A Framework with Enriched Fluorinated Sites for Stable Li Metal Cycling

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Abstract: In past decades, lithium-ion batteries (LIBs) were the dominant energy storage systems for powering portable electronic devices because of their reliable cyclability. However, further increase in the energy density of LIBs was met by a bottleneck when low-specific-capacity graphite was used at the anode. Li metal has long been regarded as the ideal anode material for building the next high-energy-density batteries due to its ultrahigh capacity of 3860 mAh·g⁻¹, which is ten times higher than that of graphite. However, using Li metal as an anode in rechargeable batteries is challenging due to its high

uncontrolled volume expansion and aggressive side reactions with liquid electrolytes. In this study, we demonstrate the effect of a three-dimensional (3D) framework with enriched fluorinated sites for Li metal protection. This framework is obtained *via* a facile integration of down-sized fluorinated graphite (CF_x) particles into Li⁺ conducting channels. Thermogravimetry, energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy results show that Li⁺ conducting channels rich in lithium fluoride (LiF) are formed *in situ* across the embedded CF_x particles during the initial lithiation process, leading to fast Li⁺ transfer. Scanning electron microscopy results show that residual CF_x particles could act as high-quality nucleation sites for uniform Li deposition inside the framework. These features could not be achieved with a 2D structure consisting of large CF_x flakes, due to the limited Li⁺ transfer paths and low utilization ratio of CF_x for conversion into LiF-based solid electrolyte interphase (SEI) layers. Consequently, better performance of Li metal anodes in a 3D framework with enriched fluorinated sites is demonstrated. Stable Li plating/stripping over 240 cycles is obtained at a current density of 0.5 mA·cm⁻² for a fixed capacity of 1 mAh·cm⁻² by maintaining a voltage hysteresis below 80 mV. Improved Li-LiFePO₄ full cell performance with a practical negative/positive capacity ratio of 3 is also demonstrated. These results show the rational combination of well-developed 3D Li⁺ transfer channels and enriched fluorinated sites as an optimized interfacial design beyond the single use of a 2D fluorinated interface, giving new insight into the protection of Li metal anodes in high-energy-density batteries.

Key Words: Li metal battery; Li metal anode; Fluorinated graphite; Solid electrolyte interphase; Coulombic efficiency

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一种有助于稳定锂金属循环的富氟化位点框架结构

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摘要: 锂金属是下一代高能量密度二次电池的理想负极材料, 然而它的应用仍然受制于较差的循环稳定性。近期, 二维氟化界面被广泛用于改善锂金属负极的成核机制、沉积形貌和循环稳定性。本工作通过将体积缩小化的氟化石墨颗粒与锂离子传导网络结合, 获得了一种富氟化位点的三维框架结构。实验结果证明此类三维氟化结构可显著提升锂金属负极在不同电流密度和容量下的循环稳定性, 且优于二维氟化界面结构。通过本工作的研究, 证明了相较于单纯的二维氟化界面, 三维锂离子传导网络和富氟化位点的合理结合可以成为一种改进的界面结构用于锂金属负极保护, 为高能量密度锂金属电池的负极保护提供了新的设计思路。

关键词: 锂金属电池; 锂金属负极; 氟化石墨; 固液界面; 库伦效率

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1 Introduction

The state-of-the-art lithium ion batteries (LIBs) are approaching their theoretic energy limit, and can hardly respond to the requirements from the ever-growing market of portable electronics, electric vehicles and smart energy storage grids^{1,2}. During the last decade, Lithium (Li) metal have aroused wide attentions with aim of building next high-energy-density Li metal batteries (LMBs), due to its ultrahigh specific capacity (3860 mAh·g⁻¹) and the lowest redox potential (−3.04 V *vs* Standard Hydrogen Electrode). The high Fermi level of Li metal often leads to large energy gaps against most of the conventional electrolyte solvents, forming a solid electrolyte interphase (SEI) which is helpful to separate Li from electrolyte in static conditions³. However, unlike the graphite anode in LIBs, the native SEI layers pre-formed on the Li surfaces are not able to withstand the uneven deposition and huge volumetric change caused by the delocalized Li⁺ flux on “hostless” Li surface, while the regenerations of SEI layers posterior to the surface cracks are often accompanied by Li and electrolyte consumptions, internal impedance increase and fast fading of coulombic efficiency (CE) of the LMBs^{4,5}.

