Dendrite-Free Lithium Electrodeposition Enabled by 3D Porous Lithiophilic Host toward Stable Lithium Metal Anodes

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Abstract

Lithium metal is a promising anode utilized in cutting-edge high-energy batteries owing to the low density, low electrochemical potential, and super high theoretical capacity. Unfortunately, continuous uncontrollable lithium dendrite growth and ‘dead’ lithium result in capacity decay, low coulombic efficiency, and short circuit, severely hindering the practical utilization of lithium anode. Herein, we propose a three-dimensional porous lithiophilic current collector for lithium storage. The conductive 3D structure constructed by carbon fiber (CF) can well accommodate the deposited lithium, eliminating volume change between the lithium depositing/stripping process. Moreover, the polydopamine (PDA) coating on the CF surface possesses a large number of polar groups, which can homogenize Li$^+$ ions distribution and apply as the sites for lithium deposition, decreasing nucleation overpotential. As a result, under the 1 mA cm$^{-2}$ current density, the PDA coated CF (PDA@CF) electrode exhibits high CE (~98%) for 1000 cycles. Galvanostatic measurements demonstrate that the Li anode using PDA@CF achieves 1000 h cycling life under 1 mA cm$^{-2}$ with a low overpotential (<15 mV). The LiFePO$_4$ full cell shows enhanced rate performance and stable long-term cycling.

Keywords: Lithium metal, Lithium metal battery, Lithium dendrites, 3D host, Polydopamine, Carbon fiber


1. Introduction

Rechargeable lithium-ion batteries have been extensively utilized in various fields, including small electronic equipment, electric vehicles, and energy storage grid.\(^1\) However, due to the relatively low specific capacity of traditional electrodes, such as graphite electrodes (372 mAh g\(^{-1}\)), it is difficult to satisfy the expanding demand for more capacity and power.\(^2\) To address this difficulty, lithium metal battery (LMB) are considered as an ideal substitute owing to their high energy density. Compared to other anode materials, lithium metal has an unprecedented theoretical capacity of 3860 mAh g\(^{-1}\) and the lowest electrochemical potential (-3.04 V vs. the SHE).\(^3\) Therefore, lithium metal is relied upon to supplant graphite as the first choice of the next generation high-energy Li-S and Li-O\(_2\) batteries.\(^4,5\)

As early as 1976, lithium anode has already been studied and fabricated by Exxon.\(^6\) Unfortunately, its cycling instability and safety concerns limit the commercialization of lithium metal batteries. Unlike lithium intercalation compounds, lithium ions are directly deposited on the lithium anode surface during charging, so the surface morphology has a great impact on the lithium-ion deposition behaviors.\(^7\) There may be an uneven local Li\(^+\) flux between the electrolyte and electrode because of the rugged morphology. Subsequently, Li\(^+\) tend to plate on the protrusions of the electrode, leading to the formation of lithium dendrite, further increasing the surface roughness.\(^8,9\) Besides, the solid electrolyte interface (SEI) can’t accommodate the tremendous volume change of lithium metal in the cycling process, which falls into repeated rupture and regeneration, prompting capacity loss, low coulombic efficiency and lifetime degradation.\(^10,11\) The uncontrollable sharp dendrites can poke through the separator, eventually causing the short circuit.\(^12\)

Different electrolyte additives have been created to optimize the liquid electrolytes, including fluoroethylene carbonate,\(^13-15\) Cs\(^+\) ions,\(^16,17\) CO\(_2\),\(^18\) LiF,\(^19,20\) and ionic liquid.\(^21,22\) These additives participate in the formation of SEI, improving its uniformity and stability. However, in most cases, the additives are continuously consumed during cell cycling, which is difficult to remain sustainable over a long period of time.\(^23,24\) Artificial protective SEI films coated on the out layer of lithium ex situ are also developed. The protective layer is usually composed of polymers or inorganic materials, such as Cu\(_3\)N+SBR layer,\(^25\) LiF/PVDF-HFP composite film,\(^26\) and lithium silicate (Li\(_x\)SiO\(_y\)),\(^27\) which has good chemical stability and mechanical properties to restrain the
formation of lithium dendrite. However, owing to the high reactivity of lithium metal, the coating process may be cost unfriendly, which is not suitable for mass production. The solid electrolyte, considered an ideal choice for lithium metal anode, has reliable mechanical strength and can inhibit the growth of lithium dendrites in a physical barrier way.\textsuperscript{28, 29} Nevertheless, the solid electrolyte often leads to higher polarization voltages owing to their high interfacial impedance and low ionic conductivity.\textsuperscript{30, 31}

