Stable Li metal anode by crystallographically oriented plating through *in-situ* surface doping

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ABSTRACT Lithium (Li) metal is regarded as the holy grail anode material for high-energy-density batteries owing to its ultrahigh theoretical specific capacity. However, its practical application is severely hindered by the high reactivity of metallic Li against the commonly used electrolytes and uncontrolled growth of mossy/dendritic Li. Different from widely-used approaches of optimization of the electrolyte and/or interfacial engineering, here, we report a strategy of *in-situ* cerium (Ce) doping of Li metal to promote the preferential plating along the [200] direction and remarkably decreased surface energy of metallic Li. The *in-situ* Ce-doped Li shows a significantly reduced reactivity towards a standard electrolyte and, uniform and dendrite-free morphology after plating/stripping, as demonstrated by spectroscopic, morphological and electrochemical characterizations. In symmetric half cells, the *in-situ* Ce-doped Li shows a low corrosion current density against the electrolyte and drastically improved cycling even at a lean electrolyte condition. Furthermore, we show that the stable Li|LiCoO₂ full cells with improved coulombic efficiency and cycle life are also achieved using the Ce-doped Li metal anode. This work provides an inspiring approach to bring Li metal towards practical application in high energy-density batteries.

Keywords: Li metal anode, crystallographically oriented plating, *in-situ* cerium doping, low surface energy

INTRODUCTION

Nowadays, there is a growing need to develop high-energy-density batteries for power applications, such as portable electronic devices, and electric vehicles [1–3]. Decades after the commercialization, conventional lithium (Li) ion batteries (LIBs) have reached a performance close to their theoretical limitation in terms of

gravimetric/volumetric energy densities. Li metal batteries using metallic Li as anodes have the potential to reach an energy density beyond the limitation of LIBs as a result of the ultrahigh theoretical specific capacity (3860 mA h g⁻¹) of metallic Li, the low electrochemical reduction potential (−3.04 V vs. standard hydrogen electrode) and the low density (0.534 g cm⁻³) [4–6]. However, Li metal batteries typically show low coulombic efficiency (CE) and thus poor cycling life due to the high reactivity of Li metal with the commonly used liquid electrolytes and the formation of mossy and dendritic Li, which hinder their realization in practice [7,8]. The high reactivity readily promotes aggressive formation of a solid electrolyte interphase (SEI) on Li metal [8–10]. The as-formed SEI alters the local electric field and the Li-ion flux during plating/stripping, which stimulates the growth of a mossy/dendritic Li. The SEI has poor passivation and insufficient mechanical strength to suppress the growth of mossy/dendritic Li and, consequently, the SEI breaks down with further exposure of Li and reaction with electrolyte. This repeated process leads to accumulation of isolated mossy/dendritic Li covered by a thick SEI and continuous consumption of electrolyte, resulting in failure of the cell [11–15].

Many approaches have been taken to address the above-mentioned issues in order to improve Li plating/stripping [16–18]. Optimization of the electrolyte is a widely used approach to improve SEI formation and facilitate uniform deposition of Li metal [19], including using new electrolytes [20–23], highly concentrated electrolytes [24–27] and/or new additives [28–30]. Another efficient method is the modification of the interface between Li metal and electrolyte by applying an artificial layer of materials such as organosulfide, polyvinyl alco-

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hol, highly elastic polyrotaxane, LiF/h-BN or $\text{Li}_2\text{S}_6/\text{P}_2\text{S}_5$ [31–38].