The native SEI layers are generally an inhomogeneous mixture of inorganic species such as LiF or Li₂O, and organic species such as ROLi and ROCO₂Li, exhibiting poor uniformity for Li⁺ conduction, Li nucleation and deposition⁶. Interfacial engineering to regulate the SEI layers has been devoted as a main roadmap to stabilize the Li/electrolyte interfaces, including the SEI modification by electrolyte formulations^{7–13} and construction of artificial SEI layers and host structures^{14–20}. In particular, fluorine (F) has recently been revealed as a critical element to affect the interfacial stability of Li metal anodes. Enriching the F content in the SEI layer *via* electrolyte additives^{21–24}, or constructing artificial fluorinated layers have

shown prominent effects to boost the cyclability of Li metal anodes^{25–28}.

Although the F-containing interfaces exhibit reinforced mechanical stability, high Li⁺ diffusivity and inhibition of dendritic Li growth, the actual efforts are mainly emphasized on the designing of two dimensional (2D) F-containing protective layers to suppress side reactions between Li metal and electrolytes. Further improvements of using fluorinated structures to afford stable Li metal cycling for higher current densities and capacities are still expected. Herein, we report a three dimensional (3D) framework with enriched fluorinated sites, leading to fast Li⁺ transfer and abundant nucleation sites for uniform Li deposition inside the framework (Fig. 1b), significantly outperforming the 2D structure consisted of large CF_x flakes (Fig. 1a). The related physic-chemical properties and electrochemical performances of the investigated protective structure for Li metal anodes are explored.

2 Experimental

2.1 Material preparations

Fluorinated carbon (CF_x) flakes with F content above 50% were purchased from Shanghai CarFluor Chemicals Co., Ltd., and were used as received. The down-sized CF_x particles were obtained using a ball-mill (PM200, Retsch GmbH Inc., Germany) operated at a grinding speed of 400 r·min⁻¹ for 10 h in ethanol medium, and denoted as CF_x-400. The obtained CF_x-400 particles were dried under 80 °C until the ethanol was completely evaporated.

2.2 Materials characterizations

The crystalline phases were characterized by X-ray diffraction (XRD) with a Bruker D8 advanced diffractometer using Cu K_α (λ = 0.15406 nm) radiation (Bruker axs, D8 Advance). The microstructure analysis was conducted by scanning electron

Fig. 1 Schematic representations of (a) large CF_x flakes based 2D structure and (b) down-sized CF_x particles based 3D framework for Li metal cycling.

microscopy (SEM, FEI, QUANTA 250 FEG) under the emission voltage of 5 kV, while 10 kV was applied during the measurements of electron dispersive spectrometer (EDS). All the samples were coated with Au thin film to obtain high-quality images. Surface analysis was carried out with an X-ray photoelectron spectrometer (XPS, Axis Ultra DLD), which was excited by $\text{Mg } K_{\alpha}$ radiation source at a constant power of 100 W (15 kV, 6.67 mA). The weight ratio of organic species in the investigated structures were evaluated using Thermo-gravimetry (TG, PerkinElmer Diamond TG/Differential Thermal Analysis (DTA)) on a temperature range of 30–800 $^{\circ}\text{C}$, with a ramping rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under an argon atmosphere. Brunauer-Emmett-Teller (BET) surfaces were obtained through nitrogen gas adsorption measurements with an ASAP2020HD88 analyzer from Micromeritics, Inc.

2.3 Electrochemical measurements

2032R coin cells were used for cell assembly. The separator films with a thickness of 20 μm were purchased from Celgard, and cut into discs with a diameter of 19 mm, in which 50 μL electrolyte of 1 $\text{mol}\cdot\text{L}^{-1}$ LiPF_6 in ethylene carbonate (EC) and diethyl carbonate (DEC) 1 : 1 by volume, with 5% (volume fraction) fluoro-ethylene carbonate (FEC) was added. The CF_x -based structures were prepared by mixing CF_x or CF_x -400: polyvinylidene fluoride (PVDF) at a mass ratio of 8 : 2 in *N*-methyl pyrrolidone (NMP). The slurries were cast onto copper (Cu) foils, followed by vacuum drying at 120 $^{\circ}\text{C}$ for 12 h to obtain the electrodes. The mass loading of CF_x or CF_x -400 is $\sim 5 \text{ mg}\cdot\text{cm}^{-2}$. Li cycling CE on CF_x or CF_x -400 structures were assessed in Li-Cu cells, by plating Li at desired current density and capacity followed by stripping Li to a cut-off voltage of 0.5 V vs Li/Li^+ . The LiFePO_4 electrodes were obtained by mixing LiFePO_4 : Super-P: PVDF (8 : 1 : 1 by wt.) in NMP. The slurries were cast on aluminum foils, followed by vacuum drying at 120 $^{\circ}\text{C}$ for 12 h. The capacity loading of the obtained LiFePO_4

