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Super-three-dimensional lithiophilic Cu-based current collector for anode-free lithium metal battery

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ABSTRACT

The formation of Li dendrites and dead Li, which causes short circuits, continuous side reactions, low Coulombic efficiency (CE) and thermal runaway, severely hinders the development of anode-free lithium metal batteries. Here, Cu-based current collector with super-three-dimensional lithiophilic modification layer is developed by the pyrolysis of resorcinol formaldehyde on 3D engineered copper mesh (a-RF@3D CM). The modification layer, consisting of highly dispersed CuO_x sites in the O-containing defective carbon, together with the super-three-dimensional microstructure exhibits excellent lithiophilicity and capability to effectively reduce the nucleation overpotential, accommodate the uniform dendrite-free lithium deposition, promote stable and inorganic-rich solid electrolyte interphase formation, and improve the cycle stability. As a result, the a-RF@3D CM current collector exhibits reduced nucleation overpotential of 14.2 mV and prolonged cycling life over 400 cycles with average CE >98.5%. In the LiFePO₄||a-RF@3D CM anode-free cell, average CE of 99.50% and capacity retention of 60.66% are successfully achieved after 100 cycles. Meanwhile, average CE 99.78% and capacity retention of 64.43% are successfully achieved in LiFePO₄||Li@a-RF@3D CM cell (N/P = 1.6) after 200 cycles. The work provides feasible way to realize the fabrication of anode-free lithium metal batteries and also enhance the understanding of solid electrolyte interface evolution and regulation strategy of Li plating-stripping in advanced Li metal-based batteries.

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1. Introduction

Rapid development of electric vehicles and portable devices leads to continuously increasing demands for high-energy-density batteries. Conventional commercial lithium-ion battery, which consists of graphite (372 mAh/g [1]) as anode and layered oxides as cathode, is approaching its energy-density limit and hard to meet the growing demand. Lithium metal with ultrahigh theoretical capacity (3860 mAh/g), the lowest redox potential (-3.04 V vs.

standard hydrogen electrode), and low density (0.59 g/cm³) is the most promising anode candidate for next-generation battery [2]. However, the commercial application of lithium metal faces many challenges, among which the excess usage of Li metal in cells results in overvalued energy density. The use of limited lithium (\leq 30 µm, or \leq ~6 mAh/cm²) is highly desired to substantially improve the energy density of Li metal battery [3]. The high-cost and limited ready availability of thin lithium foils bring about the latest research on anode-free lithium metal battery (AFLMB) system. In the AFLMB system, a bare current collector is used as anode instead of lithium metal foil, and lithium ions from the cathode are in-situ plated on the current collector. The elimination of lithium foil results in potentially significant increase in the energy density (Wh/kg or Wh/L) by more than 50% relative to conventional Li-ion batteries. In addition, the energy and cost associated with anode







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production (including electrode slurry preparation, slurry coating, and drying) are saved. However, the direct use of in-situ plated Li metal is highly problematic due to its high reactivity, severe side reactions with electrolyte and thus low Coulombic efficiency (CE), which is usually less than 80% in most electrolytes [4,5]. Mean-while, the dendrite growth and volume change of lithium during cycling are also severe problems which could diminish the cycling life of the battery and may lead to short circuit and other safety issues [6,7]. As consequence, the in-situ-plated Li supplied by the cathode will be completely consumed, resulting in cell failure, within a few cycles and the application of AFLMB is still quite challenging.

To solve these problems, strategies including advanced electrolyte formulations [8–10], current collector engineering [11,12], modification of separator [13,14] and so on have been reported. The engineering of anode current collector is decisive to achieve uniform and dendrite-free lithium deposition since it directly influences the uniformity and morphology of lithium plating. Cu foil is the most commonly used current collector in the rechargeable lithium battery; however, it is not ideal for lithium metal deposition due to its poor lithiophilicity [15]. Three-dimensional (3D) microstructured materials, like 3D Cu mesh [16], 3D porous Cu foil [17], and so on, attract many efforts since they could reduce the local current density, accommodate Li deposition, minimize volume change of Li, and thus suppress dendrite formation to prolong the cycle life. However, the low lithiophilicity of the 3D structured Cu current collectors results in high nucleation barrier and poor homogeneity of plated Li [18,19]. Therefore, improving the lithiophilicity of the current collector is a key to uniform deposition of lithium [20]. Various materials, like polymer (polyacenequinone [21] and polyethylene oxide [22]), alloy (Li-Sn [23,24], Cu-Zn [25], and Ni-Co [26]), metal oxides (CuO [27] and ZnO [28]), and so on, have been employed to enhance the lithiophilicity of Cu. Among the candidate materials for surface modification, carbon with light weight, high electronic conductivity, excellent chemical and physical stability is an ideal material to regulate the deposition behavior of lithium [29]. For example, Zhang et al. [30] constructed a buffer layer using carbon nanotubes to improve the stability of current collector. Yan et al. [31] developed a nanocapsule structure consisting of hollow carbon spheres with nanoparticle seeds inside, which effectively promoted the uniform Li deposition. Moreover, Kim et al. [32] fabricated lithiophilic Au nanoparticle incorporated 1D hollow carbon fiber as Li host to regulate Li plating/stripping, thereby the cell achieved high CE of 99.9% under 1 $\,m\text{A}/cm^2$ and 2 mAh/cm². However, the introduction of precious metals would raise the cost. Although various methods have been proposed to synthesize lithiophilic modification layer on current collector, the mechanical strength and adaptability of the modification layer to the AFLMB is still not satisfactory. More efficient methods to regulate lithium plating/stripping in the AFLMB are still highly desired.