Intrinsically, Li is a kind of alkali metal with a body centered cubic (BCC) crystal structure [39–41]. The plating of metallic Li is electrochemical nucleation and growth of Li crystals that is strongly related to the crystal structure and orientation as well as surface energy of Li metal substrate, along with the electrolyte and interface properties as mentioned above [42–47]. Following the thought, herein, we developed an approach of an *in-situ* elemental doping to Li metal and surprisingly found Li metal can plate/strip with a preferred crystalline orientation with low surface energy and thus result in a low reactivity against the electrolyte. By this *in-situ* elemental doping into Li metal, we demonstrated Ce doping at the top surface of Li metal facilitated the crystallographically oriented growth of Li metal along the [200] direction with uniform Li plating morphology verified by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Density functional theory (DFT) calculations further confirmed that Ce-doped (200) crystal facets had the lowest surface energy, even lower than any low-surface-energy facets of the native Li crystal. Benefiting from low-surface-energy facets exposed to the electrolyte, the decrease in reactivity of Li metal towards the electrolyte was verified by the observation of a low corrosion current density. As a result, Li plating/stripping showed an improved CE in Li|Li symmetric cells, even at lean electrolyte condition (8.6 μL electrolyte per 1 mA h Li metal). Furthermore, Li|LiCoO₂ full cells utilizing the *in-situ* Ce-doped Li metal demonstrated a superior cycling stability. The crystal-orientation controlled growth of Li metal provides a novel pathway to address the challenge of Li metal anodes and to improve the performances of high-energy-density Li metal batteries.

EXPERIMENTAL SECTION

Pre-treatment of lithium metal anode

Firstly, 500 mg of cerium fluoride (CeF_3) and 200 mg of polyvinylidene fluoride (PVDF) were dispersed in 50 g of dimethyl sulfoxide (DMSO). The mass percent of PVDF for total solid materials is 28.6%. The mixture was magnetically stirred overnight. Subsequently, the slurry was coated on a Li foil in an argon-filled glove box ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). The Li foil with the CeF_3 coating was transferred into a vacuum oven and dried at 60°C for 12 h. Before use, the modified Li foil was punched into electrodes with a diameter of 15.0 mm. Lithium metal coated by lithium fluoride (LiF) was prepared with the

same procedure and used as the control sample.

Preparation of LiCoO₂ cathode

The slurry of lithium cobalt oxide (LiCoO_2) for the cathode was made by mixing LiCoO_2 , Super-P and PVDF in a weight ratio of 8:1:1. The mixture was magnetically stirred for 1 h to make uniform slurry and the obtained slurry was cast onto the aluminium (Al) foil and then dried at 100°C in vacuum overnight. The cathode was punched into electrodes with a diameter of 12.0 mm. The loading of active materials is approximately 8.0 mg cm^{-2} .

Electrochemical measurements

All electrochemical measurements were carried out in standard CR2032 coin-type cells assembled in an argon-filled glove box ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). The electrolyte was 1 mol L^{-1} lithium hexafluorophosphate (LiPF_6) in ethylene carbonate/diethyl carbonate=1:1 (EC/DEC=1:1). To assemble the symmetrical cell, Li foil, separator (Celgard 2400) and Li disk (15 mm diameter) were placed in a sandwich structure with 40 μL (sufficient) and 15 μL (lean) of electrolyte, respectively. The capacity for Li plating-stripping was set as 1.0 mA h cm^{-2} . The CE was investigated in Li|Cu half-cells, using Ce-doped Li metal as anode, Cu as cathode and 1 mol L^{-1} LiPF_6 in EC/DEC=1:1 as electrolyte. The Li|Cu half-cells were operated at a current density of 1.0 mA cm^{-2} and a capacity density of 2.0 mA h cm^{-2} . Li|LiCoO₂ full cells were assembled in a standard CR2032 type coin cell with 20 μL electrolyte. The voltage range was limited to 3.0–4.2 V in each cycle. The corrosion test was conducted at a CHI electrochemical station with a voltage range from –0.15 to 0.15 V at a scanning rate of 1.0 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was carried out on a Solartron analytical instrument within a frequency range from 0.1 Hz to 1 MHz at room temperature.

Characterization

An XRD-6100 powder diffractometer was used to record XRD patterns with Cu K α radiation, in the range from 20° to 80° with a scanning speed of 5° min^{-1} . The sample was covered by Kapton membrane to avoid air exposure. The ESCALAB Xi+ was used for X-ray photoelectron spectroscopy (XPS) with monochromatic Al K α radiation under a vacuum of 2×10^{-6} Pa. The morphologies of the electrodes after cycling were characterized by a Gemini SEM 500 field-emission scanning electron microscope (FESEM).

