CellPress

Article

Covalent Organic Frameworks Construct Precise Lithiophilic Sites for Uniform Lithium Deposition



A boroxine covalent organic framework (COF-1) is employed to construct a lithiophilic host for Li metal batteries. The well-defined COF-1 structure enables well-defined lithiophilic sites and homogeneous site distribution at the atomic level, providing maximum efficiency and exposure of the lithiophilic sites. Consequently, the COF-1-based anode exhibits superior electrochemical performance with dendrite-free morphology.



Understanding

Dependency and conditional studies on material behavior Song et al., Matter 4, 253–264 January 6, 2021 © 2020 Published by Elsevier Inc. https://doi.org/10.1016/j.matt.2020.10.014

Yun-Wei Song, Peng Shi, Bo-Quan Li, ..., Xue-Qiang Zhang, Xiao Chen, Qiang Zhang

zhang-qiang@mails.tsinghua.edu.cn

HIGHLIGHTS

A COF-based strategy is proposed to construct a lithiophilic host for a Li metal anode

Lithiophilic B_3O_3 sites with precise structure and uniform distribution are achieved

A high-performance Li metal anode is realized on the COFbased host

Article

Covalent Organic Frameworks Construct Precise Lithiophilic Sites for Uniform Lithium Deposition

Yun-Wei Song,^{1,2} Peng Shi,^{1,2} Bo-Quan Li,¹ Xiang Chen,¹ Chang-Xin Zhao,¹ Wei-Jing Chen,¹ Xue-Qiang Zhang,¹ Xiao Chen,¹ and Qiang Zhang^{1,3,*}

SUMMARY

Lithium (Li) metal represents one of the most promising anode materials for constructing high-energy-density rechargeable batteries. However, uncontrolled Li dendrite growth induces limited lifespan and safety hazards, impeding the development of Li metal batteries severely. Introducing a Li host has been shown to effectively relieve dendrite growth, while further construction of lithiophilic sites will significantly facilitate uniform Li deposition for stably cycling Li metal batteries. Herein, a boroxine covalent organic framework (COF-1) is employed to construct a lithiophilic host for dendrite inhibition in working Li metal batteries. The well-defined boroxine sites demonstrate ideal lithiophilicity to reduce the Li nucleation energy barrier, and the ordered framework structure of COF-1 affords a uniform distribution of the lithiophilic sites. As a result, the COF-1based Li host affords a more than doubled lifespan of routine anodes in both half- and full cells. This work demonstrates the promising potential of applying advanced framework materials to essential energy-related processes.

INTRODUCTION

The rapid development of modern society puts forward ever-growing demands for rechargeable batteries with high energy density.¹ Lithium (Li) metal affords an ultrahigh theoretical specific capacity (3,860 mAh g^{-1}) and low reduction potential (-3.04 V versus standard hydrogen electrode),² providing lithium metal batteries (LMBs) with theoretical energy density much higher than that of the current Li-ion batteries based on graphite anodes.³ Therefore, LMBs constitute one of the most promising candidates for next-generation energy storage systems.

Compared with the traditional graphite anode with stable Li ion intercalation during cycling,^{4,5} the Li metal anode is intrinsically "hostless" and suffers from virtually infinite volume fluctuations during Li plating/stripping.^{6,7} Due to the dramatic dimensional change, uneven Li deposition and the resulting uncontrolled Li dendrites lead to a short lifespan and even safety hazards, including internal short circuit and thermal runaway, which severely limit the practical applications of LMBs.^{8–10}

To address the above issues, host materials are introduced to regulate the Li plating/ stripping behaviors and are expected to alleviate the dimensional fluctuations and inhibit the growth of Li dendrites.^{11–14} On this basis, lithiophilicity, referring to the affinity between Li species and the host material, is indispensable and highly considered during host design.¹⁵ The lithiophilic hosts are expected to reduce the Li nucleation energy barrier and guide uniform Li deposition owing to the strong

Progress and Potential

Lithium (Li) metal represents a promising anode material for constructing high-energy-density rechargeable batteries but is severely limited by uncontrolled Li dendrite growth. Introducing a Li host effectively relieves Li dendrite growth, while precise construction of the lithiophilic sites is essential but insufficient among the current strategies.

In this contribution, a covalent organic framework is employed as a Li host to precisely construct the lithiophilic sites with well-defined chemical structure and uniform geometric distribution at the atomic level. The precisely constructed structure delivers maximum efficiency and exposure of the lithiophilic sites. Consequently, the G@COF-1 host reduces Li nucleation overpotentials and favors prolonged lifespan with uniform deposition morphologies, and the G@COF-1-Li composite anode realizes stable cycling in LFP and NCM full cells.









interactions between the lithiophilic sites and the Li species,¹⁶ and thus dendrite growth can be inhibited in Li metal anodes.¹⁷

