeneous SEI layer enriched in nitrides, favorating lower barriers for Li+ transport.

The solvation structure in the presence of NO3− plays a vital role in the formation of SEI and attracts much attention.22,41,44 Nevertheless, deep insight into its electrified solvation sheath near a specific Li electrode has not been shown yet. To obtain the molecular understanding of interfacial solvation sheaths, we calculated the number density function of Li+−NO3− within a region of 0.48 nm adjacent to the negatively charged Li surface. As shown in Figure 4 d, the number density of NO3− to Li+ indicates stronger involvement of NO3− in the solvation sheaths of Li+. The nearly double-increased coordinated number of Li+−NO3− at 100 mV is also reported in the surface region. It means a higher appearance frequency of NO3− in the solvation shell during the charging process in CV modes, which originates from the enhanced internal electric field.
Li+ was conducted to charge the cells with a cut-off voltage of 1.9 V vs Li/ Li0.5. All the batteries were cycled at a mild current of 3.33 mA cm−2 in Figure 5c with a peak up to 27 mA cm−2. As shown in Figure 5a, cells in two charging modes exhibit almost the same steady discharge capacity of 110 mAh cm−2. The voltage selection principle is shown in Figure S18. As lithium titanium oxide (Li4Ti5O12, LTO) has been extensively evaluated with sulfur batteries, we assembled and tested coin cells with either CC (1C, 3.33 mA cm−2) or CV (2.55 V) charging methods. A free-standing matrix of carbon nanofibers was used as the cathode substrate, and the sulfur loading is about 2 mg cm−2. As shown in Figure 6a and Figure S26, the capacity and CE sustainably drop off after the charging current turning to 3.33 mA cm−2 in CV mode because of a fast “active Li” depletion and isolated “dead Li” formation. In comparison, cells in CC mode exhibit a stable specific capacity of 700 mAh g−1 over 70 cycles with the charging time below 12 min (Figure 6b). In addition, it is worth noting that the Li/S batteries deliver higher capacity when they are charged at 2.55 V. It is supposed that the internal electric field in CV mode not only plays a beneficial role in stabilizing Li deposits during fast charging process but also promotes polysulfide anions migrating to the cathode, thus resulting in the mitigation of shuttling effects and higher utilization of sulfur. The role of higher constant voltage during charging in the S cathode side is beyond interest here, and will be focused on this in our future works.

Fast Charging Performance of Li/S and Li/S Batteries. The electrochemical performance of full cells using limited Li as an anode has been tested to demonstrate the potential of CV charging methods for its practical application. The nominal thickness of commercially obtained Li foil is 45 μm, and the specific capacity is measured to be 8.9 mAh cm−2 (Figure S19). As lithium titanate oxide (Li4Ti5O12, LTO) has been extensively evaluated with sufficient data supporting its extraordinary fast-charging stability,32 the cycling performance of LiliTO battery here should be hindered by the Li metal side. All the batteries were cycled at a mild constant current condition for 5 cycles to activate the electrodes. In CV mode, a constant voltage of 1.9 V vs Li/ Li0.5 was conducted to charge the cells with a cutoff current of 3 mA cm−2. The voltage selection principle is shown in Figure S19. As shown in Figure 5a, cells in two charging modes exhibit almost the same steady discharge capacity of 110 mAh g−1. In a conventional CC charging way of 6C, the capacity declines obviously after cycling for just 40 cycles because of the formed dead Li and the exhaustion of the active Li resource (Figure S20 and Figure S21). It depicts that a higher polarization averaged about 150 mV (Figure S22) are also available in the charging procedure. Benefiting from the adaptively enhanced internal electric field, stable cycling performance is achieved in CV after 100 cycles with an extremely short charging time less than 3 min. The charging current profile in Figure 5c with a peak up to 27 mA cm−2 agrees well with that in Li/LiCu models (Figure 2e). As shown in Figure S23, SEI derived from the CV mode verifies its enrichment in nitriles. The robust SEI greatly improves the reversibility of metallic lithium and reduces the cell resistance (Figure 5b). Furthermore, the capacity retention of the LiliTO cells using a thick Li metal as anode remains at 80.1% after 550 cycles in CV, further demonstrating its good stability. Figure 5e,f shows the morphologies of Li deposits with CC and CV methods after cycling. It can be seen that a huge constant current makes dendrite-like Li after 40 cycles and further deteriorates it after 80 cycles. As shown in Figure 5f, a dense surface formed by Li particle is obtained after cycling, showing less mossy Li or fewer dendrites. Traces of densification and convergence still can be found after continuous plating and stripping, suggesting the beneficial impact during XFC for increasing the number of Li+ and constructing a more NO3− involved solvation structure at Li surface in CV. We also conducted an atomic force microscopy (AFM) characterization using an environment controlled AFM (Nanonavi E-Sweep) to avoid air damage to the lithium metal. The relevant data are shown in Figure S24. The morphology measured by AFM shows much smoother Li deposition in CV charging mode which agrees well with that in SEM characterizations. The lithium–sulfur (Li/S) battery is one of the most promising candidates to replace traditional lithium-ion batteries because of its ultrahigh theoretical cathode capacity (1675 mAh g−1) and energy density (2500 Wh kg−1).33 The Li/S battery has a notorious challenge called the shuttling effect.33 The issue originated from the dissolved polysulfide in the electrolyte which can shuttle to the anode surface, making it much more intractable to achieve Li dendrite inhibition due to their severe chemical side reaction. To confirm the positive impact of CV charging mode in Li/S batteries, we assembled and tested coin cells with either CC (1C, 3.33 mA cm−2) or CV (2.55 V) charging methods. A free-standing matrix of carbon nanofibers was used as the cathode substrate, and the sulfur loading is about 2 mg cm−2. As shown in Figure 6a and Figure S26, the capacity and CE sustainably drop off after the charging current turning to 3.33 mA cm−2 in CC mode because of a fast “active Li” depletion and isolated “dead Li” formation. In comparison, cells in CC mode exhibit a stable specific capacity of 700 mAh g−1 over 70 cycles with the charging time below 12 min (Figure 6b). In addition, it is worth noting that the Li/S batteries deliver higher capacity when they are charged at 2.55 V. It is supposed that the internal electric field in CV mode not only plays a beneficial role in stabilizing Li deposits during fast charging process but also promotes polysulfide anions migrating to the cathode, thus resulting in the mitigation of shuttling effects and higher utilization of sulfur. The role of higher constant voltage during charging in the S cathode side is beyond interest here, and will be focused on this in our future works.
CONCLUSIONS

