Conducting and Lithiophilic MXene/Graphene Framework for High-Capacity, Dendrite-Free Lithium-Metal Anodes

Haodong Shi^{†,‡,¶}, Chuanfang (John) Zhang^{#1}, Pengfei Lu[†], Yanfeng Dong^{†,§}, Pengchao Wen[†],
Zhong-Shuai Wu^{†*}

[†] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

[‡] University of Chinese Academy of Sciences, 19 A Yuquan Rd, Shijingshan District, Beijing, 100049, China

[#] Swiss Federal Laboratories for Materials Science and Technology (Empa), ETH domain, Überlandstrasse 129, CH-8600, Dübendorf, Switzerland

[§] Department of Chemistry, College of Sciences, Northeastern University, 3-11 Wenhua Road, Shenyang 110819, China

ABSTRACT:

Li-metal anode is widely acknowledged as the ideal anode for high-energy-density batteries, but seriously hindered by the uncontrollable dendrite growth and infinitely volume change. To this goal, seeking suitable stable scaffolds for dendrite-free Li anodes with large current density ($> 5 \text{ mA cm}^{-2}$) and high Li loading ($> 90\%$) are highly in demand. Herein, a conductive and lithiophilic three-dimensional (3D) MXene/graphene (MG) framework is demonstrated for dendrite-free Li-metal anode. Benefiting from its high surface area ($259 \text{ m}^2 \text{ g}^{-1}$) and lightweight nature with uniformly dispersed lithiophilic MXene nanosheets as Li nucleation sites, the as-formed 3D MG scaffold showcases an ultrahigh Li content ($\sim 92\%$ of the theoretical capacity), as well as strong capabilities in suppressing the Li-dendrites formation and accommodating the volume changes. Consequently, the MG based electrode exhibits high Coulombic efficiencies ($\sim 99\%$) with a record lifespan up to 2700 h, and is stable for 230 cycles at an ultrahigh current density of 20 mA cm^{-2} . When coupled with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or sulfur, the MG-Li/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ full-cell offers an enhanced capacity of 142 mAh g^{-1} after 450 cycles while the MG-Li/sulfur cell delivers improved rate performance, implying the great potential of this 3D MG framework for building long lifetime, high-energy-density batteries.

KEYWORDS: MXene, Li metal anode, 3D framework, dendrite free, graphene

The ever-increasing demands for electric vehicles and portable electronics have accelerated the continuous development of high-energy-density rechargeable batteries.¹⁻³ Lithium (Li) metal possesses an ultrahigh theoretical capacity (3860 mAh g⁻¹) and the lowest redox potential (-3.04 V vs standard hydrogen electrode) comparing to the rest possible candidates, thus has been received substantial research focuses in the electrochemical energy storage field.⁴⁻⁷ When matched with high-capacity cathodes of such as sulfur (S) and O₂, the corresponding theoretical energy densities are predicated to be as high as 2600 Wh kg⁻¹ for Li-S batteries and 11400 Wh kg⁻¹ for Li-O₂ batteries.⁸⁻¹¹ However, their commercialization applications have been seriously hindered by the uncontrollable growth of Li dendrite and infinite volume changes during charge-discharge processes.¹²⁻¹⁴

The growth of Li dendrite is known to be influenced by several factors, including (i) inhomogeneous distribution of space-charge and current density on the anode surface, (ii) the chemical and electrochemical reactions between the anode and electrolyte, and (iii) the crack of solid electrolyte interphase (SEI).¹⁵⁻¹⁶ To overcome these issues, a number of strategies have been proposed either focusing on new electrolyte systems (including highly concentrated electrolytes, dual or ternary-salt electrolyte and additives),¹⁷⁻²⁰ or Li-based alloys (*e.g.*, Li-Au, Li-Zn, Li-Al, Li-Si).²¹⁻²⁵ For instances, Zhou *et al.* reported on a concentrated ternary-salts electrolyte (LiTFSI-LiNO₃-LiFSI) for stable Li-metal anode and achieved a high Coulombic efficiencies of 99.1%;¹⁷ Xu *et al.* employed LiPF₆ as an additive in LiTFSI-LiBOB dual-salt electrolyte, and a cyclability of 97.1% capacity was retained after 500 cycles.¹⁸ On the other hand, Nazar *et al.* demonstrated the formation of Li-Zn (In) alloy which exhibited stable performance over 1500 cycles with a Li₄Ti₅O₁₂ cathode.²¹ Aside from these endeavors, designing stable artificial physical protective barrier also represents delicate strategies to suppress the Li dendrite formation and realize long

cycle life batteries.^{26,27} However, these strategies to some extent can't fully accommodate the infinite volume changes during Li electrochemical cycling, which result in huge internal stress fluctuations and unstable interface.

