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Coralloid Carbon Fiber-Based Composite Lithium Anode for Robust Lithium Metal Batteries



Lithium (Li) metal is among the most promising anode materials for nextgeneration high-energy-density batteries. However, both dendrite growth and unstable solid electrolyte interphases have hindered its practical applications. Herein, we propose a coralloid carbon fiber-based composite lithium anode, which is an initially Li-containing structured anode. Such electrode design renders dendrite-free morphology during repeated stripping/plating cycles and extraordinary electrochemical performance in Li-LiFePO₄ and Li-sulfur cells. Rui Zhang, Xiang Chen, Xin Shen, ..., Chong Yan, Chen-Zi Zhao, Qiang Zhang

cxb12@mails.tsinghua.edu.cn (X.-B.C.) zhang-qiang@mails.tsinghua.edu.cn (Q.Z.)

HIGHLIGHTS

Coralloid carbon fibers were achieved by electroplating Ag onto their surface

Ag coating layer endows electrodes with lithiophilic nature to syphon molten Li

The composite Li electrode can cycle without dendrite growth or volume change

The composite Li can match Licontaining (LiFePO $_4$) and Li-free (sulfur) cathodes

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Coralloid Carbon Fiber-Based Composite Lithium Anode for Robust Lithium Metal Batteries

Rui Zhang,¹ Xiang Chen,¹ Xin Shen,¹ Xue-Qiang Zhang,¹ Xiao-Ru Chen,¹ Xin-Bing Cheng,^{1,*} Chong Yan,¹ Chen-Zi Zhao,¹ and Qiang Zhang^{1,2,*}

SUMMARY

Lithium metal is among the most promising anode materials in next-generation energy-storage systems. However, Li dendrite growth and unstable solid electrolyte interphase have hindered its practical applications. Structured current collectors have been widely proposed to settle these issues, whereas the prefilling of Li metal into structured anode is challenging. We proposed a coralloid silver-coated carbon fiber-based composite Li anode (CF/Ag-Li) through Ag electroplating and molten Li infusion. The molten Li can be infused into the carbon fiber framework due to the lithiophilic nature of Ag. In addition, a dendrite-free morphology and extraordinary electrochemical performance are achieved in Li-LiFePO₄ and Li-sulfur cells. The CF/Ag-Li|Li symmetrical cells can cycle for 160 cycles at 10.0 mA cm⁻² and 10.0 mAh cm⁻². The CF/Ag-Li|S cells exhibited a high initial discharge capacity of 785 mAh g⁻¹ and a large capacity retention rate after 400 cycles at 0.5C.

INTRODUCTION

With the rapid development of high-end electronic devices such as mobile phones and electric vehicles, the currently widely used lithium (Li)-ion batteries are finding it very difficult to meet the growing demand for energy storage. The practical applications of next-generation rechargeable batteries with much higher energy densities have become the most challenging concerns in recent years. Li metal, the "Holy Grail" electrode, is recognized as the most promising anode due to its ultrahigh theoretical specific capacity of 3,860 mAh g⁻¹ and the lowest negative electrochemical potential (-3.040 V versus standard hydrogen electrode).¹⁻⁴ However, the practical applications of Li metal batteries such as Li-sulfur (Li-S) and Li-oxygen (Li-O₂) batteries have been severely hindered by severe challenges (such as Li dendrite growth, unstable solid electrolyte interphase [SEI], and large volume change during repeated charge-discharge cycles), which induces low discharging capacity and short cycling life accompanied by safety hazards.^{5–8}

Grand strategies have been proposed to settle these issues. (1) Various electrolyte additives have been employed to build a stable SEI layer on the surface of Li metal anode, by which the plated Li can be protected from irreversible reactions with organic electrolytes.^{9–12} (2) Artificial SEI layers, including inorganic compounds and organic polymers, have been extensively investigated for their ability to inhibit Li dendrite growth and therefore render dendrite-free morphology and high cycle performance.^{13–17} (3) Concentrated liquid electrolytes, solid-state electrolytes, and hybrid electrolytes have also been reported to exhibit outstanding effects in

Context & Scale

With the rapid development of electric vehicles and portable electronics such as mobile phones and laptops, the widely used lithium (Li)-ion batteries are having many difficulties in meeting the growing demands for high-energy-density energystorage systems. Li metal, with an ultrahigh theoretical specific capacity of 3,860 mAh g^{-1} and the lowest negative electrochemical potential (-3.040 V versus standard hydrogen electrode), has become one of the most promising anode materials for next-generation batteries. Unfortunately, the practical application of Li metal anode has been hindered by its low cycling efficiency, short lifespan, and potential safety hazards. Herein we propose a Li-containing composite electrode based on coralloid carbon fibers that exhibited extraordinary electrochemical performance in full cells of Li-S and Li-LiFePO₄ batteries. Such proof of concept on Li-infused structured electrodes sheds fresh light on the dendrite-free plating of Li metal anodes in working rechargeable batteries.