In summary, the electrochemical performances of the Li metal anode in XFC are promoted by applying a constant voltage charging method which constructs the enhanced internal electric field in the battery, compared with the constant current charging mode. The enhanced electrical field stress can physically mitigate the ion concentration gradient while chemically optimizing the nanostructure of SEI. The nitride-enriched SEI is derived from the electrified interfacial structure which contains more NO$_3^-$ anions. As a result, higher CE and dendrite-suppressive morphologies have been achieved in traditional ether-based electrolytes in Li/Cu, Li/LTO, and Li/S batteries in XFC. CV methods using a mild voltage may bridge a brand-new way to drastically shorten the charging time of low-voltage Li metal systems, especially the Li/S battery. The electrolyte components and the working voltages should be further optimized to reach their practical use. Therefore, this work not only enriches the fundamental understanding of the interfacial nanostructure but also provides a practicable way to stabilize Li deposits in XFC.

EXPERIMENTAL SECTION

Materials. The salts LiTFSI (99.8%), lithium hexafluoroarsenate (Li$_2$AsF$_6$) (99.9%) and the solvents DOL (99.95%), DME (99.95%), ethyl methyl carbonate (EMC) (99.9%), fluoroethylene carbonate (FEC) (99.9%) are purchased from DodoChem. LiNO$_3$ (99.99%) is bought from Aladdin reagent Co., Ltd. The preparation is illustrated: 1 M LiTFSI in DOL/DME (1:1; v- (v)) with 2 wt % LiNO$_3$ and 1 M Li$_2$AsF$_6$ in FEC/EMC (3:7, v- (v). Ultrathin Li metal foils are supported by China Energy Lithium Co., Ltd. The lithium titanium oxide (LTO) electrode is prepared by mixing LTO, conductive carbon, and PVDF binder with a ratio of 8:1:1. The mass loading of LTO is about 5.5 mg cm$^{-2}$. The C electrode is prepared as our earlier report$^{[45]}$ and the sulfur loading is 2 mg cm$^{-2}$.

Electrochemical Measurements. The LAND Electrochemical Testing System and Solartron Analytical Electrochemical Workstation were used to study the electrochemical performance of lithium metal-based cells. Li/Cu cells were precycled at $-0.01$–$2$ V in $0.1$ mA cm$^{-2}$ for $5$ cycles to fully remove the contamination. Ten cycles in which a fixed amount of Li (1 mA cm$^{-2}$, 1 mA h cm$^{-2}$) was plated on Cu and stripped at 1 mA cm$^{-2}$ until the cutoff voltage to 1 V vs Li$^+$/Li$^-$, were conducted for both CC and CV methods to form a preliminary SEI on the Cu current collector in advance. The first formal plating cycle was then started in a constant current or a constant voltage, followed by complete lithium stripping to 1 V vs Li$^+$/Li$^-$. The CE was calculated as the Li stripping capacity divided by the Li plating capacity during a single cycle. Impedance measurements were performed in the frequency range of 100 kHz to 0.01 Hz with a 10 mV amplitude. The electrolyte used for the Li/LTO and Li/S batteries was 1 M LiTFSI in DOL/DME (1:1, v- (v) with 2 wt % LiNO$_3$. No unexpected or unusually high safety hazards were encountered in the experimental protocols.