In addition to the above strategies, the modifications on the current collector have also been extensively studied to defeat the drawbacks of lithium anode.\textsuperscript{32, 33} These modifications are mainly to construct current collector with a 3D structure, which could increase the electrode surface area and reduce the local current density.\textsuperscript{34, 35} Simultaneously, empty space inside the 3D structure can well accommodate the deposited lithium, greatly eliminating the negative impact of volume change.\textsuperscript{36} Herein, we propose a novel electrode with 3D porous lithophilic host to stabilize lithium metal. The modified current collector not only has the advantages of the 3D structure but also introduces polydopamine (PDA) to improve the lithiophilicity of the current collector. The host structure is mainly composed of carbon fiber (CF) coated with strong adhesive PDA. The PDA coating layer, possessing lithophilic functional groups (such as hydroxyl and amino), is expected to serve as lithium nucleation sites, thereby realizing uniform lithium distribution and deposition. Under the synergy of the 3D CF and PDA, the modified current collector effectively improves the deposition behaviors of Li\textsuperscript{+} and suppresses the growth of lithium dendrites. The prelithified PDA@CF electrode shows outstanding cycle life, high coulombic efficiency, and low overpotential. When paired with LiFePO\textsubscript{4}, the full cells exhibit excellent capacity retention and superior cycle stability.

2. Experimental section

2.1. Preparation of lithium polyacrylate

Lithium polyacrylate (LiPAA) was prepared by ion exchange reaction. A 10\% polyacrylic acid (PAA) solution was prepared by dissolving PAA (average M\textsubscript{v} \sim 250000, Sigma-Aldrich) in deionized water. Then the aqueous solution of lithium hydroxide (98\%, Aladdin) of equal molar amount was added to PAA drop by drop for a final solution pH \approx 7. Then, the prepared LiPPA solution was placed in an open container to allow the majority of water to evaporate, followed by vacuum drying under
60 °C for 24 hours.

2.2. PDA@CF Preparation

The carbon fibers (CF, purchased from MREDA) were dispersed in the dopamine (98%, Aladdin) solution (10 mM in methanol) with the Tris-HCl buffer (10 mM, pH 8.5). After stirring at 800 rpm for 2 h and standing at room temperature for 24 h, the products were filtrated, followed by ethanol washing, and vacuum dried under 50 °C for 24 hours, which was denoted as PDA@CF. The PDA layer is about 80 nm thick.

2.3. Material Characterization

The field emission scanning electron microscope (Hitachi S-4800) was utilized to obtain scanning electron micrographs (SEM). The JEM-2100F microscope was used to obtain high-resolution TEM (HRTEM) images and EDS images. An AXIS Supra (Kratos Analytical Ltd., UK) was applied to obtain X-ray photoelectron spectrometer (XPS) element analysis while using Al Kα X-ray as radiation source. The Rigaku Ultima was utilized to collect the X-ray diffraction (XRD) pattern. The FTIR spectrophotometer (Thermo Fisher Scientific) was used to characterize the chemical structure of the PDA. The DXRxi (Thermo Fisher Scientific) was applied to collect the Raman spectra. To observe Li deposition morphology, Li/Cu cells were disassembled after different electrochemical processes (dissolution/deposition). Then the lithium foil to be tested was gently washed with 1,2-Dimethoxyethane three times to eliminate the residual electrolyte, and then followed by vacuum drying.

2.4. Electrochemical measurements

To prepare the electrodes, the PDA@CF and LiPAA were stirred in distilled water with the mass ratio of 2:1 for 12 h to get a homogenous slurry. Then, the slurry was cast onto a copper foil by a doctor blade. After vacuum drying under 60 °C for 24 hours, the PDA@CF electrode was obtained.

Coin-type cells (CR-2032) were utilized in this work, while the working electrode is PDA@CF electrode or Cu and the counter electrode is the Li metal foil. The electrolyte is 1 M lithium bis(trifluoromethanesulfonyl)imide in DOL/DME (1:1 v/v) with 2 wt% LiNO₃. Electrochemical analyzer (CHI650C) was utilized for the impedance measurements and LANHE CT2001A battery tester was used in the cycling measurements.