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Li dendrite inhibition.^{2,4,18–23} However, Li metal anode is a hostless electrode and the interfacial films constructed by the aforementioned strategies are not strong and stable enough to suppress the dendrite growth when the electrode experiences a sharp volumetric change. A structured composite metallic electrode with a preexistent framework for Li plating is the prerequisite for a high-capacity and long-life-span Li metal anode.

The structured composite anode can regulate the Li⁺ deposition and induce dendrite-free morphology, which is very helpful in realizing a high-capacity and long-lifespan Li metal anode.^{24–36} Great progress has been made in the rational design of novel matrices for Li deposition, such as carbon-based frameworks and 3D metal-based current collectors.^{31,37–42} However, these structured anodes are mainly the initially Li-free anodes, and cannot be directly paired with Li-free cathode materials (such as the high-specific-capacity S and O₂ cathodes) to assemble rechargeable high-energy-density batteries. Even matching the Li-containing cathode (such as LiFePO₄), these initially Li-free anodes cannot provide excess Li to offset the irreversible consumption in the chemical formation and later cycling processes. Therefore, it is crucial to pre-fill the structured anode with an appropriate amount of Li to obtain a composite Li metal electrode.

In this contribution, we proposed a coralloid carbon fiber (CF)-based composite Li anode. Coralloid CFs were achieved by electroplating silver (Ag) particles onto the surface of CFs. Compared with the conventional high-temperature chemical vapor deposition and atomic layer deposition (such as Si, ZnO, Al_2O_3),^{30,31,43–45} this electroplating strategy is facile and cost-effective in achieving a lithiophilic matrix. Ag particles can not only endow electrodes with lithiophilic nature to syphon molten Li to obtain a composite Li metal anode (CF/Ag-Li), but can also regulate Li nucleation and growth during Li plating. The CF/Ag-Li composite anode exhibits improved cycling stability during repeated cycles with dendrite-free morphology, even at an extremely high current density of 10.0 mA cm⁻² and a high cycling capacity of 10.0 mA cm⁻². The CF/Ag-Li|LiFePO₄ cells exhibit stable cycles with high specific capacity for more than 500 cycles at 1.0C. The CF/Ag-Li|S cells indicate a very high initial discharge capacity of 785 mAh g⁻¹ and a large capacity retention rate of 64.3% after 400 cycles at 0.5C.

RESULTS

Fabrication and Characterization

Conductive CF is a suitable matrix for Li metal anode due to its high electrical conductivity and large porosity for metallic Li storage.^{33,46–48} It is necessary for a matrix with a high porosity to accommodate more metallic Li and therefore exhibit high-capacity performance in full batteries. However, the CF framework cannot be wetted by molten Li due to its poor lithiophilic nature, since a compact lithiophilic coating layer is necessary to pre-fill Li through a molten-infusion method. Herein, we propose a facile and energy-saving method to synthesize size-controlled lithiophilic Ag particles by directly electroplating Ag on the CF framework. After coating Ag particles on CF, the as-obtained composites exhibit a coralloid morphology (Figure S1). With this Ag coating layer, the CF/Ag framework can be fully infused by molten Li in 1–3 min to produce the Li-filled CF-based Li metal anode (CF/Ag-Li).

The synthesis procedure of the CF/Ag-Li includes two key steps: Ag coating and Li infusion (Figure 1A). The Ag particle coating is conducted by pulse electroplating of Ag on CF framework (Figure S2). The pristine CF consists of crosslinked CFs with a

¹Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P.R. China

²Lead Contact

*Correspondence: cxb12@mails.tsinghua.edu.cn (X.-B.C.), zhang-qiang@mails.tsinghua.edu.cn (Q.Z.) https://doi.org/10.1016/j.joule.2018.02.001

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Figure 1. Fabrication of CF/Ag-Li Composite Electrode

(A and B) Schematic diagrams (A), scanning EM images (B), and (inset figures) digital photos for pristine CF, coralloid CF with electroplated Ag layer (CF/Ag), CF/Ag with molten Li infused at the surface of CF (CF/Ag-Li(I)), and metallic Li fully infused in CF framework (CF/Ag-Li(II)).

uniform diameter of 10 μ m (Figure 1B). The pores constructed by these CFs have a size of several tens of micrometers, which affords enough space for high-capacity Li metal storage and low resistance for Li⁺ transport. After the pulse electroplating at a current density of 20 mA cm⁻² for a total 180 s (repeat 18-s electroplating 10 times, each time followed by 18-s break time), the CFs are compactly covered by uniform Ag grains with the size of 10 μ m. The shape, size, and numerical density of Ag grains can be regulated by the electroplating method, current density, and plating duration (Figure S3). More compact and smaller Ag grains can be electroplated onto CF by the pulse electroplating method at a high current density. It is noteworthy that Ag is plated as tree-like dendrites rather than compact cubic grains when the current density is higher than 40 mA cm⁻² (Figure S3C). The morphology does not interfere the lithiophilic nature of Ag metal. Both cubic Ag grains and tree-like Ag dendrites can effectively guide molten Li to infuse into CF/Ag frameworks.