cathode is $\sim 0.85 \text{ mAh}\cdot\text{cm}^{-2}$ ($170 \text{ mAh}\cdot\text{g}^{-1}$). The Li- LiFePO_4 cells were cycled between 2.5 and 4.4 V vs Li/Li^+ with charge/discharge rates of 0.5C/0.5C. The anodes used in Li- LiFePO_4 cells were bare Cu or CF_x -400 on which $2.5 \text{ mAh}\cdot\text{cm}^{-2}$ Li was pre-deposited (corresponding to a negative/positive capacity, N/P ratio ~ 3), denoted as Cu@Li and $\text{CF}_x\text{-400@Li}$, respectively. It should be mentioned that 10 cycles of discharge/charge process between 0–1 V vs Li/Li^+ at a current density of $0.5 \text{ mA}\cdot\text{cm}^{-2}$ were applied to the CF_x -400 electrode to complete the formation of the inner Li^+ conducting channels prior to the fabrication of composite anode. The electrochemical impedance spectroscopy (EIS) spectra were measured using a potentiostat/galvanostat 1470E equipped with a frequency response analyzer 1455A from Solartron. The EIS measurements were performed under potentiostatic mode, from 1×10^5 to 1×10^{-1} Hz with a voltage perturbation of 5 mV.

3 Results and discussion

The morphology of CF_x flakes is shown in Fig. 2a, with a typical size of dozens of micrometers. An evident down-sized morphology was observed for CF_x -400 particles, which are ranged on 1–2 μm (Fig. 2b). The down-sizing of CF_x also involved the increased BET surface, which is $\sim 196.84 \text{ m}^2\cdot\text{g}^{-1}$ for CF_x -400, compared to $\sim 156.78 \text{ m}^2\cdot\text{g}^{-1}$ for CF_x (Fig. S1b, Supporting Information). It should be mentioned that the sharply changed morphologies from CF_x to CF_x -400 do not affect their crystal structures and chemical compositions, as shown by their quasi-identical XRD patterns (Fig. S1a, Supporting Information), similar mass ratio of F element ($\sim 60\%$) on the C and F overlapped uniform surfaces (Table S1, Figs. S2a and S2b, Supporting Information). XPS wide scans indicate that C and F are the main elements on pristine CF_x and CF_x -400 except some traces of O impurities (Fig. S3a, Supporting Information), and obvious peaks of $-\text{CF}$ (688.6 eV), $\text{C}-\text{C}$ (284.6 eV), $\text{C}-\text{CF}_2$

Fig. 2 SEM images of pristine (a) CF_x and (b) CF_x-400; (c) F 1s and (d) C 1s XPS spectra of pristine CF_x and CF_x-400.

(286.5 eV), -CF (290.1 eV) and -CF₂ (291.6 eV) are observed on the amplified F 1s and C 1s spectra (Figs. 2c and 2d). Thus, the CF_x and CF_x-400 based structures could be used as very representative model structures to assess the down-sizing effect of CF_x on the protection of Li metal anodes.