To evaluate the cycling performance, Li of 6 mAh cm⁻² was pre-deposited into the pristine Cu and PDA@CF electrodes using the half cell, obtaining the Cu-Li and PDA@CF-Li electrodes, respectively. Then the Cu-Li and PDA@CF-Li electrodes
were extracted from the half cells and assembled into the symmetrical cell, respectively. Galvanostatic cycling was conducted at various current densities, and the voltage was recorded with time. Electrochemical impedance spectra (EIS) were measured with an amplitude voltage of 5 mV at room temperature, and the frequency range was set in 0.1 Hz ~ 1 MHz.

To test the full cell, LiFePO₄ (LFP) was utilized as cathode material. LFP, polyvinylidene difluoride, acetylene black (weight ratio of 85:10:5) were mixed in the solvent of N-methylpyrrolidone (NMP). After being stirred for 24 hours, the homogenous slurry was cast on aluminum collector by a doctor blade. After vacuum drying under 100 °C for 24 hours, the LFP cathode was obtained (mass loading ~6 mg cm⁻²).

3. Result and Discussion

Fig. 1a schematically illustrates the fabrication procedure of the PDA@CF. The carbon fibers (CF) were immersed in the dopamine-tris(hydroxymethyl)aminomethane-HCl buffer solution to allow dopamine (DA) to self-polymerize and deposit on the surface of CF. Subsequently, the PDA@CF electrodes were prepared with the typical slurry-making process using polymer lithium polyacrylate (LiPAA) as binder. The PDA@CF has a cross-linked 3D porous structure, shown in the SEM image (Fig. 1b). FTIR spectrum of the prepared PDA is shown in Fig. 1c. The broad absorption peaks at 3700-3300 cm⁻¹ are ascribed to ν(N-H) and ν(O-H) stretching modes, the aliphatic ν(C-H) stretching modes are at around 2900 cm⁻¹. The absorption peaks around 1614 and 1518 cm⁻¹ are attributed to the νᵣᵣᵣᵣ(C=C) of indoline structure and νᵣᵣᵣᵣ(C=N) stretching vibration of indole structure in the PDA. Raman spectrum (Fig. 1d) shows three characteristic bands of carbon, which are the 2D band at 2698 cm⁻¹, the G band at 1580 cm⁻¹, and the D band at 1355 cm⁻¹. The presence of 2D band indicates that the carbon material has a graphene-like structure. Besides, the intensity ratio of D band to G band (Iᵢᵣᵢᵣ∕Iᵢᵢᵢᵢ = 0.122) indicates insignificant defects in the carbon material, which is coincided with a sharp peak (002) in the XRD pattern (Fig. S1). XPS was employed to detect the elements change of the CF after PDA modification (Fig. S2). The existence of O and N peaks in PDA@CF indicates that PDA coating has been successfully introduced to the surface of carbon fibers. Besides, the HRTEM and elemental mapping results of the modified carbon fibers further confirm the uniform element distribution in PDA@CF (Fig. 1e).
The Li plating morphology is a significant factor to assess the Li electrochemical behaviors on the electrode. Galvanostatic cycling of the Li/ PDA@CF half cell was carried under a current density of 0.5 mA cm\(^{-2}\) and the voltage was recorded with time. (Fig. 2a). During the process of lithium deposition, the insertion process of Li\(^+\) into carbon fibers is reflected in the voltage drop from \(\sim 1\) V to -0.025 V. The capacity contributed by the intercalation does not exceed 0.5 mAh cm\(^{-2}\). Subsequently, the voltage plateau at -0.02 V is ascribed to the stable nucleation and deposition stage of Li\(^+\) on the surface of CF. The morphological evolution of lithium deposition within PDA@CF was analyzed by SEM. The surface SEM images show that lithium was continuously deposited on the PDA@CF host and partially filled the porous structures (Fig. 2c). It can be observed that pancake-like Li deposited evenly on the electrode with the increase of Li deposition areal capacity (Fig. 2d, e). Especially at the edge of deposition, the lithium, embedded with fibers, shows a flat and smooth surface without any visible dendrites, indicating the good compatibility between lithium and PDA@CF (Fig. S3c, d). The dendrite-free and compact lithium deposition is mainly ascribed to a 3D porous structure constructed by carbon fibers and multiple deposition sites provided by PDA. On the one hand, the uniform distribution of Li\(^+\) guided by lithiophilic sites in PDA ensures that the edges of deposited lithium have the same chance to contact with lithium ions, thus avoiding local over-deposition. On the other hand, the three-dimensional space formed by the carbon fibers can well accommodate lithium. The synergy of the two factors positively affects the lithium deposition behaviors and prevents the formation of lithium dendrite. Besides, the deposited Li could be reversibly stripped from the PDA@CF as well. As shown in Fig. 2f-h, along with the charging process, the Li was continuously stripped from the PDA@CF, and the pancake-like lithium became smaller. While the delithiation process was completed after charging to 1 V (Fig. 2h), the pancake-like lithium disappeared totally with the PDA@CF structure recovered to the initial state. The 3D structure of the carbon fibers remains intact during the total cycling process, indicating the excellent robustness of PDA@CF, which is beneficial to long-term cycling. After continuous plating/stripping Li of 4 mAh cm\(^{-2}\) 20 times, the deposited lithium in PDA@CF electrode remains a flat surface without any observable Li dendrites, suggesting the outstanding electrochemical behaviors of Li. In contrast, the pristine Cu foil exhibited obvious lithium dendrites at the first deposition (Fig. S4c). What's more, due to the low reversibility, a lot of lithium debris remained on the surface of the copper electrode after the stripping of lithium metal (Fig. S4h).
The residual debris further increased the non-uniformity of charge distribution on the electrode, resulting in the deterioration of the subsequent lithium deposition. After 20 cycles (Fig. S4i), there were not only lithium dendrites, but also a significant amount of ‘dead’ lithium on Cu foil, which reflects the superiority of the 3D carbon fibers structure and multiple deposition sites of PDA.