In retrospect, tremendous effort has been put into developing lithiophilicity, such as with heteroatom-doped carbon^{18,19} and composites of carbon and metal,^{20,21} metal oxide,^{22,23} and metal nitride.²⁴ Nevertheless, it remains challenging to construct an ideal lithiophilic host for dendrite-free Li metal anodes. On one hand, higher lithiophilicity is required for further facilitating the Li plating/stripping processes. On the other hand, many of the reported Li host scaffolds offer a uniform distribution of lithiophilic nanoparticles at the micrometer scale,^{25,26} while the lithiophilic sites are expected to be homogeneously distributed at the atomic level rather than spatially aggregated to guide uniform Li deposition. Therefore, precise construction of the lithiophilic sites with the favored chemical structure and ordered geometric distribution is essential but insufficient among the current designing strategies. Covalent organic frameworks (COFs) are a new class of materials with specific organic groups covalently connected to a periodic network.^{27–36} These merits endow COFs with precisely pre-designed chemical structures and provide opportunities to construct well-defined highly lithiophilic sites with homogeneous distribution.^{37–40}

In this contribution, a boroxine COF (COF-1) is employed to construct a lithiophilic host for Li dendrite inhibition in working LMBs (Figure 1). According to previous work, the boron-oxygen dipole is predicted to have higher lithiophilicity than other doping structures,⁴¹ yet such structure is very difficult to precisely fabricate within carbon skeletons.^{42,43} COF-1 felicitously addresses the above issue with well-defined lithiophilic boroxine rings and uniform distribution of the boroxine rings confined within its framework skeleton.^{44–46} Furthermore, COF-1 is composited *in situ* with graphene (named G@COF-1) to construct the lithiophilic host to overcome the inherent poor conductivity and bulk morphology of the COF materials. Consequently, the G@COF-1 host demonstrates a stable coulombic efficiency (CE) of 98% within 240 cycles, and the G@COF-1-Li anode affords superior stability in full cells with LiFePO₄ (LFP) and LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523) cathodes, both of which exhibit dendrite-free morphologies.

RESULTS AND DISCUSSION

G@COF-1 was synthesized following a solvothermal method with graphene (named as G) as the template.⁴⁷ The morphology of G@COF-1 was evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The COF-1 nanoflakes, with an average diameter of 30 nm, were uniformly distributed on the G substrate without self-aggregation, ensuring the conductivity and full exposure of the boroxine sites (Figures 2A, 2B, S1, and S2). Meanwhile, the N₂ isothermal of G@COF-1 also demonstrated enlarged specific surface area and abundant mesopores compared with pure COF-1 to efficiently guide Li deposition (Figure S3). Elemental analysis indicated that the mass ratio of G:COF-1 was \sim 1:4.5 by X-ray photoelectron spectroscopy (XPS), combustion method, and yield analysis (Figure S4 and Tables S1–S3).

Further characterization was carried out by aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 2C). The COF-1 nanoflakes afforded brighter contrast than the G substrate, with morphology resembling that on the SEM and TEM images. The chemical composition of a COF-1 nanoflake was further confirmed by energy-dispersive X-ray spectroscopy with quantitative line-scan and mapping analysis (Figures 2C-2E). The

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

²These authors contributed equally

³Lead Contact

*Correspondence: zhang-qiang@mails.tsinghua.edu.cn https://doi.org/10.1016/j.matt.2020.10.014





Figure 1. Schematic Illustration of Li Deposition on Different Li Hosts COF-1 provides well-defined lithiophilic boroxine rings and uniform site distribution to guide

uniform Li deposition, thereby affording dendrite-free morphology.

line-scan analysis afforded synchronous results for C, B, and O signals. Meanwhile, the local mapping analysis demonstrated the atomic ratio of C:B:O to be \sim 3:1:1, in agreement with the theoretical value.

The structure of G@COF-1 was evaluated by Fourier transform infrared (FTIR) spectrum, solid-state ¹³C NMR spectrum, and powder X-ray diffraction (XRD) tests. Typical adsorption peaks of B_3O_3 rings were identified in the FTIR spectrum, confirming the successful construction of the lithiophilic boroxine sites (Figure 2F).⁴⁵ In addition, XRD patterns and NMR signals of G@COF-1 exhibited characteristic peaks of COF-1, indicating the well-defined ordered framework architecture of COF-1 on G (Figures 2G and S5).^{45,48} The highly crystalline COF-1 endows the lithiophilic boroxine sites with precise chemical structures and uniform geometric positions. Thereby, uniformly distributed highly lithiophilic sites are precisely constructed as Li host materials for Li dendrite inhibition in working LMBs.

Li nucleation overpotential was evaluated as an indicator to quantitatively characterize the lithiophilicity of G@COF-1. Compared with bare G, the G@COF-1 electrode demonstrates much lower nucleation overpotentials of 8.7, 19.8, and 38.8 mV at current densities of 0.5, 1.0, and 3.0 mA cm⁻², respectively (Figures 3A and 3B). The reduced nucleation overpotentials indicate enhanced Li nucleation kinetics owing to ideal lithiophilicity from the boroxine sites. Density functional theory (DFT) calculations, including binding energy and differential charge density analyses, further indicate that the boron-oxygen dipole structure in the boroxine ring plays an important role in determining the lithiophilicity by providing strong ion-dipole interactions with Li atoms (Figure S6). Moreover, the lithiophilic advantages of the G@COF-1 host were probed in cycling half-cells. The CE of the G@COF-1 electrode retains over 98% for more than 240 cycles, while the control G electrode fails after only 75 cycles at the current density of 1.0 mA cm^{-2} and areal capacity of 1.0 mAh cm^{-2} , with a cycling number improved by 220% (Figure 3C). The voltage hysteresis of the G@COF-1 electrode is also reduced compared with the G electrode as the cycle number increases



Figure 2. Characterization of G@COF-1

CellPress

(A–C) (A) TEM image of graphene (G); (B) TEM and (C) HAADF-STEM images of G@COF-1 with energy-dispersive X-ray spectroscopy mapping corresponding to (C). B, boron; C, carbon, and O, oxygen.