Herein, this work developed a super-three-dimensional copper current collector by constructing lithiophilic carbon-coated copper fibers on engineered three-dimensional copper mesh (3D CM) through the pyrolysis of resorcinol formaldehyde (a-RF@3D CM). The three-dimensional microstructure not only provides capability to regulate lithium deposition spatially but also effectively reduces the local current density to alleviate dendrite growth. The superthree-dimensional lithophilic modification layer established on 3D CM effectively reduces the nucleation barrier of lithium deposition and leads to homogeneous lithium plating behavior, resulting in the reduced nucleation overpotential of 14.2 mV and stable dendrite-free lithium plating/stripping. As a result, improved cycling life with more than 400 cycles at 0.6 mA/cm² is achieved on the Li||Cu half-cell using a-RF@3D CM. Moreover, the anode-free LiFePO₄||a-RF@3D CM full cell without active anode material and LiFePO₄||Li@a-RF@3D CM (N/P = 1.6) full cell with limited lithium exhibits high average CE of 99.50% and 99.93% after 100 cycles, and the capacity retention reaches 60.66% and 92.93%, respectively. This work provides a feasible and promising way to develop structurally engineered lithiophilic current collector for high-energy-density AFLMB.

2. Experimental section

2.1. Preparation of 3D Cu current collector

Pristine CM (Shanghaihuadong) was washed by acetone, hydrochloric acid, and deionized water to remove the surface impurities. And then the CM was placed in the mixed solution with 10 mol/L sodium hydroxide (Aladdin, AR) and 1 mol/L ammonium persulfate (Aladdin, \geq 98%) for 5 min. Finally, the resulting sample was heated in 5% H₂/Ar flow at 350 °C for 2 h, and the obtained sample was denoted as 3D CM.

2.2. Fabrication of a-RF@3D Cu current collector

The resorcinol formaldehyde was synthesized on the 3D CM by the polymerization of resorcinol (Canrd, AR) and methanol (Canrd, \geq 99.5%) in the mixed solution of deionized water and ethanol (Canrd, AR) for 12 h. Then, the resulting sample was calcined in 5% H₂/Ar flow at 750 °C for 2 h to obtain the product denoted as a-RF@3D CM.

2.3. Characterizations

The Young modulus of the modified current collector was measured using atomic force microscope (Bruker Dimension Icon). The X-ray diffraction (XRD) patterns were measured on a Rigaku D/ MAX-2500 powder diffractometer with Cu-Ka radiation $(\lambda = 0.154 \text{ nm})$ operated at 40 kV, 200 mA. Raman spectra were recorded on a Renishaw in Via Raman microscope (Renishaw, Gloucestershire, United Kingdom) with an Ar ion laser at the excitation wavelength of 532 nm. The X-ray photoelectron spectrum was tested to analyze the sample surface structure on a VG ESCALAB MKIIX-ray photoelectron spectrometer using Mg-Ka as the exciting source and PHI5000VersaProbell in situ X-ray photoelectron spectrometer using Al-K α as the exciting source. The scanning electron microscope (SEM) images and the energy dispersive X-ray spectroscopy (EDS) images were obtained by HITACHI SU8010 cold field emission SEM (Japan, 5 kV). The selected area electron diffraction (SAED) patterns were acquired on Thermo Fisher Tecnai G2 F30 microscope operated at 300 kV. OLYMPUS SZX16 optical microscopy were used to observe the Li deposition behavior during cycling.

2.4. Electrochemical measurements

The standard CR2032 type coin half-cells were assembled using Li foil (16 mm in diameter) paired with CM, 3D CM, and a-RF@3D CM current collectors ($\emptyset = 12$ mm) in an Ar-filled glovebox (H₂O and O₂ < 0.01 ppm). The Celgard 2325 were used as separator. 70 µL of LiTFSI (1 M) in DOL/DME (1:1, by volume) with 2 wt% LiNO₃ additive was used as the electrolyte. The cells were cycled at plating/stripping current of 0.3 mA/cm²/0.5 mA/cm² with 1 mAh/cm², 0.3 mA/cm²/0.5 mA/cm² with 2 mAh/cm², 0.6 mA/cm²/1 mA/cm² with 1 mAh/cm², and 1.2 mA/cm²/2 mA/cm² with 1 mAh/cm² using battery tester station (Land CT3001A, China), before which the cells were initially cycled 2 times at 0.1 mA/cm² as formation cycles.

Anode-free coin cells were assembled using LiFePO₄ electrodes (~1.6 mAh/cm²) paired with bare Cu foil, a-RF@3D CM, Li@Cu, and Li@a-RF@3D CM ($\emptyset = 12$ mm), respectively, in an Ar-filled glovebox (H₂O and O₂ < 0.01 ppm). The Li@Cu and Li@a-RF@3D CM were obtained by pre-depositing 1 mAh/cm² Li on the current collector. The Celgard 2325 was used as separator, and 70 µL of LiTFSI (1 M) in DOL/DME (1:1, by volume) with 2 wt% LiNO₃ additive was used as the electrolyte. The anode-free coin cells were tested between the potential window of 3.0–3.8 V with the charge/discharge rate of 0.2C/0.3C in a typical electrolyte of 1 M LiTFSI (DOL: DME 1:1). Before cycling, all cells were initially cycled 2 times at 0.1C for electrochemical activation. The electrochemical impedance spectroscopy test was performed on CHI660e electrochemical work-station (Chenhua, China) in the frequency ranges of 0.01 HZ to 10⁵ HZ.