The Li-infusing process is operated by immersing Ag-coated CF electrodes (CF/Ag) into molten Li at the temperature of 300°C (Figure 2A and Movie S1). When the CF/Ag electrode is placed onto the glossy molten Li, with the siphonic effect provided by the lithiophilic Ag coating layer, molten Li can be automatically infused into CF/Ag frameworks. Molten Li can then spread onto the whole electrode in 2 min. The as-obtained CF/Ag-Li electrode exhibits a silvery-white luster appearance with legible CF skeletons. Such Li-infused CF/Ag with only the surface of each CF covered by molten Li is termed CF/Ag-Li(I) herein (Figures 1A and 2A). Finally, when the CF/Ag electrode is fully immersed into the molten Li, the pores of CF framework can be fully filled with molten Li, and the CF/Ag-Li electrode is obtained (Figure S4), which herein is termed CF/Ag-Li(II) (Figures 1A and 2A). The final CF/Ag-Li has a smooth silvery-white glossy surface with the same appearance as a piece of fresh Li foil. The thicknesses of pristine CF and CF/Ag-Li electrode are both around 150 µm (Figures 2B and 2C), exhibiting a structural stability during Li infiltration and therefore providing a possibility to suppress volumetric changes during repeated Li plating/stripping processes in working batteries. By contrast, the CF framework without a lithiophilic Ag coating layer cannot be filled with molten Li (Movie S2), indicating the indispensable role of the Ag coating layer in the Li-infusing process.

The lithiophilicity of the Ag coating layer is attributed to the formation of Ag-Li alloy once Ag contacts with excessive amounts of molten Li at high temperature. Ag can

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Figure 2. Li-Infusing Process

(A) Digital photos of Li-infusing process: molten Li, different times (0, 30, and 60 s) after the CF/Ag contacted with molten Li, and the as-obtained composite lithium metal anodes (CF/Ag-Li(I) and Li(II)).

(B and C) Cross-sectional scanning EM images of (B) pristine CF framework and (C) CF after Li was fully infused, indicating the unchanged thickness of 150 μm after Li was fully infused.

be easily dissolved in molten Li when the atomic percentage of Li is higher than 71.6% above 170°C from the Ag-Li binary phase diagram (Figure S5).^{49,50} As a result, when the CF/Ag electrode contacts with the molten Li, every fiber in CF/Ag can be automatically and rapidly covered with molten eutectic Ag-Li alloy and molten Li metal, leading to the fully infused Li electrode (Figure S6). When the solid solution of Ag-Li is cooled to room temperature, the Ag-Li alloy phase (Ag-Li, Ag-Li₃, etc.) and pure phase of Li metal freeze and precipitate successively. X-ray diffraction (XRD) was employed to analyze the chemical components at different stages during the fabrication of CF/Ag-Li (Figure 3A). When the pristine CF is covered with an electroplated Ag layer, the peaks of Ag phase arise signally in the XRD spectra of CF/Ag. For CF/Ag-Li(I) the Ag phase disappears, while the Ag-Li alloy phase (especially the Ag-Li component) emerges. The peak of C is replaced with the peak of LiC_x (mainly LiC₆), which indicates that graphite crystals in CFs can be intercalated with Li at such temperatures. The LiAgC₂ three-phase alloy ($2\theta = 27.2^{\circ}$) can also be observed in CF/Ag-Li. Therefore, the alloy components are complicated in the CF/Ag-Li electrode. In contrast, the peak of Aq-Li becomes weak and the peak of pure Li phase grows significantly for the fully infused Li electrode CF/Ag-Li(II). As a result, the metallic Li is the main phase in the fully infused CF/Ag-Li electrode.