(D and E) (D) Line scan and (E) local area scan across a COF-1 nanoflake (#1 and #2 as in C).

(F and G) (F) FTIR spectrum and (G) XRD patterns of G, COF-1, and G@COF-1.

(Figure 3E). When the current density and capacity are elevated to 3.0 mA cm^{-2} and 3.0 mAh cm^{-2} , respectively, the G@COF-1 electrode still exhibits stable charge-discharge profiles and prolonged cycling lifespan of 50 cycles beyond the G electrode lifespan of only 25 cycles (Figures 3D and 3F). XPS characterization before and after cycling indicated that the lithiophilic boroxine sites were stable during cycling, where additional signals suggest the decomposition of the electrolyte on a lithium metal surface (Figure S7). Therefore, the promoted stability of Li plating/stripping with the G@COF-1 host is attributed to the uniformly distributed lithiophilic boroxine sites, which provide abundant and dispersive nucleation sites for uniform Li deposition.

The morphology of Li plating/stripping on different host materials was further investigated by SEM characterization. When Li metal is deposited on the G@COF-1 host at 1.0 mAh cm⁻² and 1.0 mA cm⁻², the electrode exhibits a dense and smooth morphology, indicating that the Li metal is evenly plated within the host (Figures S8 and 4A). After Li stripping, the G@COF-1 electrode recovers to the pristine morphology without obvious remaining dead Li (Figure 4B). The thickness of the G@COF-1 electrode is also stable around 26 µm after 10 cycles (Figures 4C, S9A, and S9B). In contrast, the G electrode shows distinct morphology differences, with messy Li after plating/stripping and unmitigated volume expansion from 21 to 47 µm in thickness (Figures 4D–4F, S9C, and S9D). With the







(C-F) (C and D) Cycling CE of half-cells with G or G@COF-1 electrodes and (E and F) corresponding voltage profiles.

current density and capacity increasing to 3.0 mA cm^{-2} and 3.0 mAh cm^{-2} , respectively, the same trend can be observed, that the G@COF-1 electrode is superior in morphology and dimensional stability (Figure S10). It is therefore concluded that the lithiophilic G@COF-1 host guides uniform Li deposition to render reduced volume expansion, relieved dendrite growth, and limited dead Li, which are crucial for long-cycling LMBs.

To explore the feasibility of G@COF-1 for practical applications, G@COF-1-Li anodes were fabricated and evaluated in full cells with LFP and NCM523 cathodes. Ultrathin Li foils (33 μ m) and G-Li anodes were employed as the control anodes with the same anode capacity. A low negative/positive electrode ratio of 4.4 was applied in order to approach practical conditions. The cycling performance of the LFP full cells at 1.0 C (1 C = 170 mA g^{-1}) is shown in Figure 5A. The LFP full cell with the G@COF-1-Li anode stably performed 60 cycles at the benchmark of 80% retention of the initial capacity; meanwhile, the shorter lifespan of the G anode indicates that routine host materials with limited lithiophilicity cannot afford stably cycling LMBs. For the cell with the G@COF-1-Li anode, the voltage gap between the charge and the discharge plateaus of the first cycle is 88 mV, almost half that of the ultrathin Li anode (160 mV)





Figure 4. Morphology Characterization of Li Hosts at 1.0 mA cm⁻² and 1.0 mAh cm⁻² Top-view SEM images of (A) G@COF-1 and (D) G after Li plating, and (B) G@COF-1 and (E) G after Li stripping. (C and F) Cross-sectional SEM images of (C) G@COF-1 and (F) G before cycling and after 10 cycles. (A–C) The G@COF-1 electrode, (D–F) the G electrode.

(Figure 5B). The voltage gap remains stable toward the 45th cycle with the G@COF-1-Li anode, while it dramatically increases with the ultrathin Li anode. These results are attributed to the lithiophilic sites in COF-1 and the stable electronic paths provided by the high-surface-area G skeleton.

Furthermore, morphology evolution of the anodes in LFP full cells was performed. Notably, all of the pristine anodes share the same thickness of 33 μ m and exhibit similar smooth surfaces (Figure S11). After 60 cycles, the G@COF-1-Li anode was still dendrite free, with a denser surface morphology and an increase in thickness to 143 μ m. In contrast, both the G-Li anode and the ultrathin Li anode demonstrated massive Li dendrites and more severe volume change to 180 and 270 μ m, respectively (Figures 5C, 5D, and S12). The above results indicate that the G@COF-1 host effectively inhibits Li dendrite growth in practical full cells and stabilizes Li plating/stripping over a long lifespan.