3. Result and discussion

3.1. Characterization of a-RF@3D CM current collector

The preparation procedure of the modified current collector a-RF@3D CM is shown in Fig. 1a, which is realized through aldol condensation to introduce carbon-modified layer on engineered 3D CM. The 3D fibers were prepared by oxidizing the surface of the CM. Then the resorcinol formaldehyde (RF) resin layer, which is an excellent carbon source synthesized by efficient and controllable alkali-catalyzed aldol condensation, was grown on the 3D Cu(OH)₂ fibers without annealing. Finally, the resulting sample was annealed in argon-hydrogen gas, in which Cu(OH)₂ was dehydrated and reduced to Cu and resorcinol formaldehyde resin was pyrolyzed and carbonized to amorphous carbon, which results in a super-three-dimensional microstructure [33,34]. Resorcinol has more hydroxyl groups than phenol and can provide more lithophilic oxygen for resin. During the pyrolysis process, the resin was gradually transformed into amorphous carbon with oxygencontaining function groups (Fig. 1b). There are three main steps to this process. First, the methylene is cleaved at high temperatures to produce volatile substances such as CH₄ and H₂O. In the second step, hydroxyl radicals generated at high temperatures oxidize methylene, produce carbon dioxide, carbon monoxide, and other gases which lead to the formation of some intermediate products (Fig. S1) [35,36]. In the third step, polycyclic reaction occurs among these intermediate products, and the resin is gradually transformed into amorphous carbon [36-38]. Super-three-dimensional structure constructed by RF and Cu(OH)₂ on the current collector can be well preserved in the obtained modification layer, which is expected to regulate the lithium deposition behavior on the current collector.

The surface morphology of the CM, 3D CM, and a-RF@3D CM were characterized using the SEM. As shown in Fig. 1c and Fig. S2a, the pristine CM substrate consists of copper wire networks. After the pretreatment in sodium hydroxide and ammonium persulfate, the 3D microstructure of CM is well maintained (Fig. 1d and Fig. S2b). The surface of the 3D CM is uniformly covered by 3D fibers with an average diameter of ~240 nm and varied length, which are generated by Cu(OH)₂ during calcination. The introduction of RF resin and following calcination further increases the roughness of the 3D networks (Fig. S2c). Extra deposits are effectively coated on the fibers in 3D CM (Fig. 1f), and the final product a-RF@3D CM exhibits super-three-dimensional structure, which is a more subtle and microscopic 3D structure further constructed on the basis of a 3D structure [39]. In this paper, the super-three-dimensional structure refers to the modification layer constructed on the basis of the original 3D CM. Due to the more microscopic 3D structure, the superthree-dimensional structure can exhibit superior properties compared with the 3D structure to regulate Li deposition since it can effectively reduce the local current density, homogenize the Li⁺ flux, and thus alleviate dendrite growth. Moreover, the super-three-dimensional structure can effectively suppress the volume change during lithium deposition/dissolution and avoid the structural degradation [40,41]. The cross-sectional SEM image of a-RF@3D CM in Fig. 1f shows that the average thickness of the super-three-dimensional composite layer on the CM substrate introduced by the two-step synthesis is ~2 μ m. As revealed by atomic force microscopy in Fig. S3, the Young's modulus of the modification layer is ~4.065 GPa, comparable with the reported modification layers on the Cu anode current collectors [42].

As shown above, the surface modification layer in a-RF@3 M CM is rough with nanosized spherical domains. The EDS mapping was applied to the fiber to further understand the composition of the modification layer and the super-three-dimensional structure. As shown in Fig. 1g–j, C (Fig. 1h) and O (Fig. 1i) are homogeneously distributed in the modification layer either on the surface or the spherical domains. Moreover, Cu (Fig. 1j) also exists in the modification layer as well as in the superficial spherical domains. It demonstrates that the surface modification layer mainly consists of carbon species incorporated with O and Cu. The contact angle of CM, 3D CM, and a-RF@3D CM with the electrolyte is 65.1°, 19.3°, and 22.3°, respectively (Fig. S4). Compared with the pristine CM, the three-dimensional processing significantly improves the wettability of electrolyte on the current collector. This phenomenon may be caused by the difference of surface tension, which results from the predominance of metallic bonds in the Cu substrate and covalent bonds in the modification layer [43]. In lithium metal batteries. poor wettability would prevent the electrolyte from infiltrating, resulting in uneven transport of lithium ions and the generation of lithium dendrites. Therefore, the better the wettability of the electrolyte, the more uniform the current density distribution on the anode surface, which can effectively prevent the generation of lithium dendrites.

The XRD patterns of the CM, 3D CM, and a-RF@3D CM are presented in Fig. S5 to understand the crystalline structure of the modification layer. The XRD profiles of these samples only consist of characteristic diffraction peaks of Cu (PDF#04-0836) without any diffraction peaks from the introduced modification substance, which may be related to the low content. Raman spectra of the a-RF@3D CM in Fig. 2a exhibit characteristic Raman shift of carbon materials at 1360 cm (D band) and 1589 cm (G band), indicating the presence of defective carbon on the surface of the modified current collector. The I_D/I_G values are 0.836, indicating that there are abundant defects in the modification layer due to the low degree of crystallization.

The chemical states of the modification layer were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS results indicate that C and O are dominant in the surface layer of a-RF@3D CM with contents of 66.57 at.% and 18.36 at.%, respectively. The content of Cu in the a-RF@3D CM occupies 15.07 at.%, which includes the contribution from copper species in the modification layer as well as those in Cu substrate. Table S1 shows the binding energy and relative content of different species in a-RF@3D CM. Compared to carbon, oxygen is more lithiophilic to improve the lithiophilicity of the current collector. There are four peaks at 284.7 eV, 285.3 eV, 286.4 eV, and 288.3 eV in the C1s spectra (Fig. S6), corresponding to the C–C, C]C, C–O, and C]O bonds, respectively [44]. The deconvolution of the O1s spectra (Fig. 2b) consists of four peaks at 530.3 eV, 531.0 eV 532.2 eV, and 533.3 eV, which are assigned to CuO_x, C]O bond, C–OH bond, and O–C–O, respectively [45]. It suggests that carbonyl groups are widely present in the modification layer, which are lithiophilic due to the conjugated structure [46]. The conjugated groups can effectively improve the charge