X-ray photoelectron spectroscopy (XPS) was also carried out to reveal the surface chemistry of the as-fabricated CF/Ag-Li electrode (Figure S7). The binding energy peak of Ag 3d (368.5 eV for Ag $3d_{5/2}$, 374.5 eV for Ag $3d_{3/2}$) relating to the Ag appears clearly in the XPS spectra of CF/Ag electrode (Figures S7A and S7B). As for the CF/Ag-Li electrode, no Ag peak can be observed, indicating that the CF/Ag framework is perfectly covered with Li metal by our molten-infusion method. When CF/Ag-Li electrodes are cycled in electrolytes such as ether-based electrolyte (1.0 M LiTFSI in DOL/DME in 1:1 volume), the chemical components of the formed SEI is similar to that formed on Li foil electrode in the same electrolyte. The main components of the SEI layers are LiF, Li₂CO₃, and some other organic lithium salts

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Figure 3. Chemical Characterization of CF/Ag-Li

(A) XRD spectra of CF, CF/Ag, and the two stages of CF/Ag-Li.(B and C) Calculated binding energies of a Li atom with (B) Ag atoms and (C) C atoms.

(Figure S7B). The Ag coating layer is stable during electrochemical cycles due to its high electrochemical potential of 3.839 V (versus Li⁺/Li).

The alloy in the CF/Ag film guides the course of molten Li infusing into CF frameworks by reducing interfacial tension of molten Li and CF, which is thermodynamically attributed to the large binding energy between Li and Ag atoms. Density functional theory (DFT) calculations were employed to determine the binding energies between a Li atom and Ag or C (graphene) slab (Figures 3B and 3C). The Ag (111) surface exhibits a much larger binding energy of -2.07 eV than that of pristine CF, -1.14 eV, indicating that the electroplated Ag layer is much more lithiophilic than pristine CF. Such lithiophilic Ag coating can decrease the electroplating overpotentials, guiding the smooth Li deposition.^{38,40} Compared with the pristine CF electrode, the electroplating overpotential of Li deposition on the CF/Ag electrode decreased from 31.0 to 6.5 mV, and the nucleation overpotentials were also reduced from 11.4 to 6.8 mV (Figure S8).

Morphology Evolution

The Li-stripping process of Li fully infused CF/Ag-Li electrode was observed by *in situ* optical microscopy (Figures 4A–4C and Movie S3). The pre-filled Li in the CF framework (CF/Ag-Li electrode) was stripped at a current density of 2.0 mA cm⁻². During the stripping process, the Li metal dissolved from the side at electrolyte (top side in Figures 4A–4C) to the opposite side at the based current collectors (bottom side in Figures 4A–4C). No "dead Li" is observed in this gradual stripping process of Li metal from top to bottom in the CF-based composite Li metal anode. Nearly all of the Li filling this framework can contribute to its active capacity during the stripping process. Importantly, the thickness of CF/Ag-Li is nearly constant after all Li is stripped out, indicating the nearly zero volume change during the stripping process.

To investigate the morphology after replating of metallic Li during cycles, we recorded the morphology after Li stripping and replating at a current density at 1.0 mA cm⁻² and a cycle capacity of 1.0 mAh cm⁻² by scanning electron microscopy (EM) images (Figures 4D and 4E). Metallic Li is stripped evenly at the surface of the CF/Ag-Li electrode. There is no Li dendrite growth when Li is replated on the stripped CF/Ag-Li electrode. The scanning EM images after the first and fifth stripping and replating of Li on CF/Ag-Li also exhibit uniform stripping morphology and dendrite-free replating morphology (Figures 4F and 4G,

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Figure 4. Morphology Evolution of CF/Ag-Li Electrode after Repeated Li Plating/Stripping (A–C) Cross-sectional *in situ* optical microscopy photos of the stripping process of CF/Ag-Li at a current density of 2.0 mA cm⁻² after (A) 0 hr, (B) 2 hr, and (C) 5 hr.

(D–G) Scanning EM images of CF/Ag-Li after (D) first Li stripping, (E) first Li replating, (F) fifth Li stripping, and (G) fifth Li replating with a cycle capacity of 1.0 mAh cm⁻² at a current density of 1.0 mA cm⁻².

(H and I) Scanning EM images of CF/Ag-Li after Li stripping with high cycle capacity of (H) 5.0 mAh cm⁻² and (I) 10.0 mAh cm⁻² at the same high current density of 5.0 mA cm⁻².

high-resolution scanning EM images in Figure S9). Besides, the thicknesses of CF/Ag-Li electrodes after the first and fifth cycle are both around 150 μm (Figures S10A and S10B), which is the same as pristine CF/Ag-Li electrode before the cycling test (Figures 2B and 2C). The consistency in the thickness of CF/Ag-Li electrode before and after repeated Li plating/stripping processes illustrates a nearly zero volume-change property of CF/Ag-Li electrode, which is crucial for a practical electrode. As for Li foil electrode (Figure S11), a large amount of uneven pits emerge after the first Li stripping. After Li replating and a few later cycles, the surface of Li foil is covered with a layer of pulverized Li, indicating the formation of dendritic Li and "dead Li." By contrast, the conductive CF framework endows CF/Ag-Li electrode with dendrite-free and "dead Li"-free plating morphology. Such morphology is attributable to the enlarged active surface area provided by CFs in CF/Ag-Li electrode, which can decrease the local current density and enhance the transportation of electrons and Li ions at the interface between electrode and electrolyte.