When matched with a high-voltage NCM523 cathode, the G@COF-1-Li anode also demonstrated promising cycling stability. The G@COF-1-Li | NCM523 full cell exhibits a comparable initial capacity of 155 mAh g⁻¹, superior capability retention (80% after 80 cycles), and dendrite-free morphology at 0.4 C (1 C = 180 mA g⁻¹), whereas the Li | NCM523 or the G-Li | NCM523 full cells undergo rapid capacity fade after 40 or 55 cycles, respectively (Figures S13 and S14). The good rate performance of the G@COF-1-Li | NCM523 cell also reveals that the lithiophilic G@COF-1 host can support rapid Li plating/stripping at higher current densities (Figure S15). Moreover, the G@COF-1-Li anode can stably afford 100 cycles with an elevated cathode capacity of 2.0 mAh cm⁻² where no obvious capacity decay is observed when changing the electrolyte from ethylene carbonate/diethyl carbonate (FEC/DMC) (v/v = 1/1) to 4-fluoro-1,3-dioxolan-2-one/ dimethyl carbonate (FEC/DMC) (v/v = 1/4) (Figure S16), further confirming the potential of the COF-1-based lithiophilic Li host to construct stable LMBs. In addition, symmetric cell evaluation was performed to confirm the performance



Article



Figure 5. Electrochemical Performance in LFP Full Cells

(A–D) (A) Cycling performance and (B) charge-discharge profiles of LFP full cells at 1.0 C. (C) Crosssectional and (D) top-view SEM images of G@COF-1-Li, G-Li, and ultrathin Li anodes after 60 cycles.

improvements contributed by the G@COF-1-Li anode. As shown in Figure S17, the G@COF-1 anode affords stable Li plating-stripping cycles for 300 h with a reduced overpotential of \sim 30 mV and surpasses the ultrathin Li anode, showing that the superior performance promotion in full cells is contributed by the advanced G@COF-1 lithiophilic host.

In conclusion, a boroxine-based COF (COF-1) was applied to construct a lithiophilic host to inhibit Li dendrite growth in LMBs. As afforded by the well-defined chemical structure of COF-1, highly lithiophilic boroxine sites are homogeneously distributed within the framework skeleton to guide uniform Li deposition under working conditions. The growth of Li dendrites is significantly relieved by the COF-1-based host, rendering reduced overpotential and prolonged cycling life in both half-cells and full cells. The design strategy of introducing lithiophilic sites by using COF materials not only provides a new family of lithiophilic candidates, but also inspires the application of advanced materials for energy-related processes, especially for next-generation rechargeable batteries.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fullilled by the lead contact, Qiang Zhang (email: zhang-qiang@mails. tsinghua.edu.cn).

Materials Availability

1,4-Benzenediboronic acid (BDBA; 98%), mesitylene (99%), tetrahydrofuran (THF; 99%), and 1,4-dioxane (99%) were purchased from Alfa Aesar Chemical Co., Ltd., and directly used without further purification. Copperfoils, Celgard 2400 polypropylene membranes, and polyvinylidene fluoride (PVDF) were purchased from Shenzhen Kejing Star Technology Co., Ltd. Li metal foils were purchased from China Energy Lithium Co., Ltd. 1,2-Dimethoxyethane (DME) (99%), 1,3-dioxolane (DOL) (99%), FEC (99%), DMC (99%), lithium nitrate (LiNO₃) (99.98%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (98%) were





purchased from Alfa Aesar Chemical Co., Ltd., and kept in a glovebox. Battery-grade 1.0 M hexafluorophosphate (LiPF₆) in EC/DEC (1:1 by volume) electrolyte and N-methyl pyrrolidone (NMP, 98%) were purchased from Beijing Institute of Chemical Reagents.

Data and Code Availability

All data needed to evaluate the conclusions in the paper are presented in the paper and/or Supplemental Information. Additional data related to this paper may be requested from the authors.

Synthesis of COF-1 and G@COF-1

Synthesis of G@COF-1

G@COF-1 was fabricated by a solvothermal method. Typically, 800 mg BDBA and 80 mg G were added into a mixture of 20 mL mesitylene and 20 mL 1,4-dioxane. The suspension was stirred for 15 min and then ultrasonically treated for 20 min to get a homogeneous suspension. Then the suspension was transferred to a Teflon hydrothermal kettle reactor to conduct the solvothermal reaction. The reactor was sealed and kept at 125°C for 72 h to produce G@COF-1. The resulting product was thoroughly washed with THF three times and dried at 60°C for 24 h. The yield of G@COF-1 was 58%.

Synthesis of COF-1

First, 1.27 g BDBA was dispersed in a mixture of 20 mL mesitylene and 20 mL 1,4dioxane; then the same procedures for the synthesis of G@COF-1 were followed. The yield of COF-1 was 68%.

Materials Characterization

A JSM 7401F scanning electron microscope, a JEM 2010 transmission electron microscope, and an FEI Titan Cubed G2 300 double spherical aberration-corrected scanning transmission electron microscope were employed to characterize the morphology of the samples. The operation voltage of the scanning electron microscope, transmission electron microscope, and scanning transmission electron microscope was 3.0, 120.0, and 300.0 kV, respectively. The Li metal anodes were protected in argon (Ar) in a glass container before morphology characterization to avoid contact with the air during the transferring process. Energy-dispersive X-ray spectrometer analysis was performed using the JEM 2010 or the FEI transmission electron microscope equipped with an Oxford Instrument energy-dispersive X-ray spectrometer. The XRD patterns were recorded on a Bruker D8 Advanced diffractometer with Cu-Ka radiation at 40.0 kV and 120 mA as the Xray source. XPS was done on an ESCALAB 250Xi system (Thermo Fisher Scientific, Inc., USA) to analyze the surface chemistry of the samples. All the samples were cleaned by argon plasma before measurements. The XPS spectra were calibrated using a C 1s line at 284.6 eV. FTIR spectrometry was performed on a NEXUS 870 spectrograph to reveal the chemical structure. Solid-state ¹³C cross-polarization magic-angle spinning (MAS) NMR spectrum test was performed using the JNM-ECZ600R spectrometer with a resonance frequency of 150 MHz and a MAS frequency of 12 kHz. The N₂ isotherm was measured by an Auto-IQ2-MP-C physical adsorption system at 77 K. The corresponding pore size distribution and specific area were calculated by the non-local DFT method and the Brunauer-Emmett-Teller method, respectively.