On the other side, three dimensional (3D) hosts with excellent chemical stability and large surface areas are expected to simultaneously suppress the growth of Li dendrite and minimize the volume changes of Li metal anodes.^{28,29} So far, various 3D porous frameworks based on porous Cu foil,³⁰ nickel foam,^{31,32} and 3D polyimide,³³ were reported as effective hosts for Li metal. However, the reported 3D lithium anodes either suffer from a relatively low Li content (< 60%) or poor electrical conductivity, limiting the achievable energy density. 3D conductive carbon framework is thus frequently employed as lightweight host for Li, especially at a high loading amount. For example, 3D reduced graphene oxide (rGO) film and carbon nanotube (CNT) paper were studied as the Li flexible hosts, achieving a capacity up to 3390 mAh g⁻¹ and a mass loading of 80.7%, respectively.^{34,35} Unfortunately, most of nanocarbon frameworks are poor in the lithiophilicity, leading to inhomogeneous nucleation/deposition processes and loose contact between Li and host carrier. The subsequent cycling inevitably results in the formation of Li dendrite and "dead Li". This is especially true at high current density (> 5 mA cm⁻²).

To this end, introducing lithiophilic species into 3D highly conductive nanocarbon hosts without compromising the homogenous nucleation sites are urgently in demand for realizing both high lithium loading and dendrite-free metallic Li anodes.³⁶⁻³⁸ Of particular attention is given to 2D MXene (Ti₃C₂T_x, the most extensively studied MXene), a family of two-dimensional (2D) carbides and nitrides of transition metals (M), where X stands for carbon or nitrogen and T_x represent hydroxyl-, oxygen-, and/or fluorine-terminated groups.^{39,40} The excellent electrical conductivity and abundant lithiophilic functional groups (O, F) on the MXene surface endow it an

ideal platform for Li deposition.⁴¹⁻⁴⁴ However, upon drying and electrode fabrication, which decreases the achievable sites and uniformity for Li deposition.^{45,46} Said otherwise, designing 3D MXene/carbon conductive, lightweight framework with high lithium mass loading and large current density has been proved to be quite difficult.^{47,48}

Herein, we report on a highly conductive, lithiophilic and lightweight MXene/graphene (MG) framework as the Li scaffold *via* a thermal infusion strategy. Such a 3D MG framework possesses a high surface area ($259 \text{ m}^2 \text{ g}^{-1}$) and interconnected pore structure, allowing a high Li loading amount while preserving excellent mechanical properties. The structure design in the flexible lithium-metal anode (MG-Li) ensures a capacity up to 3560 mAh g^{-1} coupled with Coulombic efficiencies ($> 99\%$) and cycling stability up to 2700 h in the absence of Li dendrite. The cell can withstand extremely high current density of 20.0 mA cm^{-2} with very small potential polarization (30 mV). The MG-Li anode also demonstrates improved rate capability and cyclability in the assembled full cell, showcasing promising applications for future long lifetime, high-energy-density batteries.