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With regard to the structural stability of CF/Ag-Li electrode at high cycling current and capacity, scanning EM images of CF/Ag-Li electrode cycled at a stripping capacity of 5.0 mAh cm⁻² and an extremely high stripping capacity of 10.0 mAh cm⁻² at the same current density of 5.0 mA cm⁻² are exhibited as Figures 4H and 4I, respectively. After such a high-capacity stripping of Li metal, the CF paper skeleton emerged completely, indicating the outstanding structural stability of such CF/Ag-Li electrode at an extremely high stripping capacity. After the same high-capacity stripping capacity.

pacity replating of Li metal in CF/Ag-Li electrode, the even surface morphology as pristine CF/Ag-Li electrode re-emerges (Figure S12). Moreover, the thickness of the CF/Ag-Li electrode after 10 cycles with such a high capacity of 5.0 mA cm⁻² is also ~150 μ m (Figure S10C). The stability in plating/stripping morphology at an ultrahigh current/capacity demonstrates the potential applications of the CF/Ag-Li composite electrodes in the practical cells, usually with a large current density.

Electrochemical Cycling Performance

Galvanostatic cycles of Li|Li symmetrical cells were conducted to probe the longterm cycling stability of CF/Ag-Li electrode. CF/Ag-Li and Li foil electrodes were assembled with Li foil as the counter electrode. When the cells were cycled at a current density of 1.0 mA cm^{-2} with a cycling capacity of 1.0 mAh cm^{-2} , the Li|Li cell exhibited a gradually increasing hysteresis to 80 mV in less than 70 cycles, while the CF/Ag-Li|Li cell maintained a much lower and more stable hysteresis of ~60 mV for more than 200 cycles (Figure 5A). It can be observed that the hysteresis of CF/Aq-Li|Li cell at the initial process is a little larger than that of the Li|Li cell in Figure 5A. This is due to the larger amount of SEI formation of CF/Ag-Li electrode than routine Li foil at the initial few cycles, which is produced by the exposure of the CF framework after Li stripping. When the SEI is mature and becomes stable after the initial few cycles, the hysteresis of CF/Ag-Li|Li cell reduces and becomes smaller than that of the Li|Li cell due to the conductivity of the CF framework playing the critical role in later long cycles. At a higher cycling current of 3.0 mA cm⁻² and capacity of 3.0 mAh cm⁻², the CF/Ag-Li electrode produced hysteresis lower than that of the Li foil electrode, in which the hysteresis increased in 30 cycles (Figure S13A). These symmetrical cells were also conducted at an extremely high current density of 10.0 mA $\rm cm^{-2}$ and a capacity of 10.0 mAh cm⁻². The hysteresis of CF/Ag-Li|Li cells (\sim 120 mV) was lower than that of Li foil|Li cells (~200 mV) in the first 30 cycles (Figure S13B). These good electrochemical results are due to the lower Li ionic transport resistance in CF/ Ag-Li electrode. When part of the Li is stripped from the CF/Ag-Li electrode, the structured anode affords more specific surface area and interconnected transfer channels for plating/stripping and migration of Li⁺ in a working battery. Therefore, the lower hysteresis is achieved during repeated cycles, and hence a superior stability in long-term cycling.

Electrochemical impedance spectroscopy (EIS) was employed to investigate the interfacial transport behavior (Figure S14). It is noteworthy that both the electronic resistance in solid/liquid phase (referring to the intercept at ultrahigh frequency of EIS) and the interfacial ionic resistance in the SEI layer (referring to the semicircle in high frequency of EIS) reduce with the prolonged cycles in CF/Ag-Li|CF/Ag-Li cells. This indicates the effect of the conductive CF framework in CF/Ag-Li electrodes and the stable SEI layer provided by the stable CF skeleton. By contrast, the electronic resistance and the interfacial ionic resistance of Li foil|Li foil cells increase with prolonged cycles, due to the "dead Li" layer with more SEI formation and unstable surface structure on Li foil (Figures S11B–S11D). Furthermore, the resistance in CF/Ag-Li|CF/Ag-Li cell is smaller than that in Li|Li cell in prolonged cycles (e.g., 100th cycle). Consequently, the CF/Ag-Li electrode can effectively enhance



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Figure 5. Long-Term Electrochemical Cycling Performance

(A) Voltage profile of CF/Ag-Li|Li and Li foil|Li cells with a cycle capacity of 1.0 mAh $\rm cm^{-2}$ at 1.0 mA $\rm cm^{-2}.$

(B and C) Discharge capacity and Coulombic efficiency (B), and charge and discharge curves (C) at different cycles of CF/Ag-Li|LFP and Li foil|LFP cells at 1.0C (1.0C = 170 mA g^{-1} for LFP cathode). (D and E) Discharge capacity and Coulombic efficiency (D), and charge and discharge curves (E) at different cycles of CF/Ag-Li|S and Li|S cells at 0.5C (1.0C = 1,675 mA g^{-1} for sulfur cathode). (F) Discharge capacity and Coulombic efficiency of CF/Ag-Li|S and Li|S cells at 1.0C. (G) Rate performance of CF/Ag-Li|S and Li|S cells.

the electronic conductivity in anode and the interfacial charge transfer at the electrode surface.