As above-mentioned, the down-sized CF_x-400 particles are expected to form a framework in which fast Li⁺ conducting channels are formed. To assess the latter, CF_x and CF_x-400 based electrodes were fabricated *via* doctor blade coating of CF_x:PVDF and CF_x-400:PVDF mixtures on Cu foils, which were subjected to lithiation process down to 0 V vs Li/Li⁺ (Fig. 3a and Table S2, Supporting Information). For CF_x, a specific capacity of 1.16 mAh·mg⁻¹ Li was achieved at 0 V vs Li/Li⁺, corresponding to the formation of SEI layers and lithiation of CF_x flakes. Meanwhile a higher specific capacity of 1.64 mAh·mg⁻¹ Li was achieved for CF_x-400, whereas the additional capacity contribution should arise from the formation of Li⁺ conducting channels in the framework consisted of down-sized CF_x-400 particles. The lithiation capacities for thinner CF_x and CF_x-400 with a mass loading ~1 mg·cm⁻² were also compared. As shown in Fig. S4 (Supporting Information), similar lithiation capacities were obtained, which were ~1.24 and ~1.78 mAh·g⁻¹ for CF_x and CF_x-400, respectively, showing the intrinsic lithiation capacities for these CF_x materials. The formation of Li⁺ conduction channels in the CF_x-400 framework was further demonstrated by TG measurements, whereas the TG curves of the lithiated CF_x and CF_x-400 showed the continuous weight loss from the initial stage of temperature ramping, while the weight loss of pristine CF_x and CF_x-400 powders only take place above 400 °C (Fig.

S5, Supporting Information). These results show that the weight loss occurring at early stage of TG measurements (below 400 °C) for the lithiated CF_x and CF_x-400 should arise from the organic species in the SEI layers and/or Li⁺ conducting channels. Furthermore, a weight loss of ~18% was observed for the lithiated CF_x-400 electrode, while it was only ~9% for the lithiated CF_x (Fig. 3b). Since the weight ratio and absolute quantity of CF_x and CF_x-400 in the coating slurry mixtures were strictly fixed at the same values, the higher weight loss observed on the TG curves should arise from the formation of the inner Li⁺ conducting channels including partially organic species in the CF_x-400 framework.

The morphologies of lithiated CF_x and CF_x-400 are shown in Fig. 3c, d, and Fig. S6a, S6b (Supporting Information). Evident cracks and pulverizations are observed on CF_x flakes (Figs. 3c and S6a (Supporting Information)), depicting their structural instability during lithiation and eventual collapse for further Li deposition. The amplified SEM images of pristine and lithiated CF_x flakes are shown in Fig. S7 (Supporting Information), whereas evident cracks could be observed on the lithiated flake surfaces, which are mainly caused by the strain rooted in the lithiation process. This feature further demonstrates the necessity of down-sizing the CF_x particles to mitigate the deformation caused by mechanical strain during lithiation process. In contrast, intact structure is maintained for the CF_x-400 framework (Figs. 3d and S6b (Supporting Information)), indicating that the initial lithiation was mainly rooted in the formation of Li⁺ conducting channels without affecting the overall structure of the framework, which are beneficial to

Fig. 3 (a) The 1st discharge curves of CF_x and CF_x-400 with a mass loading ~1 mg·cm⁻²; (b) TG curves of lithiated CF_x and CF_x-400; SEM images of lithiated (c) CF_x and (d) CF_x-400; (e) F 1s and (f) C 1s XPS spectra of lithiated CF_x and CF_x-400.

enable uniform Li deposition in subsequent cycling. The surface components of the lithiated electrodes were analyzed by EDS and XPS, showing similar chemical compositions with co-existence of C, O and F elements (Table S1, Fig. S2c, S2d and S3b, Supporting Information). Besides C and F, the presence of O should arise from the solvent decompositions. On the F 1s XPS spectra, in addition to the peak of -CF (688.5 eV), the peak of LiF (685.5 eV) appeared (Fig. 3e), indicating the conversion of CF_x into LiF during the lithiation process. It should be mentioned that FEC from the electrolyte could also be reductively decomposed into LiF²¹, thus a FEC-free electrolyte (1 mol·L⁻¹ LiPF₆ in EC : DEC 1 : 2 by vol.) was used to perform the lithiation of CF_x and CF_x-400. As shown in Fig. S8, Supporting Information, evident peaks of LiF were clearly observed for both CF_x and CF_x-400, demonstrating the formation of LiF through the lithiation of CF_x materials. Meanwhile, the formations of organic species are observed on C 1s spectra, shown by the peaks of C-C-O (285.6 eV) and CO-CO₂Li (288.4 eV) which should correspond to the organic species included in the SEI layers on CF_x or in the Li⁺ conducting channels in CF_x-400.