The Li nucleation overpotential \( \mu_n \), defined as the voltage gap between the voltage dip and the subsequent plateau on the discharge profile, is introduced to quantitatively evaluate the lithiophilicity of electrodes. As shown in the discharge curves of the electrodes (Fig. 3a), the \( \mu_n \) is only 15 mV for PDA@CF electrode at the 0.5 mA cm\(^{-2}\) current density while is that of 90 mV for copper foil. As the current density increase, the \( \mu_n \) of copper foil increases drastically, which is 92 mV, 126 mV, and 136 mV at the current density of 1, 2, and 5 mA cm\(^{-2}\), respectively, whereas the PDA@CF electrode always exhibits a relatively small \( \mu_n \) below 25 mV, indicating the lower energy barrier for Li nucleation in electrochemically plating. This could be attributed to the lithiophilic O and N heteroatoms in PDA, providing multiple deposition sites for Li\(^+\) ions, decreasing the nucleation overpotential. The comparative test of CF electrode (without PDA modification) proves the superiority of lithiophilic PDA. As shown in Fig. S5a, the CF electrode has a deeper voltage drop and a larger nucleation overpotential at different current densities. The morphology of deposited lithium (Fig. S5b) shows local accumulation rather than uniform distribution. These comparisons display the advantage brought by the lithiophilicity of PDA, which overcomes the heterogeneous nucleation barrier of lithium ions on CF and homogenize lithium deposition.

To cross the heterogeneous nucleation barrier caused by huge thermodynamic mismatch between lithium and copper (poor lithiophilicity), the copper foil possesses a large overpotential of \( \sim 100 \) mV, which leads to a deep drop when starting discharge. Theoretically, the lithium-ion deposition potential is 0 (relative to Li/Li\(^+\)), but during the discharge process, there are a heterogeneous nucleation barrier, concentration polarization, and ohmic polarization on the electrode surface, all of which result in an overpotential. Therefore, only a negative potential can drive lithium ions to undergo a reduction reaction on the electrode surface to form lithium metal.

The Li/Cu cell was used to monitor the coulombic efficiency (CE) and cycling stability to assess the cycling performances of PDA@CF electrode. We adopted two methods to determine the coulombic efficiency. The most common method is depositing a given amount of Li metal \( (Q_D) \), and then stripping lithium metal \( (Q_S) \) from
the copper electrode to a cut-off voltage. The CE can be calculated:

$$CE = \frac{Q_S}{Q_D}$$

As shown in Fig. 4a, except for the first cycle, the CE of the cells using PDA@CF electrode could be stabilized at about 99% under the 0.5 mA cm$^{-2}$ current density for 500 cycles. In contrast, the CE of cells with pristine copper electrode is unstable, sometimes exhibits a low value, and then followed with an abnormally high value (>100%) in later cycles, which is mainly due to the disconnection of dendrites and electrical reconnection of ‘dead’ lithium. When the current density further rises to 1 and 2 mA cm$^{-2}$, the PDA@CF cells still present a CE of about 98.2% and 97.8%, respectively. However, the cells using Cu display poor cycling performance with fluctuant CE and shorter lifetimes. The CE of Li/Cu cells shows a continuous decrease after 120 cycles under 1 mA cm$^{-2}$ and 50 cycles under 2 mA cm$^{-2}$ because of the irreversible formation of unreactive ‘dead’ lithium. When rising to a high current density of 5 mA cm$^{-2}$, PDA@CF could deliver a high CE of about 97% for over 400 cycles, exhibiting more stability than that of the pristine copper electrodes. More prominently, when further increasing the deposition capacity, the PDA@CF electrode could maintain excellent cycling with a high CE (Fig. S6, S7). Especially under the current density of 2 mA cm$^{-2}$ and the capacity of 4 mAh cm$^{-2}$, stable 200 cycles could be achieved with a high CE of ~95.8%. In comparison, the CE of Cu exhibits rapid decay after 50 cycles under extreme conditions. Fig. 4b, c show the detailed voltage curves of Li depositing/stripping under the 5 mA cm$^{-2}$ current density. The cells using the PDA@CF electrode possess almost identical voltage curves in different cycles, accompanied by low voltage hysteresis of ~60 mV. Such outstanding performance is mainly due to the numerous deposition sites on the PDA guiding the uniform deposition of lithium, reducing the cell polarization and thus preventing the growth of lithium dendrites. In comparison, pristine Cu manifests terrible Li plating/stripping behaviors. As the increase of cycles, the charging voltage profiles of pristine Cu shift leftward gradually, which indicates the existence of ‘dead’ lithium, leading to massive irreversible capacity loss. Table S1 (supporting information) compares the coulombic efficiency of the PDA@CF electrode with results from a wide variety of previous state-of-art studies.

During the lithium depositing process, Li loss includes the side reaction of Li with electrolyte or Cu substrate surface.$^{37}$ To eliminate the possible lithium loss caused by
the substrate, we choose another charge/discharge mode to measure CE. An excess given amount of Li metal \((Q_T)\) is deposited onto the copper electrode as a lithium reservoir in the initial cycle, and then a small part of lithium \((Q_C)\) is utilized to plate and strip. After running for \(n\) cycles, stripping the remaining Li metal \((Q_S)\) from copper electrode to a cut-off voltage. The average coulombic efficiency for \(n\) cycles could be calculated:

\[
\text{CE}_{\text{avg}} = \frac{nQ_C + Q_S}{nQ_C + Q_T}
\]

In the practical LMBs, lithium metal is not completely stripped from the substrate, so the CE\(_{\text{avg}}\) measured by this method can better reflect the practical situation of the electrode. Under the current density of 1, 2 mA cm\(^{-2}\), the initial \(Q_T\) of 6 mAh cm\(^{-2}\) and cycling \(Q_C\) of 0.5 mAh cm\(^{-2}\) (Fig. 5a, b), PDA@CF shows excellent cycling stability, illustrated by the lower polarization overpotential, and smooth delithiation process in the last cycle, which exhibits the high CE\(_{\text{avg}}\) of 99.6% and 99.5%, respectively. By contrast, the cells using pristine Cu foil show larger overpotential and inferior stripping behaviors, such as the fluctuant voltage curves. As the amount of cycling lithium \((Q_C)\) increasing to 1 mAh cm\(^{-2}\) (Fig. S8), the copper foil displays worse cycling behaviors. Particularly at the 2 mA cm\(^{-2}\) current density (Fig. S8b), the voltage rises with several abrupt drops in the last cycle, indicating the existence of micro short circuit triggered by lithium dendrite puncture. While the dendrites piercing the separator and contacting the counter electrode, the short circuit for a moment generates heat and melts the tips of dendrites, so the voltage drops in a short time and then rises normally. The amount of electricity that flows through in a short circuit is counted as part of the charging capacities, so causing the illusion that the CE\(_{\text{avg}}\) exceeds 100%. However, the PDA@CF electrode still maintains stable cycling and high CE\(_{\text{avg}}\) nearly to 99% under the test condition of the \(Q_C\) of 1 mAh cm\(^{-2}\), deriving from the uniform lithium deposition and storage in 3D carbon fibers skeleton and less Li loss caused by side reactions.