Li|LiFePO₄ (LFP) cells were firstly assembled to evaluate the full-cell performance of CF/Ag-Li electrode, as the LFP electrode is relatively stable. The specific capacity of

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CF/Ag-Li|LFP reaches 137 mAh g^{-1} at the first cycle and gradually decreases to 86 mAh g^{-1} at the 500th cycle (Figures 5B and 5C). While the specific capacity of Li foil|LFP is initially 110 mAh g^{-1} and rapidly fades to nearly 20 mAh g^{-1} after 500 cycles. The Li|LFP cells assembled with CF/Ag-Li composite electrode exhibited higher and more stable specific capacity than Li foil electrode, indicating the robust ionic and electronic channels in the CF/Ag-Li electrode.

Such a superior CF/Aq-Li electrode is also employed in Li-S cells, which have been considered one of the most promising next-generation rechargeable batteries because of its extremely high theoretical energy density of 2,600 Wh kg^{-1,5,51,52} Unlike the LFP cathode, the S cathode is a Li-free electrode on the cathode side, which indicates that all of the active Li in Li-S cells comes from the anode electrode. To ensure an equitable comparison, routine Li foil and CF/Ag-Li have the same activated areal capacity of 10 mAh cm^{-2} , meaning that Li foil in this experiment has a thickness of 50 µm. When conducted in prolonged cycles, the CF/Ag-Li|S cell exhibited a high initial discharge capacity of 785 mAh g^{-1} and a high capacity retention rate of 64.3% after 400 cycles at 0.5C, which is higher than ultrathin Li|S cells with a capacity retention rate of 52.7% after 400 cycles (Figures 5D and 5E). We noticed that the capacity retention of both CF/Ag-Li|S cells and ultrathin Li|S cells after prolonged cycles are not very high, which is due to the polysulfide-shuttle behavior in Li-S cells, especially when the sulfur cathode is paired with limited Li in CF/Aq-Li and ultrathin Li electrodes. At a current density of 1.0C, the CF/Aq-Li|S cells exhibited a high initial discharge capacity of 781 mAh g^{-1} , which is higher than ultrathin Li|S cells that have an initial discharge capacity of only 215 mAh g^{-1} (Figures 5F and S15). The CF/Aq-Li electrode in Li-S cells has also exhibited a superior rate performance (Figure 5G). The discharge capacity of CF/Ag-Li|S cells can reach 1,111, 941, and 714 mAh g^{-1} with the increasing current density of 0.1C, 0.2C, and 1.0C (1.0C = 1,675 mA g^{-1}), while those of ultrathin Li|S cells were only 957, 863, and 231 mAh g^{-1} , respectively. Of note, the discharge capacity of ultrathin Li|S cells at a current density higher than 1.0C is very low (Figures 5F and 5G). Such a significant difference is due to the inhomogeneous stripping of Li from capacitylimited ultrathin Li foil, in which the activated Li is reduced due to the increasing of high-proportion "dead Li" with prolonged cycles. By contrast, Li in the similarly capacity-limited CF/Ag-Li can be uniformly plated/stripped without "dead Li" ascribed to the conductive CF framework. Therefore, the CF/Ag-Li anode exhibited much higher discharge capacities attributable to the efficient composite electrode. As a result, the Li-containing structured anode, such as the CF/Ag-Li electrode, is much more promising than routine Li foil anodes in full cells because of its high efficiency in suppressing dendritic Li growth and "dead Li" formation.

DISCUSSION

A lithiophilic Ag coating layer is proposed to guide molten Li infusion into the CF framework to fabricate an initially Li-containing structured Li metal anode. The lithiophilic Ag coating layer is achieved by a facile pulse electroplating, which is economical, generally applicable, and finely controlled. Such an Ag layer can be coated on various conductive structured current collectors such as C-based and metal-based frameworks. By infusing molten Li into these structured current collectors, the Li-filled metal anode exhibits better electrochemical performance. This introduces following merits:

(1) The molten Li-infusion method observably increases the active Li content in composite anode electrode. The strategy with Li pre-filled by electroplating



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is not only complicated but also introduces extra irreversible SEI components and useless "dead Li," which severely reduces the energy density. On the contrary, the strategy with Li pre-filled by molten Li avoids contact of Li metal with the electrolyte and guarantees an extremely high energy density.