Based on the above results, it can be concluded that the solvent decompositions and conversions of CF_x into LiF occurred during the lithiation processes of CF_x and CF_x-400, leading to the formation of LiF-imbudded SEI layers on the CF_x flakes or LiF-incorporated Li⁺ conducting channels in the CF_x-400 framework. Meanwhile the higher content of organic species from the Li⁺ conducting channels (weight loss on TG curves, Fig. 3b) can maintain the integrity of the CF_x-400 framework as a stable host to accommodate Li deposition. It should be mentioned that the CF_x materials have a low electronic conductivity, while no electronic conductive agents were added into the CF_x-400 framework. However, the latter could be a beneficial feature that

forces the initial Li deposition to occur in the bottom of the framework whereas the reduction into Li metal could be achieved by receiving the electrons from the current collector, and this initially deposited Li layer could further serve as electron conductor for subsequent Li deposition that progressively fills the void space of the framework. Based on the synergism of the LiF-incorporated Li⁺ conducting channels and down-sized CF_x-400 particles, the stability of Li metal cycling could be much improved in the CF_x-400 framework, as shown in the following paragraph.

The EIS measurements were conducted to assess the interfacial stability of Li-Cu cells using bare Cu, CF_x or CF_x-400 coated Cu as working electrodes. Before cycling, large impedances were observed for all the samples due to the lack of Li⁺ conducting interphase (Fig. 4a). After the formations of SEI layers by cycling the Li-Cu cells for 10 cycles, the typical semi-circles representing the interfacial impedances were clearly observed for all the samples, which are 33.57, 134.64 and 45 Ω for bare Cu, CF_x and CF_x-400, respectively (Fig. 4b). Herein, the interfacial impedances of CF_x and CF_x-400 are higher than that of bare Cu, indicating that these artificial structures engender unavoidable additional impedances to the interfacial charge transfer. It should be mentioned that the bulk electronic conductivity of fluorocarbon is depending on the fluorination degree, higher the fluorination degree, lower the electronic conductivity. In the present case, the F content is above 50%, leading to relatively poor electronic conductivity. However, the CF_x-400 framework exhibits much smaller interfacial impedance increase, thanks to the well cross-linked Li⁺ conducting channels. After 30 cycles, the interfacial impedances were increased to 60.86 and 157.09 Ω for bare Cu and CF_x, respectively, while it was stably maintained at ~45 Ω for CF_x-400 (Fig. 4c). These results depict the serious side product

Fig. 4 Nyquist plots of Cu, CF_x and CF_x-400 electrodes (a) before cycling, at the (b) 10th and (c) 30th cycles; SEM photos of (d) Cu, (e) CF_x and (f) CF_x-400 electrodes after 30 cycles of 1 mAh·cm⁻² Li plating/stripping; (g, h) typical voltage profiles of Li plating on (g) CF_x and (h) CF_x-400 at 0.5, 1, 2 and 3 mA·cm⁻²; (i) nucleation overpotentials of Li plating on CF_x and CF_x-400 at 0.5, 1, 2 and 3 mA·cm⁻².

accumulations on bare Cu and CF_x upon cycling, which were further confirmed by their SEM images, showing tremendous dendritic deposits (Fig. 4d, e). Although the LiF-embedded SEI layers were revealed as optimized surface layers to improve the cycling stability of Li metal anodes, the present results show that the lack of Li⁺ conducting channels still hinders uniform deposition on the 2D CF_x flakes. In contrast, an intact surface was kept for the CF_x-400 framework (Fig. 4f), depicting uniform Li plating/stripping occurring in this optimal structure, consistent to the stabilized interfacial impedances as above-demonstrated.

The measurements of interfacial impedances and Li deposition morphologies indicate a much improved Li⁺ transfer kinetic on CF_x-400. To address the latter, the Li nucleation overpotentials on CF_x and CF_x-400 were assessed by measuring the voltage profiles of Li plating at 0.5, 1, 2 and 3 mA·cm⁻², as shown in Fig. 4g, h. The as-obtained Li nucleation overpotentials (the difference between the voltage tip and plateau) are 69.1, 138.4, 154.6 and 200.2 mV for CF_x at 0.5, 1, 2 and 3 mA·cm⁻²,

respectively, and 27.8, 43.0, 54.1 and 79.4 mV for CF_x-400 at 0.5, 1, 2 and 3 mA·cm⁻², respectively (Fig. 4i). Thus, for a given current density, the nucleation overpotential on CF_x-400 is only 30%–40% of that on CF_x. These results clearly indicate the much improved Li⁺ transfer kinetic in the CF_x-400 framework.