RESULTS AND DISCUSSION

The fabrication process of 3D MG-Li anode is schematically shown in Figure 1a. First, the homogeneous mixed suspensions of MXene (Figure S1) and graphene oxide (GO) (ratio of GO and MXene was 3:1) were obtained by high-energy ultrasonication, and then freeze-dried to form 3D freestanding and lightweight MXene/GO (MGO) aerogels, with a mass density of 3.9 mg cm^{-3} . Notably, the introduction of MXene into MGO aerogels greatly improves the mechanical strength (Figure S2).⁴⁹ In this process, the small-size MXene nanosheets (300~500 nm) are uniformly dispersed on the surface of large-size GO nanosheets (1~5 μm) in 3D aerogels (Figure

S3), as observed by transmission electron microscopy (TEM) (Figure S4) and atomic force microscope (AFM) images (Figure 1b,c).⁵⁰ Second, 3D MGO aerogels were mechanically pressed (at 10 MPa) to prepare layer-stacked MGO films for lithium deposition (Figure S5). Impressively, when the MGO film was partially put into contact with molten Li, a spark reaction occurred immediately across the film and realized the rapid reduction of GO, forming a 3D MG interconnected nanoporous framework (Movie S1, Figure 1d).³⁴ In the framework, the single-layer MXene nanosheets homogeneously attach on the surface of graphene, as evidenced by the backscattered scanning electron microscope (SEM) image (Figure S6) and the energy-dispersive spectrometer (EDS) elemental mapping (Figure 1e and Figure S7). Such a 3D framework is mechanically robust (inset of Figure 1d) and effective in suppressing MXene restacking and oxidation behaviors.⁵¹ X-ray diffraction (XRD) patterns (Figure S8) and Raman spectra (Figure 1f, g) of MG aerogels reveal that MXene and rGO characteristic peaks co-existed in the MG film. X-ray photoelectron spectroscopy (XPS, Figure 1h) indicates that O and C contents in the MG aerogel have increased, which can be explained by the introduction of rGO. Further, the Ti 2p and O1s core-level XPS spectra reveal that the peaks attributed to $\text{Ti-O}_{2-x}\text{F}_x$ and C-Ti-O_x in the MG samples become more intense compared to peaks in the MXene film, implying a strong interaction between MXene and rGO. Besides, F1s signals are clearly detected in both pure MXene and MG (Figure S9), which will play a significant role in the nucleation of metallic Li during plating,⁵² as will be discussed later. Based on the Fourier transform infrared spectroscopy (FTIR, Figure S10), it is observed that after the spark reduction reaction the peak of surface -OH groups have been almost removed while other peaks attributed to oxygen-containing surface moieties are retained. Benefiting from these oxygen and fluorine-containing groups, coupled with enhanced lithiophilicity and capillary forces, Li could be readily infused into the nanoporous channels within

1 min by placing the 3D MG aerogel onto the molten media (Movie S1). In a sharp contrast, it is difficult to infuse Li into the pure MXene film (Movie S2). This discrepancy can be fairly attributed to the porosity differences in two samples. While MG possesses a 3D porous structure with high specific surface area ($259 \text{ m}^2 \text{ g}^{-1}$, Figure 1i), MXene film is typically compact and thus lack of necessary nanoporous channels (specific surface area $\sim 0.2 \text{ m}^2 \text{ g}^{-1}$, Figure S11) for Li plating. It is noteworthy that, after the Li metal was completely stripped from the MG-Li anode, the lithiophilic oxygen-containing groups of rGO are almost removed due to the strong deoxidizing ability of molten Li, indicative of the full transform of GO into graphene (Figure S12).

For practical pouch and cylindrical cell assembling, good electrode flexibility is critical for the folding or rolling processes.⁵³ Thanks to the mechanically flexible nature and layered structure of MG films (inset of Figure 1d and Figure S13), the pliability of MG-Li anode (Figure 1j) is significantly enhanced. As a result, the porous chambers of MG scaffold are uniformly infused by Li with a large thickness of $\sim 500 \text{ }\mu\text{m}$ and ultrahigh lithium mass loading up to 92% without roughening the surface, indicative of extraordinary affinity with Li and high thermal stability of MG aerogels. Furthermore, the thickness and shape of MG-Li anodes can be easily tuned by modifying the thickness and shape of the MG films (Figure S14), showcasing the wide applicability of our proposed strategy for practical applications.