Electrochemical Measurements

The electrochemical performances of G and G@COF-1 as Li host were evaluated using two-electrode cell configuration. Standard CR2025 coin-type cells were



assembled in an argon-filled glovebox with oxygen and water contents below 0.1 ppm. All the tests were performed on a NEWARE BTS-51 multichannel battery tester.

Fabrication of G and G@COF-1 Electrodes

Typically, G@COF-1 and PVDF at a mass ratio of 4:1 were added into NMP and stirred for 24.0 h to afford a homogeneous slurry. The slurry was then coated onto a Cu foil and dried in a vacuum at 80° C for 12.0 h. The areal mass loading of G@COF-1 was 1.4 mg cm⁻². After the solvent was evaporated, the coated Cu foil was punched into disks with a diameter of 13.0 mm, which directly served as the working electrode in half-cell evaluation. The fabrication of the G electrodes was otherwise identical to that of the G@COF-1 electrode except the same amount of G instead of G@COF-1 was used. The areal mass loading was same for the two electrodes.

Half-Cell Assembly and Electrochemical Measurements

In half-cells, the G or G@COF-1 electrodes were employed as the working electrodes and a Li metal foil was used as the counterelectrode. The thickness and diameter of the Li metal foil were 500 μ m and 16.0 mm, respectively. The electrolyte was 1.0 M LiTFSI in DOL/DME mixed solvent (v/v = 1/1) and the amount of electrolyte was 50 μ L in half-cells. Notably, the cells used for CE evaluation adopted the electrolyte with 5.0 wt% LiNO₃ additive, while the cells for morphology characterization were without LiNO₃ additive.

As for the testing under the conditions of 1.0 mA cm⁻² and 1.0 mAh cm⁻², the halfcells were first cycled at 0.5 mA cm⁻² and 1.0 mAh cm⁻² for five cycles, and then cycled at 1.0 mA cm⁻² and 1.0 mAh cm⁻². At the testing of 3.0 mA cm⁻² and 3.0 mAh cm⁻², the half-cells were first cycled at 0.5 mA cm⁻² and 1.0 mAh cm⁻² for three cycles, following by 1.0 mA cm⁻² and 3.0 mAh cm⁻² for three cycles, and then cycled at 3.0 mA cm⁻² and 3.0 mAh cm⁻².

Fabrication of G@COF-1-Li and G-Li Anode

G@COF-1-Li anodes were fabricated using G@COF-1-Li electrodes and ultrathin Li foils by the rolling method. Typically, a G@COF-1-Li-coated Cu foil and an ultrathin Li foil (33 µm in thickness) were stacked and rolled in a roller press (Shenzhen Kejing Star Technology Co. Ltd.). Then the Cu foil was removed. The rolling process was performed in a dry room with a dew-point temperature of -40° C. The as-obtained G@COF-1-Li foil was then punched into disks with a diameter of 13.0 mm serving as the G@COF-1-Li anodes. The G-Li anodes were fabricated following the same procedures but replacing the G@COF-1 with G.

Symmetric Cell Tests

The symmetric cells were assembled employing G@COF-1-Li or 33 µm ultrathin Li foil as the working electrode and 33 µm ultrathin Li foil as the counterelectrode. The cells were first cycled at 0.5 mA cm⁻² and 1.0 mAh cm⁻² for five cycles and then tested under the conditions of 1.0 mA cm⁻² and 1.0 mAh cm⁻². The electrolyte was 1.0 M LiTFSI in DOL/DME (v/v = 1/1) with 5.0 wt% LiNO₃ additive, and the amount of electrolyte was 50 µL in each cell.

Full-Cell Assembly and Electrochemical Measurements

The full cells were assembled employing G@COF-1-Li, G-Li, or 33 μm ultrathin Li foil as the anode and LFP or NCM523 as the cathode. The areal mass





loading of the LFP cathode was around 8.8 mg cm⁻², corresponding to the capacity of 1.5 mAh cm⁻². The Li | LFP full cells were first cycled at 0.2 C for one cycle and then cycled at 1.0 C (1 C = 170 mA g⁻¹) within a voltage range of 2.5–4.0 V. SEM characterization was carried out after 60 cycles of each cell. As for the NCM523 full cells, the areal mass loading of the NCM523 cathode was 8.0 mg cm⁻² corresponding to 1.5 mAh cm⁻². The NCM523 full cells were first cycled at 0.1 C for three cycles and then cycled at 0.4 C (1 C = 180 mA g⁻¹) within a voltage range of 2.8–4.3 V, while the rate performance was measured under 0.1, 0.2, 0.5, and 1.0 C by five cycles in each C rate. SEM characterization was carried out after 80 cycles of each cell. The electrolyte was 1.0 M LiPF₆ in EC/DEC (v/v = 1/1), or 1.0 M LiPF₆ in FEC/DMC (v/v = 1/4), and the amount of electrolyte was 50 μ L in full cells.