The Li plating/stripping morphologies were systematically carried out at various areal capacities, as shown in Fig. 5. Despite the presence of LiF in the formed SEI layer, dendritic morphologies were still observed for Li plating up to 8 mAh·cm⁻² on CF_x (Fig. 5a), indicating the sluggish Li⁺ transfer on the large CF_x flakes. Furthermore, the evidence of side products formed on CF_x could be revealed by the remaining filament species after Li stripping process to 0 mAh·cm⁻², whereas serious accumulation of side products was observed (Fig. 5a). In sharp contrast, noodle-like deposits were observed for Li plating on CF_x-400, whereas the sizes of deposits increased with the areal capacity (Fig. 5b), leading to the low-surface-area contact with electrolyte and reduced side reactions. The rounded Li deposits could also reduce the probability of

Fig. 5 Li plating/stripping morphologies at various areal capacities on (a) CF_x and (b) $\text{CF}_x\text{-400}$.

piercing the separator and improve the safety of LMBs. Furthermore, the intact surface morphology was observed after Li stripping process to $0 \text{ mAh}\cdot\text{cm}^{-2}$, demonstrating the significantly suppressed side reactions for Li plating on $\text{CF}_x\text{-400}$. These results clearly indicate the greatly improved Li^+ transfer kinetic in the $\text{CF}_x\text{-400}$ framework.

The cycling stability of Li metal anodes on bare Cu, CF_x and $\text{CF}_x\text{-400}$ were assessed in Li-Cu cells. Fig. 6a shows the cycling performances at a current density of $0.5 \text{ mA}\cdot\text{cm}^{-2}$ for a fixed capacity of $1 \text{ mAh}\cdot\text{cm}^{-2}$. Initial lithiation processes were clearly observed for CF_x and $\text{CF}_x\text{-400}$, leading to progressive increases of CEs during initial cycling. These processes are believed to undergo the formation of LiF-embedded SEI layers on CF_x flakes or LiF-incorporated Li^+ conducting channels in $\text{CF}_x\text{-400}$ framework. Posterior to the lithiation processes, more stable cycling were achieved for CF_x (~ 80 cycles) and $\text{CF}_x\text{-400}$ (~ 240 cycles), compared to that on bare Cu (~ 40 cycles), whereas the

outstanding performances of $\text{CF}_x\text{-400}$ further demonstrate the synergism of fluorinated sites and fast Li^+ conducting channels for stable Li plating/stripping. Consistently, much more stabilized Li plating/stripping curves were maintained for $\text{CF}_x\text{-400}$ upon cycling (Fig. 6d), while clear polarization enlargement and capacity fading were observed for bare Cu (Fig. 6b) and CF_x (Fig. 6c). The cycling voltage hysteresis in the condition of $0.5 \text{ mA}\cdot\text{cm}^{-2} - 1 \text{ mAh}\cdot\text{cm}^{-2}$ are shown in Fig. 6g, whereas the polarization of CF_x (from 180.7 mV at the 10th cycle to 217.0 mV at the 50th cycle) was larger than those of bare Cu (from 78.1 mV at the 5th cycle to 159.6 mV at the 50th cycle) and $\text{CF}_x\text{-400}$ (stably below 80 mV), showing the serious drawbacks of limited Li^+ transfer paths and low electronic conductivity of CF_x flakes. Although low polarization was initially achieved on bare Cu, the fast increase of voltage hysteresis during subsequent cycling still indicates large accumulation of side products, consistent to the results of EIS and SEM (Figs. 4 and 5).

Fig. 6 (a) Cycling stability of Li metal anodes on Cu, CF_x and CF_x-400 electrodes at 0.5 mA·cm⁻² - 1 mAh·cm⁻², and charge-discharge curves of (b) Cu, (c) CF_x and (d) CF_x-400 electrodes upon cycling at 0.5 mA·cm⁻² - 1 mAh·cm⁻²; cycling stability of Li metal anodes on Cu, CF_x and CF_x-400 electrodes at (e) 0.5 mA·cm⁻² - 3 mAh·cm⁻² and (f) 3 mA·cm⁻² - 1 mAh·cm⁻²; voltage hysteresis of Li plating/stripping on Cu, CF_x and CF_x-400 electrodes at (g) 0.5 mA·cm⁻² - 1 mAh·cm⁻², (h) 0.5 mA·cm⁻² - 3 mAh·cm⁻² and (i) 3 mA·cm⁻² - 1 mAh·cm⁻².