Calculation of surface energy with DFT

The Vienna *Ab-initio* Simulation Package (VASP) was

used to conduct DFT calculation with the projector augmented wave method [48]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was adopted [49]. The kinetic energy cutoff for wavefunction expansion was set to 520 eV. Monkhorst-Pack k-point grids of $19 \times 19 \times 19$, $9 \times 9 \times 1$ and $3 \times 3 \times 1$ were used for bulk BCC Li, pure Li slabs and Ce-doped Li supercell slabs, respectively. (200), (211) and (110) Li slabs were expanded to 2×2 , 4×2 and 4×2 supercell in order to keep the same total number of atoms in each slabs, and then only one Ce was doped into one surface leading to 1/95 Li/Ce ratio in every slabs. Atomic positions and lattice constants were fully relaxed in bulk Li. The relaxed lattice constant was used in two middle atomic layers for slab calculations. In addition, the two layers on surfaces of slabs were relaxed to get surface effects. The periodic boundary condition was applied along the x and y axes and vacuum space was applied along the z axis at least 20 Å to safely avoid artificial interaction between the slabs and periodic images. All relaxations were terminated until the differences of energy and forces were less than 10^{-5} eV and 0.01 eV Å^{-1} , respectively.

Calculation of texture index and total surface energy

Quantitative analyses of XRD peaks can be described by texture index (TI), obtained with the following equation:

$$TI = \frac{I_{hkl}/I_{hkl}^0}{\frac{1}{n} \sum (I_{hkl}/I_{hkl}^0)},$$

where I_{hkl} and I_{hkl}^0 are the integral intensities of the (hkl) diffraction peaks for the various electrodes and standard lithium (JCPDS 15-0401), respectively, and n is the number of diffraction peaks in the XRD patterns [39]. The total surface energy of bare Li and Ce-doped Li can be calculated with surface energy of each crystal plane and TI. It is described by the following equation:

$$\bar{E}_{\text{total}} = \sum \frac{TI_{hkl} \cdot E_{hkl}}{\sum TI_{hkl}},$$

where TI_{hkl} is the texture index of the (hkl) diffraction peak and E_{hkl} is the surface energy of (hkl) crystal plane.

RESULTS AND DISCUSSION

The *in-situ* Ce doping into Li was accomplished *via* coating a composite layer of CeF_3 nanoparticles and a polymer on fresh Li metal followed by *in-situ* chemical reduction by Li. To form the composite layer, dried CeF_3 nanoparticles and PVDF were dispersed in DMSO and

stirred to form a slurry, followed by casting on a fresh Li foil (Fig. 1a). The SEM images (Fig. 1b, c) clearly show that the surface of the Li-metal foil is covered by a composite layer containing agglomerated nanoparticles with a mean size of 20 nm (Fig. S1). The thickness of this layer is optimized to be about 1 μm (Fig. 1c).

Because of the lower reduction potential of Li compared with Ce ($\varphi_{\text{Li}^+/\text{Li}}^0 = -3.04 \text{ V}$, $\varphi_{\text{Ce}^{3+}/\text{Ce}}^0 = -2.336 \text{ V}$), CeF_3 nanoparticles can be chemically reduced by Li to form Ce(0) species (e.g., Ce metal or LiCe_x) spontaneously after coating the Li metal surface with CeF_3 . XPS was carried out to verify the chemical reaction between the CeF_3 -containing layer and Li. In the XPS spectra of the CeF_3 -coated Li, the peaks located at 883.9 and 55.7 eV are attributed to metallic Ce (Fig. 2a) and Li^+ in LiF (Fig. 2b), respectively [50]. These results confirm the successful reduction of CeF_3 , generating Ce species and LiF. The Ce species and LiF are also observed on the surface of cycled Li (Fig. S2a, b), showing the stability of this surface modification.