Computational Details

The periodic DFT calculations were conducted in the Vienna *ab initio* Simulation package with the projector-augmented-wave pseudopotentials, and the results were visualized in VESTA. The Perdew-Burke-Ernzerhof generalized-gradient approximation functional was adopted in all DFT calculations. Particularly, the van der Waals interaction was described with the DFT-D3 method. The energy cutoff was set to 520 eV. The self-consistent field and geometry convergence tolerance were set to 1 × 10⁻⁵ and 1 × 10⁻⁴ eV, respectively.

A double-layered COF-1 model was built to interact with a Li atom and the binding energy (E_b) between them was defined as the following:

$$E_{\rm b} = E_{\rm total} - E_{\rm COF-1} - E_{\rm Li},$$

where E_{total} , E_{COF-1} , and E_{Li} are the total energy of COF-1 bound with a Li atom, the pristine COF-1, and a single Li atom, respectively. In addition, a gamma-centered k-point grid through the Monkhorst-Pack method was set to 3 × 3 × 1 for COF-1 models.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.matt. 2020.10.014.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21676160, 21825501, and U1801257), the National Key Research and Development Program (2016YFA0202500), and the Tsinghua University Initiative Scientific Research Program. The authors acknowledge support from the Tsinghua National Laboratory for Information Science and Technology for theoretical simulations. We thank Jin Xie, Jia-Ning Liu, Xiao-Ru Chen, Dr. Xin-Bing Cheng, Professor Hong Yuan, and Professor Jia-Qi Huang for helpful discussions.

AUTHOR CONTRIBUTIONS

Q.Z. conceived the study and supervised this work. Y-W.S., P.S., and Q.Z. designed the experiment. Y-W.S. synthesized the materials. Y-W.S., B-Q.L., C-X.Z., and X.C. characterized the materials. P.S., X-Q.Z., and W-J.C. evaluated the electrochemical performance. X.C. performed the theoretical simulations. Y-W.S., P.S., B-Q.L., and Q.Z. wrote the paper. All authors contributed to the discussion. Y-W.S. and P.S. contributed equally to this work.





DECLARATION OF INTERESTS

The authors report no competing interests.

Received: July 23, 2020 Revised: September 22, 2020 Accepted: October 8, 2020 Published: November 4, 2020

REFERENCES

- Peng, H.-J., Huang, J.-Q., Cheng, X.-B., and Zhang, Q. (2017). Review on high-loading and high-energy lithium-sulfur batteries. Adv. Energy Mater. 7, 1700260.
- Xu, W., Wang, J., Ding, F., Chen, X., Nasybulin, E., Zhang, Y., and Zhang, J.-G. (2014). Lithium metal anodes for rechargeable batteries. Energy Environ. Sci. 7, 513–537.
- Zhao, M., Li, B.Q., Peng, H.J., Yuan, H., Wei, J.Y., and Huang, J.Q. (2020). Lithium-sulfur batteries under lean electrolyte conditions: challenges and opportunities. Angew. Chem. Int. Ed. 59, 2–19.
- Zhang, X., Cheng, X., and Zhang, Q. (2016). Nanostructured energy materials for electrochemical energy conversion and storage: a review. J. Energy Chem. 25, 967–984.
- Bruce, P.G., Scrosati, B., and Tarascon, J.M. (2008). Nanomaterials for rechargeable lithium batteries. Angew. Chem. Int. Ed. 47, 2930– 2946.
- Sun, Y., Zheng, G., Seh, Z.W., Liu, N., Wang, S., Sun, J., Lee, H.R., and Cui, Y. (2016). Graphiteencapsulated Li-metal hybrid anodes for highcapacity Li batteries. Chem 1, 287–297.
- Cheng, X.B., Zhang, R., Zhao, C.Z., and Zhang, Q. (2017). Toward safe lithium metal anode in rechargeable batteries: a review. Chem. Rev. 117, 10403–10473.
- López, C.M., Vaughey, J.T., and Dees, D.W. (2009). Morphological transitions on lithium metal anodes. J. Electrochem. Soc. 156, A726–A729.
- Bhattacharyya, R., Key, B., Chen, H., Best, A.S., Hollenkamp, A.F., and Grey, C.P. (2010). In situ NMR observation of the formation of metallic lithium microstructures in lithium batteries. Nat. Mater. 9, 504–510.
- Zhu, B., Jin, Y., Hu, X., Zheng, Q., Zhang, S., Wang, Q., and Zhu, J. (2017). Poly(dimethylsiloxane) thin film as a stable interfacial layer for high-performance lithiummetal battery anodes. Adv. Mater. 29, 1603755.
- Yang, C.P., Yin, Y.X., Zhang, S.F., Li, N.W., and Guo, Y.G. (2015). Accommodating lithium into 3D current collectors with a submicron skeleton towards long-life lithium metal anodes. Nat. Commun. 6, 8058.
- Zhang, R., Cheng, X.B., Zhao, C.Z., Peng, H.J., Shi, J.L., Huang, J.Q., Wang, J., Wei, F., and Zhang, Q. (2016). Conductive nanostructured scaffolds render low local current density to Inhibit lithium dendrite growth. Adv. Mater. 28, 2155–2162.