Characterizations. The surface morphologies of deposited Li were characterized by a field emission scanning electron microscope (SEM, SU-8010, Hitachi). The surface chemistry of Li was investigated by X-ray photoelectron spectroscopy (XPS) on ESCALAB 250Xi, Thermo Fisher Scientific Inc., U.S.A. The cells were disassembled in the Ar-filled glovebox after cycling. The electrodes were washed with DME and then dried for 6 h in the glovebox at room temperature for SEM and XPS analyses. The Young’s modulus of the interface of Li deposition in CC and CV charging methods was estimated using nanoindentation analysis (Nano Indenter G200).

Computational Procedure. Molecular dynamics (MD) simulations were utilized to investigate the electrical double layer structure of LiTFSI/LiNO$_3$/DOL/DME electrolyte at the lithium electrode surfaces. Specifically, the salts (LiTFSI and LiNO$_3$) and solvents (DOL and DME) were modeled with an all-atom force field, which has been proved to reproduce the experimentally measured properties.$^{[46]}$ A five-layer Li (001) metal facet was adopted for the lithium electrode.$^{[47,48]}$ The size of the simulation system was chosen as long enough to reproduce the bulk-like state of the electrolyte in the central region between two electrode surfaces, and the simulation cell contained 90 LiTFSI, 27 LiNO$_3$, 648 DOL, and 432 DME. All simulations were performed in NVT ensemble with the MD package GROMACS.$^{[59]}$ Temperature was controlled through the Nosé–Hoover thermostat$^{[50]}$ at 300 K with coupling constants of 1 ps. A cutoff distance of 1.2 nm was employed for the van der Waals interactions via direct summation; a similar cutoff length was adopted in the calculation of electrostatic interactions in the real space. The long-range electrostatic interactions were computed via the PME method.$^{[51]}$ An FFT grid spacing of 0.1 nm and cubic interpolation were used to compute the electrostatic interaction in the reciprocal space. The equation of motion was solved with a leapfrog integration algorithm, with a time step of 2 fs. Especially, the constant potential method (CPM)$^{[52,54]}$ was employed to allow the fluctuations of the charges on electrode atoms to ensure an adequate description of the electrode polarization effects in the presence of electrolytes. To guarantee the accuracy, the electrode charges were calculated every time step in simulation. Five different potentials were applied between two electrodes (i.e., 0, 50, 100, 400, and 1000 mV). For each simulation, the MD system was first heated at 500 K for 4 ns and then annealed to 300 K over a period of 2 ns, following by another 20 ns to reach equilibrium. After that, another 10 ns production was performed for analysis. Each case was repeated three times with different initial configurations to certify the accuracy of the simulation results.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.1c01014.

Complete experimental details and additional characterizations, including performance results, equivalent circuit for EIS, post-mortem SEM images, XPS analysis, and MD results (PDF)

AUTHOR INFORMATION

Corresponding Authors

Yi He – State Key Laboratory of Chemical Engineering, Institute of Pharmaceutical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China; orcid.org/0000-0002-8807-0892; Email: yihezj@zju.edu.cn
Guang Feng – State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong

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ACS Cent. Sci. 2021, 7, 2029–2038
University of Science and Technology (HUST), Wuhan 430074, China; orcid.org/0000-0001-6659-9181; Email: gfeng@hust.edu.cn

Yingying Lu — State Key Laboratory of Chemical Engineering, Institute of Pharmaceutical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China; ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China; orcid.org/0000-0001-9713-8441; Email: yingyinglu@zju.edu.cn

Authors

Xinyang Wang — State Key Laboratory of Chemical Engineering, Institute of Pharmaceutical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China; ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China

Ming Chen — State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

Siyuan Li — State Key Laboratory of Chemical Engineering, Institute of Pharmaceutical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China; ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China

Chang Zhao — State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

Weidong Zhang — State Key Laboratory of Chemical Engineering, Institute of Pharmaceutical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China; ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China; orcid.org/0000-0001-9556-3735

Zeyu Shen — State Key Laboratory of Chemical Engineering, Institute of Pharmaceutical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China; ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou 311215, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.1c01014

Notes

The authors declare no competing financial interest.

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