Galvanostatic cycling test was accomplished in symmetrical cell to further evaluate the cycling stability of PDA@CF electrode. The PDA@CF and copper electrode were electrochemically pre-deposited with a fixed amount of Li metal (deposition capacity of 6 mAh cm\(^{-2}\), equal to a specific capacity of 677 mAh g\(^{-1}\) base on the total mass), and tested under the 1 mA cm\(^{-2}\) current density and 1 mAh cm\(^{-2}\) cycling capacity. Fig.6a shows the voltage-time profiles, which could be utilized to analyze the stability of electrodes. Noticeably, the PDA@CF-Li exhibited superior cycling performance in
1000h with a low overpotential (~12 mV). However, the Cu-Li cells display an unstable voltage profile with a high overpotential over 30 mV and violent fluctuation at first 650 cycles. After 700 cycles, the overpotential value presents a rapid decrease, indicating that a short circuit occurred inside the cell. To show the detailed evolution of voltage curves, 100-108 and 346-354 cycles of symmetric cell are enlarged in Fig. 6b, c. The PDA@CF-Li symmetric cells maintained even voltage plateaus at charge/discharge processes throughout the 1000 h. In comparison, the Cu-Li cells displayed unstable voltage jitter especially after long-term cycling, resulting from the uncontrolled lithium dendrites and continuous consumption of electrolytes. In addition, under the higher current density of 2, 5 mA cm$^{-2}$ (Fig. S9 and S10), the PDA@CF-Li still maintained excellent stability and lower overpotential, while Cu-Li electrode exhibits inferior cycling performance and shorter cycling life. The voltage variation of the cell could be accurately revealed from the voltage hysteresis, which could be defined as the voltage gap between the lithium depositing and stripping.

As shown in Fig. 6d, the voltage hysteresis of Cu-Li cell increases continuously after 150 cycles with temporary irregular fluctuation. In contrast, the PDA@CF-Li symmetric cells always remain stable, and the voltage hysteresis is only about 16 mV, indicating the processes of uniform Li plating/stripping. Furthermore, EIS measurements of the symmetric cells were completed to evaluate the interfacial resistance and stability (Fig. 6e). The inset of Fig. 6e shows the equivalent circuit utilized to fit the impedance spectra, including bulk resistance ($R_1$), interface resistance ($R_2$), constant phase element (CPE$_1$), and Warburg resistance ($W_1$). In the impedance spectra, the semicircle at the high-frequency range shows the charge transfer resistance and interfacial resistance between the electrolyte and electrode. The cell using Cu-Li displayed a high interfacial resistance (~40 Ω) after one cycle, which is almost four times that of cell using PDA@CF-Li. After twenty cycles, the interfacial resistance of Cu-Li (15.3 Ω) is still higher than that of the PL-Li (4.2 Ω), demonstrating the faster Li plating/stripping reaction kinetics and lower hysteresis of PDA@CF-Li.

The PDA@CF-Li and Cu-Li anodes (with 6 mAh cm$^{-2}$ pre-deposited Li) were paired with LiFePO$_4$ to study full cell cycling performance. Fig. 7a, b show the rate performance and the detailed charge/discharge voltage curves of PDA@CF-Li/LFP cells at various current densities. Compared with the Cu-Li/LFP cell (Fig. S11), the PDA@CF-Li/LFP cell exhibit minor polarization potential and more stable voltage plateaus, especially at high rates. PDA@CF-Li/LFP cells render discharge capacity of
135 and 127 mAh cm\(^{-2}\) at 5 C and 10 C, respectively. In comparison, Cu-Li/LFP cells offer the lower capacity of 126 and 111 mAh cm\(^{-2}\) at 5 C and 10 C, respectively. Besides, the effective dendrite inhibition by PDA@CF ensures ultra-long cycling performance. As shown in Fig. 7c, PDA@CF-Li/LFP cells display outstanding stability for 1000 cycles with little changes in discharge capacity from 148.6 mAh g\(^{-1}\) (1\(^{st}\) cycle) to 142.4 mAh g\(^{-1}\) (1000\(^{th}\) cycle), which corresponds to high capacity retention (95.8%). However, the Cu-Li/LFP cells show poor cycling performance, the discharge capacity decays rapidly from 137.9 mAh g\(^{-1}\) to about 50 mAh g\(^{-1}\) after 400 cycles, and the capacity retention is below 37%. Moreover, another long-term cycling under a higher current density of 2 C was completed. The discharge capacities for the two cells are almost identical in the first few cycles (Fig. S12). However, the capacity of the Cu-Li/LFP cells decreases gradually after 250 cycles, while cells with PDA@CF-Li anode deliver stable cycling performance over 1000 cycles without obvious capacity loss. In ordinary graphite/LFP batteries which the graphite possesses a specific capacity of 372 mAh g\(^{-1}\), the SEI film formation consumes a number of lithium ions in the first cycle, leading to a decrease in the CE of the battery. When the PDA@CF-Li electrode (pre-deposition capacity of 6 mAh cm\(^{-2}\), a specific capacity of 677 mAh g\(^{-1}\)) is used, the deposited lithium can supplement the consumed lithium capacity, thereby maintaining a high coulombic efficiency.