XRD experiments were performed to track the evolution of the crystal structure of cycled Li metal anodes that were retrieved from symmetric Li|Li cells. The XRD patterns of the bare Li and Ce-doped Li are shown in Fig. 2a and b, respectively. In general, texture index (TI) is defined for quantification of the typical texture orientations in crystals, and the facets with TI value greater-than-1 are regarded as the preferred orientation (see details in EXPERIMENTAL SECTION) [39]. As shown in Fig. 2c, Li metal exhibits three reflection peaks related to the (110), (200), and (211) planes. Among these, the (110) plane shows the highest TI of 1.26 for bare Li metal (Table S1), indicating the (110) direction is the preferred orientation of plated Li upon cycling [39]. In contrast, the (200) planes in the Ce-doped Li metal, show the highest TI value (2.34 after 10 cycles) and are thus the preferred growth orientation (Fig. 2d). Noticeably, a reflection peak at a 2θ of 32.4° is observed and attributed to LiCe_3 [51]. We suggest that the interfacial region of Ce-doped Li exists due to the similar ionic radius of Ce with Na and K which can readily form an alloy with Li and thus fundamentally change the surface energy of Li metal and the growth orientation. To verify this hypothesis and illustrate the doping effect of Ce, DFT calculations were performed to calculate the surface energy of different crystal facets [52]. The total energy, surface area and surface energy of all slab structures are summarized in Table S2. In bare Li, the surface energy difference between the three surfaces is $\bar{E}_{\text{Li}}(110) < \bar{E}_{\text{Li}}(211) < \bar{E}_{\text{Li}}(200)$, which means that (110) is the most stable surface and

Figure 1 Schematic illustration of the fabrication process of the *in-situ* Ce-doped Li metal anode (a). Top-view (b) and cross-sectional (c) SEM images of the Ce-doped Li metal.

(200) is a high-activity surface. Interestingly, the Ce doping changes the surface energy and the energy relationship is changed to $E_{\text{Ce-Li}}(200) < E_{\text{Ce-Li}}(110) < E_{\text{Ce-Li}}(211)$. This result indicates that the Ce doping grants (200) plane to have the lowest surface energy (Fig. 2f). Collectively, the total weighted surface energy of the crystalline Li metal can be further calculated using the DFT calculated surface energy and the TI values obtained from XRD patterns (Table S3). It is found that the Ce doping prominently lowers the total weighted surface energy of Li metal upon cycling. This indicates that the Ce doping intrinsically lowers the surface energy of crystal metallic Li and potentially lowers the reactivity of Li metal against the electrolyte [53–55].

Another advantage of the process used for Ce doping is the spontaneous generation of LiF by the *in-situ* chemical reduction of CeF_3 with Li metal. The protective effects of LiF to improve the SEI and cycling of Li metal are well known [56–60]. Following previous reports, a control sample of LiF-coated Li metal (see details in EXPERIMENTAL SECTION) was fabricated, which showed improved cycle life compared with bare Li metal (Fig. S3). However, the preferred plating orientation was not observed in the case of the LiF-coated Li metal (Fig. S4). This demonstrates that the preferred oriented

growth of Li metal originates from the Ce doping rather than LiF coating. In our approach, the LiF particles are spontaneously produced by the interfacial chemical reduction of CeF_3 and are thus in intimate contact with the Li metal. With combined effects from Ce doping and intimate LiF protection, the *in-situ* Ce-doped Li metal possesses low surface reactivity and is expected to show improved electrochemical performance.