Fig. 1. (a) Schematic demonstration on the preparation of 3D CM and a-RF@3D CM. (b) The basic structure of amorphous carbon with oxygen-containing functional groups. (c–e) SEM images of CM (c), 3D CM (d) and RF@3D CM (e), respectively. (f) The cross-sectional SEM image of a-RF@3D CM. (g–j) The SEM image of the modified layer on a-RF@3D CM (f), and the corresponding EDS mapping images of C (h), O (i), and Cu (j). 3D, three-dimensional; CM, copper mesh; EDS, energy dispersive X-ray spectroscopy; RF, resorcinol formaldehyde; SEM, scanning electron microscope.

diffusion behavior and electronegativity of the material, leading to lowered barrier for Li^+ deposition on the modification layer. Meanwhile, the presence of CuO_x indicates that copper is not fully dissolved during treatment in acid and there is residue copper species in the super-three-dimensional modification layer, which is consistent with the EDS mapping results. The presence of CuO_x is also confirmed by the deconvolution of the Cu 2p spectra (Fig. 2c), which includes two peaks at 932.8 eV and 934.27 eV corresponding to Cu and CuO_x, respectively [47]. The intensity of metallic Cu species is enhanced by the copper substrate to some extent. What is interesting here is that CuO_x is also lithiophilic [27]. The ionic oxygen in CuO_x would induce strong Coulombic interactions with the incoming Li⁺ ions, which could significantly improve the overall lithiophilicity of the surface layer and regulate Li⁺ distribution.

The composition and microstructure of the super-threedimensional surface modification layer, especially the existing



Fig. 2. (a) Raman spectra of a-RF@3D CM. (b-c) Deconvoluted XPS spectra of O1s (b) and Cu 2p (c) in a-RF@3D CM. (d-i) HRTEM and corresponding SAED images of the modification layer on a-RF@3D CM. 3D, three-dimensional; CM, copper mesh; HRTEM, high-resolution transmission electron microscopy; RF, resorcinol formaldehyde; SAED, selected area electron diffraction.

state of carbon and copper species, is further investigated by the high-resolution transmission electron microscopy. As shown in Fig. 2d, carbon is uniformly coated on the surface of the fibers, and the thickness of the carbon layer is ~18 nm. There are fractures on the fibers, which may be caused by volumetric shrinkage of the copper fibers during the conversion from copper hydroxide to copper. Interplanar distance of 1.281 Å is detected for the material inside (Fig. 2e), which is attributed to the (220) plane of copper. The SAED patterns (Fig. 2f) in this area show clearly identifiable diffraction patterns with crystal plane spacing of 1.799 Å, 1.289 Å, and 0.808 Å, which are determined to be the (200), (220), and (420) plane in Cu, respectively. It further confirms the existence of copper in the super-three-dimensional structure, which could provide fast electron transfer channels inside. Meanwhile, the indistinct diffraction rings suggest the presence of amorphous carbon with oxygen-containing functional groups in the modification layer. Besides, some crystal nanoparticles of 10-25 nm evenly distribute in the modification layer (Fig. 2g), which possess interplanar distances of 2.465 Å and 1.792 Å (Fig. 2h) attributed to the lattice plane (111) of copper oxide and (200) of copper, respectively. Besides the diffraction patterns from copper, extra scattered diffraction points in the SAED images (Fig. 2i) reveal the presence of Cu₂O with $d_{200}\,=\,2.135$ Å, $d_{111}\,=\,2.398$ Å, and $d_{311}\,=\,1.227$ Å, which is consistent with the above XPS results. Similarly, indistinct diffraction rings are observed, confirming the presence of amorphous carbon. According to density functional theory calculation, the (111) facet of Cu₂O and (111) facet of CuO exhibit binding energy of -2.39 eV [48] and -3.21 eV [49] with Li⁺, which are more beneficial to facilitating uniform lithium deposition due to the reduced nucleation barrier compared to Cu (111) (-1.60 eV). The above results effectively prove that the amorphous carbon-coated copper and residue copper nanoparticles/nanofibers uniformly co-exist in the super-three-dimensional modification layer. And the highly dispersed CuO_x sites together with the O-containing defective carbon in the super-three-dimensional modification layer of a-RF@3D CM are expected to reduce the nucleation barrier of Li and effectively improve the lithiophilicity of the current collector.

3.2. Electrochemical performance of half cells

The plating/stripping behavior of Li on different current collectors was investigated by assembling half-cells with CM, 3D CM, and a-RF@3D CM current collectors and Li. Fig. 3a shows the initial voltage curve during lithium plating. The cells exhibit sharp voltage dip which is an indication of the Li nucleation barrier at the early stage of Li plating [50,51]. The nucleation overpotentials of lithium, which could effectively reflect the status of nucleation barrier, on CM, 3D CM, and a-RF@3D CM are 28.2 mV, 23.9 mV, and 14.2 mV, respectively. The current collector with good lithiophilicity usually possesses low nucleation barrier and thus low nucleation overpotential. Compared to CM, the significant decrease in nucleation overpotential on a-RF@3D CM indicates that the introduction of super-three-dimensional modification layer effectively improves the lithiophilicity of the copper substrate. The uniformly distributed Cu and CuO_x nanoparticles in the amorphous carbon play important roles in the enhancement of lithiophilicity, as discussed above, leading to reduced barrier for the nucleation and growth of lithium on the current collector. There is a reaction slope before



Fig. 3. Electrochemical evaluation of CM, 3D CM, and a-RF@3D CM in half-cells. (a) Voltage-capacity profiles recorded during lithium plating at 0.1 mA/cm² at the first cycle. (b) Voltage hysteresis of the a-RF@3D CM cell during the 25th, 50th, 200th and 300th cycle with 1 mAh/cm² of Li plating at 0.6 mA/cm²/stripping at 1.0 mA/cm². (c) Coulombic efficiency (CE) of the cells cycled with 1 mAh/cm² of Li plating at 0.6 mA/cm²/stripping at 1.2 mA/cm²/stripping at 2 mA/cm². (e) CEs of the cells cycled with 2 mAh/cm² of Li plating at 0.3 mA/cm²/stripping at 0.5 mA/cm². 3D, three-dimensional; CM, copper mesh; RF, resorcinol formaldehyde.