The pure lithium metal anode has a larger capacity than the PDA@CF-Li at the initial stage of electrochemical cycling, but as the number of cell cycles increases, the ‘hostless’ lithium anode inevitably produces lithium dendrites and ‘dead’ lithium, which greatly reduces the usable capacity. To balance capacity and life, it is probably more effective to use a modified current collector (PDA@CF) to obtain a longer cycle life when the volumetric capacity of the negative electrode is only slightly reduced.

**Conclusions**

In summary, a 3D porous lithiophilic PDA@CF electrode was created to achieve excellent cycling performance and stable lithium plating/stripping in LMBs. The conductive 3D carbon fibers not only reduce the local current density but also serves as the host to accommodate deposited Li metal, which can alleviate the large volume change of lithium metal. Moreover, the significant amount of lithiophilic O and N-based polar groups in PDA has strong interaction with Li\(^+\), which can homogenize Li\(^+\)
distribution and decreases the nucleation overpotential. Under the synergy of PDA and CF, the PDA@CF could effectively improve the electrochemical behaviors of Li\(^+\) ions, show an extremely high CE of 98.2\% at 1 mA cm\(^{-2}\) for 500 cycles. In symmetric cells, the PDA@CF-Li anode showed ultra-stable cycling life accompanied by a low overpotential of 12 mV, and 1000h duration can be achieved under 1 mA cm\(^{-2}\). When paired with LFP cathode, excellent long-term stability for 1000 cycles with high CE of about 100\% can be realized. The combination of both uniform Li nucleation and storage in the design of PDA@CF in this work is expected to be general for the designs of stable lithium metal anode.

**Supplementary Data**

Supplementary data is available at Oxford Open Materials Science online.

**Author’s contributions**

L.X. made a major contribution to the article, including idea, materials synthesis, battery tests, and initial draft. Z.Y. provided important experimental insights. J.Z., as the corresponding author, critically reviewed the article and made revisions.

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**Conflict of Interest Statement**

The authors declare no conflict of interest.
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**Fig. 1.** (a) Fabrication process of the PDA@CF. (b) SEM image, (c) FTIR spectrum, (d) Raman spectrum, (e) HRTEM image and elemental mapping for the C, O, N of the PDA@CF.

**Fig. 2.** (a) The plating/stripping curves of PDA@CF electrode in the half cell at the 0.5 mA cm$^{-2}$ current density. The surface SEM images of (b) original PDA@CF electrode and after depositing Li metal of (c) 2, (d) 3, and (e) 4 mAh cm$^{-2}$. The surface SEM images of PDA@CF electrode after stripping Li metal of (f) 2, (g) 3, and (h) 4 mAh cm$^{-2}$ (that is, recharged to 1 V). (i) The surface SEM image of PDA@CF electrode (with the deposited lithium of 4 mAh cm$^{-2}$) after 20 cycles.

**Fig. 3.** The difference in the discharge curve of Li/PDA@CF and Li/Cu half cells at various current densities of (a) 0.5, (b) 1, (c) 2, and (d) 5 mA cm$^{-2}$.