To understand the lithiophilic mechanism of Li deposition process on the MG film, density functional theory (DFT) calculations were performed to determine the adsorption energy between a Li atom with graphene and MXene clusters (Figure 2a). It is found that the MXene surface exhibits a larger binding energy of 2.93 eV than that of graphene (2.62 eV), suggesting that the former surface is indeed more lithiophilic. Meanwhile, the local charge density between MXene and Li atom is higher compared to that of graphene-Li (Figure 2b), further indicating stronger

interactions when using MXene to anchor Li. Consequently, the well-distributed lithiophilic MXene nanosheet could significantly decrease the electroplating overpotentials and guide the smooth Li deposition across the MG framework. To reflect the rate capability of Li anode, the mobility of Li atom on the surface of monolayer MXene was examined, assuming the Li atom diffuses along the path i $\rightarrow$ iv (Figure 2c). It is found that Li is preferably adsorbed on the positions of both i and iii. That is to say, the C atom sites are more favorable to form a metastable configuration (Figure 2d). Further investigations on the Li diffusion barrier in the case of C-defect and Ti-defect conclude that the Ti-defect influences the Li ion migration energy to a large extent and greatly accelerates the Li ion diffusion (Figure S15).

Adding MXene nanosheets (3600 S cm^{-1}) to the 3D scaffold also greatly improves the electrical conductivity. As seen in Figure 2e, the MG film displays an electrical conductivity of 7.6 S cm^{-1} , almost three times higher than that of pure rGO film (2.6 S cm^{-1}). To illustrate the importance of high electrical conductivity and lithiophilicity of MXene, we fabricated a counterpart of rGO film electrode with pure MXene layer coated on half of the rGO surface (Figure 2f). After deposition 1 mAh cm^{-2} Li at a current density of 0.25 mA cm^{-2} , impressively, the surface of MXene-modified part was covered by Li without any growth of Li dendrite. On the contrary, irregular Li dendrite was found on the bare rGO part (Figure 2g and Figure S16).⁵⁴ These results clearly suggest the importance of delicate structure design on highly lithiophilic MXene nanosheets decorate on rGO as preferential Li deposition sites, forming a 3D MG scaffold in the suppression of Li dendrite formation (Figure 2h).

More importantly, as confirmed by DFT calculations in Figure 2i, the energy for Li ion adsorption is much lower when electrolyte is in contact with the MG-Li surface.⁵⁵ Experimentally, it is also demonstrated that the contact angle of the electrolyte droplet on the MG-Li significantly

decreased to 0° after 1 min (Figure 2j). This is in a sharp contrast to the bare Li; whose contact angle slightly changes to $\sim 16.9^\circ$ (Figure 2k). The enhanced wettability of MG-Li anode sufficiently guarantees uniform distribution of Li ions at the interfaces between electrode and electrolyte. As a result, the 3D MG scaffold allows for the homogeneous Li metal deposition.

To examine the effect of MXene on the plating/stripping behaviors, the Coulombic efficiencies of MG aerogels with different mass ratio of MXene to GO were evaluated under deposition capacity of 0.5 mAh cm^{-2} at a current density of 0.5 mA cm^{-2} . The results are shown in Figure 3a. Apparently, the Coulombic efficiencies of pure rGO aerogels drop quickly to 88% after 35 cycles, possibly because the oxygen-containing groups consumed a lot of cyclable Li ions for SEI formation. When the mass ratio of GO to MXene decreases from 5:1 to 3:1, higher and more stable Coulombic efficiencies (98%) as well as longer lifespans are attained. When MXene content is 50%, the Coulombic efficiencies of the MG decreases to 86% for 85 cycles, implying an optimal MXene content do exist. We selected the ratio of GO to MXene = 3:1 as the optimized condition, and conducted the discussion based on this ratio unless specifically noted. The Coulombic efficiencies of MG electrode reaches 98.0% at 0.5 mA cm^{-2} for 2 mAh cm^{-2} and maintains 99.0% after 100 cycles (Figure 3b). The stable cycling performance of MG-Li anode is in sharp contrast to that of rGO-Li or bare Cu-Li electrodes, which rapidly drop to 78% only after 53 cycles and 18% after 46 cycles, respectively (Figure 3b). The cycling differences of three electrodes are more pronounced when increasing the current density to 1 mA cm^{-2} (Figure 3c) or capacity to 5 mAh cm^{-2} (Figure S17), highlighting the structure design in the realization of long cycle life lithium anodes. The rate performances of MG and Cu electrodes under increased current densities ranging from 0.25 to 2.5 mA cm^{-2} at the same plating time for 1 h were also compared. As shown in Figure 3d, the MG electrode still remains highly stable Coulombic efficiencies under a Li deposition