The great Li protection ability of CF_x-400 framework was also proved for higher current density and capacity. For cycling in high capacity condition of 0.5 mA·cm⁻² - 3 mAh·cm⁻², stable CEs were maintained for CF_x-400 over 160 cycles (Fig. 6e, h), showing its ability to accommodate high-loading Li plating/stripping which is expected in practical application. For cycling in high density condition of 3 mA·cm⁻² - 1 mAh·cm⁻², a stable cycling of 100 cycles was still obtained for CF_x-400 (Fig. 6f), with moderately maintained polarization (from ~84.9 mV at the 10th cycle to ~176.2 mV at the 80th cycle, Fig. 6i). In sharp contrast, very large polarization and poor cycling were observed for CF_x in the same condition (Fig. 6f, i), indicating the sluggish charge transfer through the 2D CF_x-based structure. Besides, the CF_x materials are well-known as a poor electronic conductor, which results in the high polarization of the substrate consisted of large CF_x flakes, as shown by the EIS and voltage hysteresis results (Fig. 4b, c and 6g-i). However, due to the significant content of LiF generated during the initial lithiation of CF_x (Fig. 3e and S8, Supporting Information), which could serve as the prominent SEI component to protect the deposited Li metal, the substrate of large CF_x flakes could still exhibit better Li metal

cycling than that on bare Cu at a relatively low current density of 0.5 mA·cm⁻². However, the increase of polarization on the large CF_x flakes became serious at the current density of 3 mA·cm⁻², leading to the Li metal cycling which was even poorer than that on bare Cu. These results further demonstrate the advantage of the framework based on the down-sized CF_x-400 particles, which exhibited stable Li metal cycling even at high current densities due to the well-established Li⁺ conducting channels that neutralize the effect of poor electronic conductivity of CF_x materials.

Based on the good Li protection ability of CF_x-400, its application in Li-LiFePO₄ full cells was also studied. Prior to the assemble of full cell, the CF_x-400 coated Cu electrode was pre-cycled in the Li-Cu cell for 10 cycles to complete the lithiation process and form Li⁺ conducting channels, as described in experimental section. 2.5 mAh·cm⁻² Li was then plated on the lithiated CF_x-400 framework to form the composite anode (denoted as CF_x-400@Li), leading to a N/P ratio about 3, which is comparable to the practical condition. As comparison, a Cu@Li anode by plating 2.5 mAh·cm⁻² Li on bare Cu was also fabricated. Fig. 7a shows the performances of the investigated

Fig. 7 (a) Capacity retentions and CEs of full cells using LiFePO₄ as cathode and Cu@Li or CF_x-400@Li as anode, and the charge-discharge curves of Li-LiFePO₄ cells using (b) Cu@Li or (c) CF_x-400@Li anode.

Li-LiFePO₄ cells, whereas the Cu@Li-LiFePO₄ cell exhibits a fast capacity fading below 0.5 mAh·cm⁻² at the 50th cycle, with unstable and low CEs, and highly polarizing and fluctuating charge/discharge curves (Fig. 7b). Remarkably, the full cell using CF_x-400@Li anode shows a stable cycling over 120 cycles (Fig. 7a), with almost unchanged polarizations upon cycling (Fig. 7c). The capacity retention of the CF_x-400@Li-LiFePO₄ full cell is ~70% at the 120th cycle, indicating a high utilization ratio of active Li in the practical condition of N/P ratio ~3.

4 Conclusions

In this work, the cycling stability of Li metal anode was studied in a CF_x-400 framework. Compared to the 2D structure consisted of large CF_x flakes, the investigated 3D framework with down-sized CF_x-400 particles and LiF-incorporated Li⁺ conducting channels could minimize the increase of interfacial impedance caused by the low electronic conductivity of fluorocarbon, and accommodate uniform and high-loading Li plating/stripping for long-term cycling. Based on the synergism of enriched fluorinated sites and fast Li⁺ conducting channels in the CF_x-400 framework, the Li metal cycling stability was significantly improved at various current densities (up to 3 mA·cm⁻²) and capacities (up to 3 mAh·cm⁻²), and improved Li-LiFePO₄ full cell performance with a practical N/P ratio of 3 was also demonstrated.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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