- Mukherjee, R., Thomas, A.V., Datta, D., Singh, E., Li, J., Eksik, O., Shenoy, V.B., and Koratkar, N. (2014). Defect-induced plating of lithium metal within porous graphene networks. Nat. Commun. 5, 3710.
- Zhang, R., Li, N.W., Cheng, X.B., Yin, Y.X., Zhang, Q., and Guo, Y.G. (2017). Advanced micro/nanostructures for lithium metal anodes. Adv. Sci. 4, 1600445.
- Liang, Z., Lin, D., Zhao, J., Lu, Z., Liu, Y., Liu, C., Lu, Y., Wang, H., Yan, K., Tao, X., et al. (2016). Composite lithium metal anode by melt infusion of lithium into a 3D conducting scaffold with lithiophilic coating. Proc. Natl. Acad. Sci. U S A 113, 2862–2867.
- Li, B.Q., Chen, X.R., Chen, X., Zhao, C.X., Zhang, R., Cheng, X.B., and Zhang, Q. (2019). Favorable lithium nucleation on lithiophilic framework porphyrin for dendrite-free lithium metal anodes. Research 2019, 4608940.
- Zhang, R., Chen, X.R., Chen, X., Cheng, X.B., Zhang, X.Q., Yan, C., and Zhang, Q. (2017). Lithiophilic sites in doped graphene guide uniform lithium nucleation for dendrite-free lithium metal anodes. Angew. Chem. Int. Ed. 56, 7764–7768.
- Lin, D., Liu, Y., Liang, Z., Lee, H.W., Sun, J., Wang, H., Yan, K., Xie, J., and Cui, Y. (2016). Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes. Nat. Nanotechnol. 11, 626–632.
- Huang, G., Han, J., Zhang, F., Wang, Z., Kashani, H., Watanabe, K., and Chen, M. (2019). Lithiophilic 3D nanoporous nitrogen-doped graphene for dendrite-free and ultrahigh-rate lithium-metal anodes. Adv. Mater. *31*, 1805334.
- Zhou, T., Shen, J., Wang, Z., Liu, J., Hu, R., Ouyang, L., Feng, Y., Liu, H., Yu, Y., and Zhu, M. (2020). Regulating lithium nucleation and deposition via MOF-derived Co@C-modified carbon cloth for stable Li metal anode. Adv. Func. Mater. 30, 1909159.
- Xie, K., Wei, W., Yuan, K., Lu, W., Guo, M., Li, Z., Song, Q., Liu, X., Wang, J.G., and Shen, C. (2016). Toward dendrite-free lithium deposition via structural and interfacial synergistic effects of 3D graphene@Ni scaffold. ACS Appl. Mater. Interfaces 8, 26091–26097.
- Zhang, H., Liao, X., Guan, Y., Xiang, Y., Li, M., Zhang, W., Zhu, X., Ming, H., Lu, L., Qiu, J., et al. (2018). Lithiophilic-lithiophobic gradient interfacial layer for a highly stable lithium metal anode. Nat. Commun. 9, 3729.
- 23. Jiang, G., Jiang, N., Zheng, N., Chen, X., Mao, J., Ding, G., Li, Y., Sun, F., and Li, Y. (2019).

MOF-derived porous Co_3O_4 -NC nanoflake arrays on carbon fiber cloth as stable hosts for dendrite-free Li metal anodes. Energy Storage Mater. 23, 181–189.

- Luo, L., Li, J., Yaghoobnejad Asl, H., and Manthiram, A. (2019). A 3D lithiophilic Mo₂Nmodified carbon nanofiber architecture for dendrite-free lithium-metal anodes in a full cell. Adv. Mater. 31, 1904537.
- Yan, K., Lu, Z., Lee, H.-W., Xiong, F., Hsu, P.-C., Li, Y., Zhao, J., Chu, S., and Cui, Y. (2016). Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. Nat. Energy 1, 16010.
- Lei, M., Wang, J.-G., Ren, L., Nan, D., Shen, C., Xie, K., and Liu, X. (2019). Highly lithiophilic cobalt nitride nanobrush as a stable host for high-performance lithium metal anodes. ACS Appl. Mater. Interfaces 11, 30992–30998.
- Cao, S., Li, B., Zhu, R., and Pang, H. (2019). Design and synthesis of covalent organic frameworks towards energy and environment fields. Chem. Eng. J. 355, 602–623.
- Cote, A.P., El-Kaderi, H.M., Furukawa, H., Hunt, J.R., and Yaghi, O.M. (2007). Reticular synthesis of microporous and mesoporous 2D covalent organic frameworks. J. Am. Chem. Soc. 129, 12914–12915.
- 29. Vitaku, E., and Dichtel, W.R. (2017). Synthesis of 2D imine-linked covalent organic frameworks through formal transimination reactions. J. Am. Chem. Soc. 139, 12911–12914.
- Chen, D., Huang, S., Zhong, L., Wang, S., Xiao, M., Han, D., and Meng, Y. (2020). In situ preparation of thin and rigid COF film on Li anode as artificial solid electrolyte interphase layer resisting Li dendrite puncture. Adv. Func. Mater. 30, 1907717.
- Yao, C.-J., Wu, Z., Xie, J., Yu, F., Guo, W., Xu, Z.J., Li, D.-S., Zhang, S., and Zhang, Q. (2020). Two-dimensional (2D) covalent organic framework as efficient cathode for binder-free lithium-ion battery. ChemSusChem 13, 2457– 2463.
- Lin, Z.-Q., Xie, J., Zhang, B.-W., Li, J.-W., Weng, J., Song, R.-B., Huang, X., Zhang, H., Li, H., Liu, Y., et al. (2017). Solution-processed nitrogenrich graphene-like holey conjugated polymer for efficient lithium ion storage. Nano Energy 41, 117–127.
- 33. Xie, H., Hao, Q., Jin, H., Xie, S., Sun, Z., Ye, Y., Zhang, C., Wang, D., Ji, H., and Wan, L.-J. (2020). Redistribution of Li-ions using covalent organic frameworks towards dendrite-free lithium anodes: a mechanism based on a Galton Board. Sci. China Chem. 63, 1306–1314.