lithium nucleation in the voltage curve of a-RF@3D CM, which corresponds to ~0.3 mAh/cm². The lithiation slope could be ascribed to the reaction between Li and carbon/CuO_x in the modification layer during solid electrolyte interphase (SEI) layer formation in the initial cycle, which allows for lithium storage through adsorption and intercalation before lithium plating and this slope no longer shows up in the subsequent cycles (Fig. S7). The lithiated carbon will act as in-situ formed lithiophilic sites to facilitate uniform lithium deposition in the subsequent cycles and improve the cycling life of the cell [52]. Besides, the lithium oxides, produced by

the reaction between lithium and oxygen containing compounds (CuO_x, O in carbon, etc.) in the modification layer, have also been reported to be beneficial inorganic components to enhancing the strength of SEI and prolong cell cycle life [53]. Fig. S7a–c show the voltage curves of CM, 3D CM, and a-RF@3D CM cells cycled at 0.6 mA/cm² plating and 1 mA/cm² stripping with the capacity of 1 mAh/cm². The CM cell fluctuates severely and quickly degrades for less than 200 cycles with deteriorative average CE of 97.48%. The 3D CM cell lasts longer with an average CE of 98.94% considering its 3D microstructure, but it fades around 300 cycles. By contrast, the

a-RF@3D CM cell remains fairly stable even after 400 cycles and maintains the average CE over 99.23%.

Fig. 3b and Fig. S7d-f show the voltage hysteresis of CM, 3D CM, and a-RF@3D CM cells in different cycles, which is an important parameter to reflect the voltage polarization and internal resistance during lithium plating/stripping. Initially at the 25th cycle, the hysteresis voltages of the CM, 3D CM, and a-RF@3D CM cells are comparable and around 32.8 mV. With prolonged cycling, there is not huge change of the voltage hysteresis before the cell is deactivated, demonstrating the effective regulation of lithium plating/ stripping by the 3D structure in the CM substrate. In addition, the hysteresis drops by 5–10% after 200 cycles, which could be related to the build-up of conductive SEI during the initial cycles. The drop of hysteresis in a-RF@3 M CM (10.06%) is relatively larger than the other two samples (2.15% for CM, 8.51% for 3D CM), suggesting that the super-three-dimensional modification layer effectively alleviate severe increase of cell impedance. Additionally, the hysteresis of the CM and 3D CM cells exhibits sharp rise before the cell fails around the 250th (38.2 mV) and 400th (43.0 mV) cycle, respectively. The formation of highly resistant interfacial layer composed of decomposed electrolyte and dead lithium is the main reason for the sharp increase of hysteresis [54]. By contrast, the voltage hysteresis in a-RF@3D CM cell remains stable even after 400 cycles, suggesting effectively suppressed internal impedance and sides reactions due to the construction of super-three-dimensional structure.

CE, which represents the efficiency between stripping and plating, is a key factor to reveal the active lithium loss during cycling and evaluate the performance of the current collectors. The lithium loss is related to lithium-electrolyte interfacial side reactions and dead lithium formation during cycling [55,56]. As shown in Fig. 3c, the a-RF@3D CM delivers superior CE and prolonged cycle life compared to the rest, indicating the super-threedimensional modification layer successfully stabilizes the anode/ electrolyte interface, reduces active lithium loss, and improves the cycling stability. However, it is worth noting that the initial CE is relatively lower for a-RF@3D CM. The formation of SEI layer due to the increased surface area in the super-three-dimensional structure and extra lithium storage through adsorption and intercalation of the introduced carbon media, which is related to the above mentioned lithiation slope in the first cycle (Fig. 3a), may be the reason for the drop of initial CE. However, the CE of a-RF@3D cell is stably maintained at relatively high level in the subsequent cycles, suggesting that the initial formed SEI is more beneficial in the modified current collector. The a-RF@3D CM cell also exhibits excellent electrochemical performance at higher currents or capacities. Increasing the plating/stripping current density to 1.2 mA/ cm²/2 mA/cm² (Fig. 3d), the Lilla-RF@3D CM cell stably cycles for more than 150 cycles, and the average CE reaches 97.76%. By contrast, the Li||CM cell only lasts for 25 cycles with CE of 96.62% and the Lill3D CM cell lasts for 100 cycles with average CE of 97.31%. Similarly, improving the capacity to 2 mAh/cm² (Fig. 4e), the Lilla-RF@3D CM cell still can stably cycle for more than 300 cycles with average CE of 99.20%, which is much superior to the Li||CM cell (49 cycles with CE of 98.24%) and the Li||3D CM cell (150 cycles with CE of 98.97%). High current density or capacity would aggravate the growth of lithium dendrites and lead to short circuit and accelerated cell failure [57]. Overall, the a-RF@3D CM current collector possesses outstanding electrochemical performance at various conditions, even at high current density and capacity. It suggests that the lithiophilic modification layer and super-threedimensional microstructure in a-RF@3D CM effectively suppress the cell degradation and enhance the cycling stability.