(2) Structured current collectors reduce the electrical and ionic resistance by the high specific surface area and large porosity. Compared with routine Li foil, structured Li metal anode has more active surface for the transport of electrons and Li ions. The interconnected pores render enough space for Li ion migration between electrodes. Besides, the structural stability can also render zero volume change during cycles.

In addition, the practical specific capacity of composite electrodes is one of the most concerning material parameters in future high-energy-density batteries. For Li pre-filled composite electrodes, the practical specific capacity of composite electrodes $Q_{\rm p}$ can be calculated by the measured practical mass fraction of Li metal in electrodes $\omega_{\rm Li,p}$ as follows:

$$Q_{\rm p} = Q_{\rm Li}\omega_{\rm Li,p}$$
, (Equation 1)

where $Q_{\text{Li}} = 3,860 \text{ mAh g}^{-1}$ is the theoretical specific capacity of Li metal. In an ideal Li pre-filled composite electrode, all of the pores in the original framework can be filled with molten Li. Therefore, the theoretical specific capacity of composite electrode Q_{t} can be controlled by the porosity φ of the structured framework (such as CF/Ag electrode) as follows:

$$Q_{t} = Q_{Li}\omega_{Li,t} = Q_{Li}\frac{\varphi\rho_{Li}}{\rho_{f} + \varphi\rho_{Li}} = Q_{Li}\frac{\varphi\rho_{Li}}{(1 - \varphi)\rho_{0} + \varphi\rho_{Li}} , \qquad (Equation 2)$$

where $\omega_{\text{Li},t}$ is the theoretical mass fraction of Li in composite electrode, ρ_{Li} , ρ_{f} , and ρ_0 are the density of Li metal, apparent density of structured framework, and the absolute density of framework material, respectively. $\varphi = 1 - \rho_{\text{f}}/\rho_0$ is the porosity of structured framework. In the CF/Ag-Li electrode, the average porosity of CF is 75% and the apparent density of CF/Ag framework is measured as 0.539 g cm⁻³. Thus the theoretical specific capacity is calculated to be 1,644 mAh g⁻¹, which is almost equal to the measured practical specific capacity can be easily enhanced by employing frameworks with higher porosity, lower apparent density, or lower absolute density according to Equation 2. Furthermore, all of the pores being filled with Li is critical for high practical specific capacity, which can be successfully achieved by the molten Li-infusion methods based on lithio-philic conductive frameworks.

In conclusion, the CF/Ag-Li composite electrode exhibits an extraordinary structural stability in the process of Li plating and stripping with dendritefree morphology. The CF/Ag-Li|Li symmetrical cells can cycle for more than 160 cycles with low hysteresis at an extremely high current density of 10.0 mA cm⁻² and very high capacity of 10.0 mAh cm⁻². Besides, the composite Li electrodes can match Li-containing (LiFePO₄) and Li-free (S) cathodes to render superb electrochemical performance. CF/Ag-Li|LFP cells exhibit stable cycles with high specific capacity for more than 500 cycles at 1.0C. These CF/Ag-Li electrodes display much more outstanding performance in high-energy-density Li-S batteries. The CF/Ag-Li|S cells achieve a capacity retention rate of 64.3% after 400 cycles at 0.5C and a high initial capacity of 781 mAh g⁻¹ at 1.0C, which is much higher than those of routine Li-S cells. Such an Ag coating layer can not only guide the molten Li infusing into structured CF frameworks at

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the fabrication of the CF/Ag-Li electrode, but also reduce the Li plating resistance and enhance the electrochemical performance during repeated cycles. More importantly, the initially Li-containing structured anodes such as CF/Ag-Li electrodes are promising for high-energy-density full cells such as Li-S and Li-O₂ batteries, which sheds new light on the dendrite-free plating of Li metal anodes in working rechargeable batteries.

EXPERIMENTAL PROCEDURES

Fabrication of CF/Ag-Li

The CF papers were purchased from Shanghai Hesen Electric. After washing with 1.0 wt% HCl and deionized water, the CF was electroplated in 0.20 M AgNO₃ aqueous solution at a pulse current of 20 mA cm⁻² for total of 180 s (repeat 10 times 18-s electroplating, each time followed by 18-s break). The obtained CF/Ag was washed by deionized water. The dried CF/Ag was then immersed into molten Li to produce the Li-infused CF/Ag-Li electrode in an Ar-filled glovebox with O₂ and H₂O content below 0.1 ppm. The Li was previously melted in a stainless-steel case on a hot plate (C-MAG HP 4, IKA) at a temperature of 300°C. The average areal CF, Ag, and Li amounts were 4.32, 3.77, and 5.54 mg cm⁻² (31.7, 27.6, 40.7 wt% of CF/Ag-Li), respectively.