More evidence of the effect of lowering the reactivity *via* Ce doping can be obtained from potentiodynamic polarization experiments (Fig. 3) [53]. The potentiodynamic polarization curves show that the Ce-doped Li exhibits a lower corrosion current density during the whole cycling life, which suggests that the Ce-doped Li exhibits a higher corrosion resistance towards the liquid electrolyte. In addition, EIS was conducted to investigate the stabilization of the interface obtained on the Ce-doped Li (Fig. S5a, b). A low and stable impedance demonstrates less accumulation of by-products on the Ce-doped Li metal, resulting from the suppressed side reactions. All above evidences confirm that Ce doping can stabilize the metallic Li metal and lower the reactivity towards electrolyte. Moreover, a Li|Cu half-cell was assembled and operated at a current density of 0.5 mA cm^{-2} and a capacity density of 1.0 mA h cm^{-2} to evaluate the

Figure 2 XPS spectra of Ce 3d_{5/2} (a) and Li 1s (b) of the Ce-doped Li metal before cycling. XRD patterns of bare Li metal (c) and the Ce-doped Li metal (d) after different numbers of cycles. (e) Slab structures of Li with and without Ce doping, atomic positions and lattice constants in fully relaxed configurations. (f) Schematic diagram for surface energy change for (200) planes of Li with/without Ce doping.

CE (Fig. S6). The CeF₃-modified Cu exhibited an ultra-high CE over the lifespan, as high as 99.04% on average over 150 cycles, confirming that the Ce-doped Li metal leads to diminished side reactions with the electrolyte.

Ex-situ SEM was performed to evaluate the morphologies of Li metal anodes after cycling. After 100 cycles, the bare Li metal exhibits a very rough and moss-like morphology (Fig. 4a, c). Moreover, a PVDF-coated (no CeF₃) Li metal shows only marginal improvement (Fig. S7a, b). As reported previously, the presence of LiF and PVDF in an artificial SEI can improve the stability of the protected Li metal, with an improved morphology and expected improved electrochemical performance [61,62]. In our case, the LiF is generated *in-situ*, ensuring an

intimate contact with the Li metal, and the LiF-coated Li metal shows an improved morphology after cycling; however, there still exist cracks and signally increased thickness of the SEI (Fig. S8a, b), which means that just the *in-situ* generated LiF that contacts with Li metal intimately shows insufficient passivating effect to improve the interfacial stability. With the *in-situ* Ce-doped Li metal, a smooth and dense morphology is found after cycling (Fig. 4b, d), further pointing to the important role of Ce doping in the stabilization of Li metal. All above results suggest that the stability of Li towards electrolyte components is remarkably improved by *in-situ* Ce doping, by which the consumption of electrolyte and the accumulation of cracked Li fragments are ef-

Figure 3 Potentiodynamic polarization curves of the Ce-doped Li metal and bare Li metal (a) before cycling, and after (b) 5, (c) 50 and (d) 100 cycles. Comparison of corrosion current density of bare Li metal and Ce-doped Li metal as a function of cycling (e).

Figure 4 Cross-sectional (a) and top-view (c) SEM images of Li metal after 100 cycles without Ce doping. Cross-sectional (b) and top-view (d) SEM images of the Ce-doped Li metal after 100 cycles.

fectively suppressed.

To confirm the improved electrochemical performance of the Ce-doped Li metal, galvanostatic cycling tests were conducted on the symmetric cells with different amounts of electrolyte. At a sufficient electrolyte condition (23 μL electrolyte per 1 mA h Li metal), the cell with Ce-doped Li metal shows no increase of the cell overpotential over 1000 h at a current density of 1.0 mA cm^{-2} (Fig. 5a) and negligible increase over 500 h at a current density of 2.0 mA cm^{-2} (Fig. S9), much better than that of Li anodes without doping (Fig. S10 for PVDF-coated Li metal, and Fig. S3 for LiF-coated Li metal). A high reactivity of Li metal will accelerate the failure of battery, particularly

under the lean electrolyte condition, which is crucial to achieve a high energy-density in practical applications. The rapid fading of the cells with bare Li metal is mainly attributed to the consumption of electrolyte under lean electrolyte condition and the loss of active Li under sufficient electrolyte condition [63,64]. In order to demonstrate the suppressed consumption of electrolyte by Ce doping, symmetric cells with lean electrolyte condition (8.6 μL electrolyte per 1 mA h Li metal) were tested. For the cell with bare Li metal, the polarization increases markedly after only 50 h of cycling, which is most likely due to the degradation and running out of electrolyte, whereas the cell with the Ce-doped Li metal shows negligible change over 300 h of cycling (Fig. 5b). Moreover, there is a retention of electrolyte and no black “dead Li” is found after cycling with Ce-doped Li metal (Fig. S11). To the best of our knowledge, the performance shown here is the best ever reported at such low electrolyte/Li ratio and high current density.