3.3. Lithium deposition behavior

To evaluate the regulating effect of the super-three-dimensional modification layer on Li deposition behavior, SEM images of the current collectors were obtained after 0.3 mAh/cm², 2 mAh/cm², and 4 mAh/cm² of lithium was deposited on CM, 3D CM, and a-RF@3D CM at 0.1 mA/cm². The initial nucleation and growth of Li on CM is quite heterogeneous and dendrites appear in the hollows even at 0.3 mAh/cm² (Fig. 4a1). The engineered structure in 3D CM regulates the Li nucleation and deposition to some extent; however, there is still obvious heterogeneity and small dendritic deposition (Fig. 4b1). By contrast, there are no dendrites on the surface of a-RF@3D CM (Fig. 4c1). As shown in Fig. S8, the surface of CM (Fig. S8a) and 3D CM (Fig. S8b) is covered by deposited lithium and Li deposition gradually forms some locally stacked particles with a diameter of ~3-5 µm. The 3D structure of 3D CM is partially destroyed. By contrast, the 3D structure on the surface of a-RF@3D CM is well maintained. The modification layer can restrain the deposited lithium with less exposed lithium directly contacting with electrolyte, thus inhibit dendrite growth. When Li deposition is increased to 2 mAh/cm², there is a great deal of lithium on the surface of the CM (Fig. S9a) and 3D CM (Fig. S9b) networks accompanied by severe dendrites. The dendrite distribution on 3D CM is reduced to some extent than that on CM, due to the 3D structure which could reduce the local current density and thus alleviate the dendrite growth [58]. By contrast, lithium deposited on a-RF@3D CM current collector (Fig. S9c) mainly exists in pellets without obvious dendrite formation. It indicates that the superthree-dimensional modification laver can effectively regulate the lithium deposition behavior by effectively suppressing the formation of lithium dendrites. As discussed above, the lithiophilic superthree-dimensional layer promotes the uniform deposition of Li⁺ flux. With the increase of lithium deposition to 4 mAh/cm² (Fig. 4a2, b2, and c2), the lithium dendrites on CM surface further exacerbate and quite porous lithium deposition is formed in the space area of CM. Some of the lithium deposited on 3D CM exists as pellets but coarse lithium dendrites dominate. The lithium deposition forms smoothly dense layer on the surface of a-RF@3D CM, and no distinct dendrites show up. It turns out that the super-threedimensional modification layer in a-RF@3D CM provides an excellent reservoir for lithium as well as regulates the lithium deposition to inhibit the dendrite growth.

The in-situ optical microscopy was conducted in the assembled light mirror electrolytic cell (Fig. S10) to observe the morphology changes during the Li deposition process. And a total Li amount of 4 mAh/cm² was deposited at a current density of 0.5 mA/cm². Fig. 4d1-f1 exhibit the initial morphology of CM (Fig. 4d1), 3D CM (Fig. 4e1), and a-RF@3D CM (Fig. 4f1) current collectors. With increasing Li deposition, the Li dendrites grew severely upwards out of control on the CM and 3D CM current collectors with obvious volume expansion. Under the same circumstances, Li spread uniformly and grew smoothly bottom-up on the a-RF@3D CM current collector with slight volume expansion. After plating for 4 h with deposition of 2 mAh/cm² (Fig. 4g2, e2, and f2), a loose Li dendrite layer appears on the CM and 3D CM current collector with varying degrees of thickness. By contrast, the thickness of a-RF@3D CM barely changes. After plating for 8 h with Li deposition of 4 mAh/ cm² (Fig. 4d3, e3, and f3), the thickness of loose Li dendrites layer on the CM and 3D CM current collectors further increases to about 104.4 μ m and 56.2 μ m, respectively. By contrast, a dense and compact deposition layer is achieved on the a-RF@3D CM without obvious dendrite growth. It should be noted that in this optical configuration, the growth of lithium dendrites is less restricted



Fig. 4. Morphology evolution and in-situ optical images of plated Li in CM, 3D CM, and a-RF@3D CM half-cells. (a–c) The SEM images of CM (a1-2), 3D CM (b1-2), and a-RF@3D CM (c1-2) with areal plating capacity of 0.3 mAh/cm² (1) and 4 mAh/cm² (2) at 0.1 mA/cm². (d–f) In-situ optical microscopy images of the side view for the CM (d1-3), 3D CM (e1-3), and a-RF@3D CM (f1-3) current collectors with Li deposition of 0 mAh/cm², 2 mAh/cm², and 4 mAh/cm² (1, 2, 3). 3D, three-dimensional; CM, copper mesh; RF, resorcinol formaldehyde; SEM, scanning electron microscope.

than that in coin cells with cell pressure. These results prove that the super-three-dimensional modification layer provides a reservoir for Li and induces the uniform nucleation and deposition of Li. Additionally, the introduction of dispersed CuO_x lithiophilic sites in a-RF@3D CM could further homogenize the nucleation of Li⁺ flux and thus regulate the Li deposition to achieve a dense and uniform platting.

3.4. SEI analysis

The interfacial structure, including the SEI layer, between the anode current collector and electrolyte is a key to regulating the lithium plating/stripping and the lithium cycling efficiency, thus the interfacial impedance and charge transfer behavior were evaluated by electrochemical impedance spectroscopy of the asymmetric cells containing the CM (Fig. S11), 3D CM (Fig. 5a), and a-RF@3D CM (Fig. 5b) current collectors paired with Li foil. Three current collectors show similar internal resistance in the fresh cells. The initial charge transfer resistance is 24.45 Ω for a-RF@3D CM, which is lower than those for CM (88.26 Ω) and 3D CM (63.34 Ω). The charge transfer resistance is reduced in all cells after cycles, which is related to the formation of the conductive SEI layer. And the interfacial charge transfer resistance is reduced to 26.49 Ω , 10.74 Ω , and 7.04 Ω , respectively, after 5 cycles (Fig. 5c). The enhanced decrease of the interfacial resistance in the a-RF@3D CM cell suggests that more conductive SEI layer is formed. The SEI layer at the anode/electrolyte interface significantly affects the interfacial transport of lithium ions, and the conductivity of SEI is dependent on its composition and thickness [59]. Repeating breakage and formation of SEI layer would occur if SEI is unstable, leading to the



Fig. 5. (a–b) EIS curves of Li||3D CM (a) and Li||a-RF@3D CM (b) cells at the fresh state and after 5th, 50th, and 100th cycle, respectively. (c) EIS curves of Li||CM, Li||3D CM and Li||a-RF@3D CM cell at the 5th cycle. (d–g) Deconvoluted XPS spectra of C1s (d), O1s (e), and F1s (f) in the SEI layer of CM, 3D CM, and a-RF@3D CM after 5 cycles. 3D, threee-dimensional; CM, copper mesh; EIS, electrochemical impedance spectroscopy; RF, resorcinol formaldehyde; SEI, solid electrolyte interphase; XPS, X-ray photoelectron spectroscopy.

formation of thick and resistive interfacial layer [60]. The above results demonstrate that more stable SEI is formed in the a-RF@3D CM cell, leading to the lowest interfacial resistance for all cycles. The stable SEI may be related to the products from the reaction between lithium and the modification layer.