Computational Method

All DFT calculations were conducted in the Vienna *ab initio* Simulation package^{53,54} and the results were visualized in Materials Studio.⁵⁵ The projector augmented-wave^{56,57} pseudopotentials and Perdew-Burke-Ernzerhof generalized-gradient approximation functional⁵⁸ were adopted in DFT calculations. The energy cutoff was set to 520 eV. The SCF and geometry convergence tolerance were set to 1 × 10⁻⁵ eV and 1 × 10⁻⁴, respectively.

The Ag (five-layer 2 × 2 × 1 super cell, (111) crystal face) and graphene slab were constructed with a 1.5-nm vacuum. A Γ -centered k-point grid by Monkhorst-Pack method⁵⁹ was set to 4 × 4 × 1 and 6 × 6 × 1 for Ag and graphene slab, respectively. When interacting with Li atom, only the bottom two-layer atoms in the Ag slab were fixed and the others were fully relaxed. The binding energy, $E_{\rm b}$, was defined as

 $E_{\rm b} = E_{\rm total} - E_{\rm slab} - E_{\rm Li},$ (Equation 3)

where E_{total} , E_{slab} , and E_{Li} are the total energy of Ag/graphene slab bound with Li atom, the pristine Ag/graphene slab, and single Li atom, respectively.

According to our previous study, the binding energy between a framework and a Li ion has a good linear relationship with that between the framework and a Li atom.⁴⁰ Therefore, only the binding energy between Ag/graphene and Li atom is considered herein. Moreover, the Li ion will be immediately reduced as soon as it contacts with the conductive framework in a working cell. Therefore, considering the binding between a framework and a Li atom is more reasonable.

Electrochemical Measurements

All cells were assembled with standard CR2025 coin-type cells in an Ar-filled glovebox with O_2 and H_2O content below 1.0 ppm. A CF/Ag-Li electrode with a diameter of 13.0 mm and 0.5-mm thick Li metal foil with a diameter of 16.0 mm (China Energy Lithium) were employed as the working and counter electrodes in symmetrical cells,

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respectively. An LFP cathode with LFP loading of 4.9 mg cm⁻² and 0.5-mm thick Li metal foil with a diameter of 16.0 mm were employed in Li|LFP cells. A sulfur cathode with sulfur loading of 1.7 mg cm⁻² and 50-µm thick Li metal foil with a diameter of 12.0 mm were employed in Li|S cells. Lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1.0 M; v/v = 1:1) (Beijing Chemical Industry Group) was employed as the electrolyte in symmetrical cells. LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1.0 M; v/v = 1:1) (Beijing Chemical Industry Group) was used as the electrolyte in Li|LFP cells. LiTFSI in DOL/DME with 2.0% LiNO₃ (1.0 M; Alfa Aesar) was employed as the electrolyte in Li|S cells. These coin cells were monitored in galvanostatic mode in a Land CT2001 multichannel battery tester. The EIS measurements were performed on a Solartron 1470E electrochemical workstation (Solartron Analytical).

Characterization

A scanning electron microscope (JSM 7401F; JEOL, Japan) operated at 3.0 kV was employed to characterize the morphology of CF, CF/Ag, and CF/Ag-Li electrodes before and after cycles. XRD patterns were recorded on a Bruker D8 Avance diffractometer equipped with a Cu-K_{α} radiation source. *In situ* optical microscopy was employed to investigate the Li-stripping process of CF/Ag-Li electrode. A quartz cell with transparent windows was used as the electrode housing, in which a symmetrical cell with Cu foil and CF/Ag-Li electrode were assembled. XPS (ESCALAB 250Xi, Thermo Fisher Scientific, USA) was employed to analyze the surface chemistry of the electrodes.

SUPPLEMENTAL INFORMATION

Supplemental Information includes 15 figures and 3 movies and can be found with this article online at https://doi.org/10.1016/j.joule.2018.02.001.

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AUTHOR CONTRIBUTIONS

Q.Z. and R.Z. conceived this work; Q.Z., R.Z., and X.-B.C. designed all experiments; R.Z. fabricated the CF/Ag-Li electrodes; X.C. performed the DFT calculations; X.S. conducted the *in situ* optical microscopic observations; R.Z. performed characterizations of CF/Ag-Li electrodes; R.Z., X.-Q.Z., X.-R.C., C.Y., and C.-Z.Z. measured the cell performance; R.Z., X.-B.C., and Q.Z. wrote the paper; all authors participated in analysis of the experimental data and discussions of the results as well as preparing the paper.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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