To demonstrate the applicability of the Ce-doped Li metal electrode in practical applications, full Li|LiCoO₂ cells were assembled and tested at rates of 2 and 5 C, respectively. The cell with Ce-doped Li metal delivers an initial specific capacity of 133 mA h g^{-1} and retains a capacity of 95 mA h g^{-1} after 300 cycles at 2 C (1 C = 140 mA h g^{-1} , Fig. 5c and e). Even at the relatively high rate of 5 C, 75% of the initial discharge capacity is retained after 300 cycles (Fig. S12). In contrast, the cells with bare Li metal show a rapid capacity fade to 25 mA h g^{-1} after 350 cycles (Fig. 5c) at 2 C and

Figure 5 Voltage profiles of Li metal electrodes tested in symmetric cells at 1.0 mA cm^{-2} with (a) sufficient electrolyte and (b) lean electrolyte conditions. Cycling performance of Li|LiCoO₂ full cells with bare Li metal and Ce-doped Li metal electrodes at rate of 2 C (c). Discharge profiles of Li|LiCoO₂ full cells with (d) bare Li and (e) Ce-doped Li metal anodes.

62 mA h g^{-1} after only 100 cycles at 5 C. The long cycle life of the full cells with Ce-doped Li metal, particularly under lean electrolyte conditions, further confirms that the suppression of side reactions on Li metal.

CONCLUSIONS

We report on an innovative approach to achieve highly stable Li metal electrodes through surface energy adjustment *via* Ce doping. The Ce doping is accomplished *in-*

situ on Li surface through the reduction of CeF_3 coating. We find that Ce doping can transform the preferred growth orientation of Li metal, from (110) to (200), during the electrochemical plating-stripping process. This change leads to a lower surface energy and significantly suppressed side reactions between Li and the liquid electrolyte. As a result, the Ce-doped Li metal exhibits smooth and dense morphology with cycling. The improved stability is realized over 1000 h cycling in symmetric cell at a current density of 1.0 mA cm^{-2} and a remarkable capacity retention is shown in $\text{Li}|\text{LiCoO}_2$ full cells. The tuning of the surface energy of metallic Li with Ce doping shows a route to low reactive Li metal electrodes for advanced rechargeable Li metal batteries.

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通过原位表面掺杂实现稳定金属锂负极的晶体定向沉积

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摘要 锂金属由于其高理论比容量(3860 mA g^{-1})而被认为是最具潜力的高能量密度锂电池用负极材料。然而, 锂枝晶的不可控生长和金属锂对电解液的高反应活性严重阻碍了其实际应用。区别于以往广泛使用的电解液优化或界面修饰工艺, 本文采用一种原位铈掺杂的策略, 从根本上改变了锂金属的电沉积行为。通过锂电极表面的原位铈掺杂促进锂在电化学过程中沿[200]方向优先沉积, 显著降低金属锂的表面能。光谱、形貌和电化学测试等结果证明, 原位铈掺杂大大降低了锂电极对电解液的反应活性, 使得电极在沉积/脱出过程中具有无枝晶形貌。采用这种策略装配的对称电池中, 锂电极具有低腐蚀电流密度, 甚至在贫液条件下循环寿命也得到显著提升。采用铈掺杂锂负极的锂-钴酸锂全电池可稳定循环300周, 库伦效率和循环寿命得到明显提高。本工作为金属锂负极在高能量密度电池中的实用化研究提供了一种具有启发性的策略。