In order to further understand the formation of stable SEI in a-RF@3D CM, XPS was employed to analyze the chemical composition of SEI layers. Fig. S12 shows the XPS spectra in the SEI layer of CM, 3D CM, and a-RF@3D CM. And the detailed contents of some key species in the SEI are listed in Table S2. In the C 1s spectra (Fig. 5d), the species of C-C/C-H (284.8 eV) increase from 34.97%/ 47.68% in CM/3D CM to 56.18% in a-RF@3D CM, due to the introduction of modification layer. The contents of C-O and O-C]O, which are related to the formation of organic components by the decomposition of electrolyte solvents, are greatly reduced in the a-RF@3D CM. It suggests that the decomposition of organic solvents and side reactions regarding solvent reduction is suppressed. It is worth noting that the peak of Li_2C_2/Li_xC_6 appears around 282.4 eV in a-RF@3D CM with content of 21.18% which is increased from 19.23%/16.19% in CM and 3D CM. This may be related to the occurrence of the lithiation of amorphous carbon species in the modification layer and the following reduction reaction of Li₂CO₃, resulting in the formation of lithium carbon compound like $Li_2C_2/$ Li_xC₆ [52,61,62].

$$Li_2CO_3 + 5Li^+ + 5e^- \to 0.5Li_2C_2 + 3Li_2O$$
(1)

The Li_2C_2/Li_xC_6 species with low Li^+ diffusion barrier would enable fast, stable plating, and stripping of lithium [63].

In the O 1s spectra, the contents of organic components including ROCO₂Li (530.7 eV) and ROR (533.2 eV), by-products from the decomposition of electrolyte solvent/lithium salts, decrease significantly (Fig. 5e) from 31.86%/31.42% in CM/3D CM to 28.38% in a-RF@3D CM, which is consistent with the above results. At the same time, among the inorganic components, the contents of LiOH (532.1 eV) are significantly increased from 16.91%/35.42% in CM/3D CM to 52.01% in a-RF@3D CM. When LiOH is the major passivation layer, less participation from solvent molecules and bistrifluoromethanesulfonimide (TFSI)⁻ during the SEI formation is expected, inducing less electrolyte side reactions and stable SEI [64]. Nevertheless, the content of Li₂CO₃ (531.5 eV) shows a large decrease from 30.41%/6.31% in CM/3D CM to 2.20% in a-RF@3D CM, which may be related to the reduced formation of organic component ROCO₂Li since the formation of Li₂CO₃ is related to the decomposition of ROCO₂Li at the later state of SEI formation [65]. Another cause for the decrease of Li₂CO₃ is related to the occurrence of Equation (1), resulting in the formation lithium carbon compound, which is consistent with the C1s spectra.

As shown in the F1s spectra (Fig. 5f), the atomic content of LiF (685.0 eV) in the SEI increases significantly from 39.25% in CM, 32.89% in 3D CM to 54.11% in a-RF@3D CM. The LiF possesses high Young's modulus and relatively low Li⁺ diffusion barrier, thus the increase of LiF can greatly enhance the mechanical strength of SEI,

resulting in stable SEI [66]. Overall, the results demonstrate that SEI with abundant inorganic lithium compounds is formed and participation of electrolyte decomposition is suppressed during SEI formation in the a-RF@3D CM, leading to stable SEI layer and elevated cycling stability.

3.5. Electrochemical performance of full cells

The anode-free full cells were assembled to investigate the potential application of a-RF@3D CM current collector in AFLMB. The commercial LiFePO₄ (LFP) in areal capacity of ~1.6 mAh/cm² was adopted as cathode, and commercial Cu foil current collector was used as reference. Fig. S13 shows the voltage curves of LFP||Cu and LFP||a-RF@3D CM anode-free coin cells at the initial cycle and Fig. 6a shows the cycling behavior of LFP||Cu and LFP||a-RF@3D CM full cells. There is a charging platform from 1.8 V to 3.5 V in LFP||a-RF@3D CM cell which can be ascribed to the initial lithiation slope of a-RF@3D, consistent with above results in Fig. 3a. However, comparing with Cu foil current collector, the a-RF@3D CM exhibits higher reversible capacity. The full cell with the a-RF@3D CM displays discharge capacities of 131.2 mAh/g, 100.2 mAh/g, and 81.0 mAh/g at the 5th, 50th, and 100th cycle, which is superior compared with Cu with discharge capacities of 119.4 mAh/g, 73.0 mAh/g, and 49.4 mAh/g, respectively. Different from the halfcell with abundant lithium sources, there is limited lithium in anode-free full-cell considering that all lithium comes from the cathode and the lithium consumed by side reactions cannot be replenished, resulting in different cycling performance from that in half-cell. As shown in Fig. 6b, average CE (ACE), initial CE (ICE), and capacity retention rate (CRR) of the Cu are 99.08%, 77.23%, and 39.82%, respectively. And these parameters in a-RF@3D CM cell are elevated to 99.50%, 84.77%, and 60.66%, respectively. The improved ICE and ACE indicate the reduced side reaction and more stable interface in the a-RF@3D CM cell, which could be ascribed to the improved SEI layer. The capacity-voltage curves for the 5th, 50th, and 100th cycles are shown in Fig. 6c. Both cells in the anode-free setup exhibit stable voltage plateaus during successive charge/ discharge cycles. And the a-RF@3D CM cell displays much slower