**Fig. 4.** (a) Coulombic efficiency of lithium depositing on PDA@CF electrode and pristine Cu foil at different current densities of 0.5, 1, 2, and 5 mA cm$^{-2}$ with a fixed 1 mAh cm$^{-2}$ deposition capacity. (b, c) Voltage curves of the lithium depositing/stripping process on (b) PDA@CF electrode and (c) pristine Cu foil under the 5 mA cm$^{-2}$ current density of and a fixed 1 mAh cm$^{-2}$ deposition capacity.

**Fig. 5.** The voltage versus time plot in CE evaluation test on PDA@CF electrode and pristine copper electrode under the current densities of (a) 1, and (b) 2 mA cm$^{-2}$ with constant $Q_C$ of 0.5 mAh cm$^{-2}$.

**Fig. 6.** (a) Galvanostatic cycling curves of Cu-Li and PDA@CF-Li symmetric cells at 1 mA cm$^{-2}$ current density and 1 mAh cm$^{-2}$ cycling capacity. And the corresponding detailed voltage curves from (b) 200 h to 216 h and (c) 692 h to 708 h. (d) Voltage hysteresis of the PDA@CF-Li and Cu-Li symmetric cells at 1 mA cm$^{-2}$ current density and 1 mAh cm$^{-2}$ cycling capacity. (e) The impedance spectra of the PDA@CF-Li and Cu-Li symmetric cells at 1$^{st}$ and 20$^{th}$ cycle under 1 mA cm$^{-2}$.

**Fig. 7.** (a) Rate performance of PDA@CF-Li/LFP cell. (b) Charge/discharge voltage curves of PDA@CF-Li/LFP cell at various current densities. (c) Long-term cycling performance of Cu-Li/LFP and PDA@CF-Li/LFP cells under the current density of 1 C.
Fig. 1. (a) Fabrication process of the PDA@CF. (b) SEM image, (c) FTIR spectrum, (d) Raman spectrum, (e) HRTEM image and elemental mapping for the C, O, N of the PDA@CF.
Fig. 2. (a) The plating/stripping curves of PDA@CF electrode in the half cell at the 0.5 mA cm\(^{-2}\) current density. The surface SEM images of (b) original PDA@CF electrode and after depositing Li metal of (c) 2, (d) 3, and (e) 4 mAh cm\(^{-2}\). The surface SEM images of PDA@CF electrode after stripping Li metal of (f) 2, (g) 3, and (h) 4 mAh cm\(^{-2}\) (that is, recharged to 1 V). (i) The surface SEM image of PDA@CF electrode (with the deposited lithium of 4 mAh cm\(^{-2}\)) after 20 cycles.

338x210mm (149 x 149 DPI)
Fig. 3. The difference in the discharge curve of Li/PDA@CF and Li/Cu half cells at various current densities of (a) 0.5, (b) 1, (c) 2, and (d) 5 mA cm\(^{-2}\).
Fig. 4. (a) Coulombic efficiency of lithium depositing on PDA@CF electrode and pristine Cu foil at different current densities of 0.5, 1, 2, and 5 mA cm⁻² with a fixed 1 mAh cm⁻² deposition capacity. (b, c) Voltage curves of the lithium depositing/stripping process on (b) PDA@CF electrode and (c) pristine Cu foil under the 5 mA cm⁻² current density and a fixed 1 mAh cm⁻² deposition capacity.
Fig. 5. The voltage versus time plot in CE evaluation test on PDA@CF electrode and pristine copper electrode under the current densities of (a) 1, and (b) 2 mA cm$^{-2}$ with constant QC of 0.5 mAh cm$^{-2}$. 

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Fig. 6. (a) Galvanostatic cycling curves of Cu-Li and PDA@CF-Li symmetric cells at 1 mA cm\(^{-2}\) current density and 1 mAh cm\(^{-2}\) cycling capacity. And the corresponding detailed voltage curves from (b) 200 h to 216 h and (c) 692 h to 708 h. (d) Voltage hysteresis of the PDA@CF-Li and Cu-Li symmetric cells at 1 mA cm\(^{-2}\) current density and 1 mAh cm\(^{-2}\) cycling capacity. (e) The impedance spectra of the PDA@CF-Li and Cu-Li symmetric cells at 1st and 20th cycle under 1 mA cm\(^{-2}\).
Fig. 7. (a) Rate performance of PDA@CF-Li/LFP cell. (b) Charge/discharge voltage curves of PDA@CF-Li/LFP cell at various current densities. (c) Long-term cycling performance of Cu-Li/LFP and PDA@CF-Li/LFP cells under the current density of 1 C.

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