- Zhi, Y., Wang, Z., Zhang, H.-L., and Zhang, Q. (2020). Recent progress in metal-free covalent organic frameworks as heterogeneous catalysts. Small 16, 2001070.
- Sun, T., Xie, J., Guo, W., Li, D.-S., and Zhang, Q. (2020). Covalent–organic frameworks: advanced organic electrode materials for rechargeable batteries. Adv. Energy Mater. 10, 1904199.
- Xu, Y., Zhou, Y., Li, T., Jiang, S., Qian, X., Yue, Q., and Kang, Y. (2020). Multifunctional covalent organic frameworks for high capacity and dendrite-free lithium metal batteries. Energy Storage Mater. 25, 334–341.
- Li, B.-Q., Zhang, S.-Y., Wang, B., Xia, Z.-J., Tang, C., and Zhang, Q. (2018). A porphyrin covalent organic framework cathode for flexible Zn-air batteries. Energy Environ. Sci. 11, 1723–1729.
- Li, B.Q., Zhang, S.Y., Kong, L., Peng, H.J., and Zhang, Q. (2018). Porphyrin organic framework hollow spheres and their applications in lithium-sulfur batteries. Adv. Mater. 30, 1707483.
- 39. Spitler, E.L., Colson, J.W., Uribe-Romo, F.J., Woll, A.R., Giovino, M.R., Saldivar, A., and

Dichtel, W.R. (2012). Lattice expansion of highly oriented 2D phthalocyanine covalent organic framework films. Angew. Chem. Int. Ed. 51, 2623–2627.

- Dogru, M., Handloser, M., Auras, F., Kunz, T., Medina, D., Hartschuh, A., Knochel, P., and Bein, T. (2013). A photoconductive thienothiophene-based covalent organic framework showing charge transfer towards included fullerene. Angew. Chem. Int. Ed. 52, 2920–2924.
- Chen, X., Chen, X.R., Hou, T.Z., Li, B.Q., Cheng, X.B., Zhang, R., and Zhang, Q. (2019). Lithiophilicity chemistry of heteroatom-doped carbon to guide uniform lithium nucleation in lithium metal anodes. Sci. Adv. 5, eaau7728.
- Wu, C., Huang, H., Lu, W., Wei, Z., Ni, X., Sun, F., Qing, P., Liu, Z., Ma, J., Wei, W., et al. (2020). Mg doped Li–LiB alloy with in situ formed lithiophilic LiB skeleton for lithium metal batteries. Adv. Sci. 7, 1902643.
- Chen, M., Li, B., Liu, X., Zhou, L., Yao, L., Zai, J., Qian, X., and Yu, X. (2018). Boron-doped porous Si anode materials with high initial coulombic efficiency and long cycling stability. J. Mater. Chem. A 6, 3022–3027.

 Furukawa, H., and Yaghi, O.M. (2009). Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications. J. Am. Chem. Soc. 131, 8875–8883.

Matter Article

- Cote, A.P., Benin, A.I., Ockwig, N.W., O'Keeffe, M., Matzger, A.J., and Yaghi, O.M. (2005). Porous, crystalline, covalent organic frameworks. Science 310, 1166–1170.
- 46. Zwaneveld, N.A., Pawlak, R., Abel, M., Catalin, D., Gigmes, D., Bertin, D., and Porte, L. (2008). Organized formation of 2D extended covalent organic frameworks at surfaces. J. Am. Chem. Soc. 130, 6678–6679.
- 47. Sun, J., Klechikov, A., Moise, C., Prodana, M., Enachescu, M., and Talyzin, A.V. (2018). A molecular pillar approach to grow vertical covalent organic framework nanosheets on graphene: hybrid materials for energy storage. Angew. Chem. Int. Ed. 57, 1034–1038.
- Jiang, C., Tang, M., Zhu, S., Zhang, J., Wu, Y., Chen, Y., Xia, C., Wang, C., and Hu, W. (2018). Constructing universal ionic sieves via alignment of two-dimensional covalent organic frameworks (COFs). Angew. Chem. Int. Ed. 57, 16072–16076.