Fig. 6. Electrochemical performance of LiFePO₄ (LFP)-based anode-free lithium metal batteries (AFLMBs). (a) Cycling performances of LFP||Cu and LFP||a-RF@3D CM full cells at the charge/discharge rate of 0.2/0.3C. (b) Average Coulomb efficiency (ACE), initial Coulomb efficiency (ICE), and capacity retention rate (CRR) of LFP||Cu and LFP||a-RF@3D CM anode-free coin cells. (c) Voltage curves of LFP||Cu and LFP||a-RF@3D CM anode-free coin cells at the 5th, 50th, and 100th cycles. (d) Cycling performances of LFP||Li@Cu and LFP||Li@a-RF@3D CM full cells at the charge/discharge rate of 0.2/0.3C with N/P = 1.6. (e) ACE, ICE, and CRR of LFP||Li@cu and LFP||a-RF@1B/2D CM anode-free coin cells. (f) Voltage curves of LFP||Li@cu and LFP||Li

capacity decay comparing with Cu cell. It demonstrates that the introduction of super-three-dimensional lithiophilic modification layer in a-RF@3D CM effectively improves the cycle stability of the AFLMB full cell.

The full cells with lean Li metal anode and LFP cathode. in which current collectors were pre-deposited with 1 mAh/cm² Li (Li@current collector), were used to further evaluate the applicability of the modified current collector (N/P ratio = 1.6). The N/P ratio is the areal capacity ratio of negative to positive electrode [67]. The ratio is defined as N/P = 1 + excess Li, thus N/P ratio in anodefree cell is 1, and the N/P ratio is larger than 1 when there is extra Li source at the anode side. Here the extra lithium is guite limited compared to the anodes using micrometer-thick lithium foils. As shown in Fig. 6d, the full cell with the Li@a-RF@3D CM displays discharge capacities of 156.0 mAh/g, 151.3 mAh/g, 145.0 mAh/g, and 125.7 mAh/g for the 5th, 50th 100th, and 150th cycles, which are higher than those in the Li@Cu cell (154.0 mAh/g, 145.8 mAh/g, 114.2 mAh/g, and 85.8 mAh/g, respectively). The ACE, ICE, and CRR of the Li@a-RF@3D CM (Fig. 6e) cell is greatly increased to 99.78%, 94.17%, 64.43% after 200 cycles, respectively, compared to the values of 99.56%, 95.47%, 41.07% in Li@Cu cell. Fig. 6f shows the capacity-voltage curves for the 5th, 50th, 100th, and 150th cycles. Similarly, the Li@a-RF@3D CM cell exhibits significantly suppressed capacity decay comparing with the Li@Cu cell, which is related to the lithiophilic modification layer and more stable SEI in a-RF@3D CM, as demonstrated above. Overall, compared with commercial Cu foil, the a-RF@3D CM with the super-three-dimensional modification layer as Li reservoir and lithiophilic sites in the composite layer is quite effective in regulating and stabilizing lithium plating/ stripping. Compared with the progress of AFLMB systems in the available literatures [22,68-74], as shown in Table S4, the research here has yielded considerable improvement of the electrochemical performance. The modification of anode current collector has made great progress in suppressing dendrite growth and guiding the uniform deposition of lithium metal. Still, more work is still needed to further enhance the cycling performance and CE. And the inadequate cycling performance of the LFP||a-RF@3D CM anode-free cells is mainly due to the irreversible consumption of lithium caused by the high surface area of current collector. To solve this problem, critical strategies to reduce the surface area of the modification layer is desired. Besides, appropriate electrolyte with good compatibility in anode-free system and lithium replenishment method in the cathode side would also be essential to reduce active lithium loss and elevate the CE.

4. Conclusion

In summary, we developed a Cu-based current collector with super-three-dimensional lithiophilic modification layer for AFLMB. The lithiophilic modification layer consists of highly dispersed CuO_x sites together with the O-containing defective carbon, which is able to reduce the nucleation barrier of Li, effectively improve the lithiophilicity of the current collector and the cycle stability. In addition, the super-three-dimensional microstructure in a-RF@3D CM successfully accommodates the uniform dendrite-free lithium deposition. As a result, the a-RF@3D CM current collector exhibits reduced overpotential of 14.2 mV and prolonged cycling life over 400 cycles with an area capacity of 1 mAh/cm² at plating/stripping 0.6 mA/cm²/1 mA/cm². In the anode-free LFP||a-RF@3D CM cell, average CE of 99.50% and capacity retention of 60.66% are successfully achieved after 100 cycles. Meanwhile, average CE 99.78% and capacity retention of 64.43% are achieved in LFP||Li@a-RF@3D CM cell (N/P = 1.6) after 200 cycles. The work here provides a feasible way to realize the fabrication of AFLMB and also enhance the understanding of SEI evolution and regulation strategy of Li plating/stripping in advanced practical Li metal-based battery systems.

Credit author statement

Nanrui Li: investigation, conceptualization, methodology, data curation, validation, writing – Original draft preparation. Tianqi Jia: methodology, investigation, writing-reviewing and editing. Yanru Liu, Yunfei Ouyang: validation, formal analysis, investigation. Yao Lv, Geng Zhong, Yufeng Wang: formal analysis, investigation, Bo Sun, Sirong Lu: supervision, resources. Shifei Huang, Feiyu Kang: investigation, funding acquisition, writing-reviewing and editing. Yidan Cao: supervision, investigation, conceptualization, methodology, data curation, validation, resources, funding acquisition, project administration, writing-reviewing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.mtener.2023.101341.

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