capacity of 2.5 mAh cm^{-2} . On the other hand, the Cu electrode fails to maintain stable Coulombic efficiencies as increasing the areal capacity. We further evaluated the rate performance of these two electrodes. Unlike the Cu electrode which quickly decays as the capacity goes beyond 0.5 mAh cm^{-2} , the MG electrode keeps excellent stability with stepwise increased capacity from 0.25 to 6 mAh cm^{-2} (Figure S18), coupled with high Coulombic efficiencies $\sim 99\%$ over 2700 h at 5 mAh cm^{-2} (Figure 3e). To the best of our knowledge, this is the longest cycle time reported under such high Coulombic efficiencies up to date. Moreover, the plating overpotential of MG electrode is $\sim 36 \text{ mV}$, much lower than that of rGO (62 mV) and Cu (71 mV) electrodes, suggesting the overall ionic transport resistance of MG is the lowest (Figure 3f and Figure S19). This is further confirmed by the electrochemical impedance spectroscopy (EIS), which reveals a much smaller interfacial charge transfer resistance for MG (10.5Ω) than those of rGO (27.9Ω) and Cu (54.1Ω) electrodes. The Li ion diffusion coefficient of MG, derived from the EIS, is calculated to be $6.99 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, which is higher than those of rGO ($1.91 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) and Cu ($1.77 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) (Figure 3g), indicative of enhanced Li lithium ion conductivity in 3D MG framework.⁵⁶

To highlight the advantage of MG-Li electrode, we compared the long-term voltage profiles of symmetric cells based on MG-Li, rGO-Li and bare Li foil, respectively. Figure 4a shows that the overpotentials of Li foil and rGO-Li symmetric cells increase sharply after 30 and 90 h , respectively, while flat and consistent voltage profiles for more than 500 h are found in the MG-Li cell. To study the evolution of the voltage profiles in detail, the 100th , 300th and 700th cycles of MG-Li cell were further enlarged (Insets of Figure 4a). Evidently, flat voltage plateau ($\sim 13 \text{ mV}$) at both the charging and discharging states can be maintained throughout the whole cycles. Increasing the current density to 5 mA cm^{-2} , the differences in the cycling stability and overpotential become more pronounced for different cells (Figure 4b). For example, the

stripping/plating overpotential for MG-Li based symmetric cell is only ~25 mV with stable life over 1000 cycles. However, symmetric cells based on bare Li and rGO-Li electrode fail quickly with substantial voltage fluctuation at the 28th (~600 mV) and 77th (~428 mV) cycles, respectively (Figure S20). Impressively, our MG-Li electrode also displays outstanding cycling stability (500 h with voltage plateau 18 mV) in highly active Li-ion battery-based carbonyl electrolyte (1 mA cm^{-2} , 1 mAh cm^{-2} , Figure S21). Further increasing the cycling capacity to 5 mAh cm^{-2} and ultrahigh current density to 20 mA cm^{-2} , the voltage curves of the MG-Li cell represent small hysteresis of only 30 mV without any indication of short circuit up to 120 h (Figure 4c), which has rarely been achieved in earlier studies. The excellent rate performance of the MG-Li symmetric cell is evidenced by the fact that no huge voltage fluctuation is observed when the current density increases from 0.5 to 5 mA cm^{-2} at a fixed stripping/plating capacity of 1 mAh cm^{-2} (Figure 4d and Figure S22). Correspondingly, the EIS reveals a lower interfacial charge transfer resistance of 31Ω for MG-Li compared to bare Li (242Ω) and rGO-Li (60Ω) (Figure 4e). The small charge transport resistance and excellent wettability of MG-Li electrode (Figure 2j) enable the uniform Li nucleation and guarantee superior electrochemical performance of symmetric cells. Moreover, the MG-Li delivers a specific capacity up to $\sim 3560 \text{ mAh g}^{-1}$ (~92% of the theoretical capacity of metal Li) based on the mass of the whole electrode when charged to 0.5 V (Figure 4f and Table S1). Such a high capacity is mainly attributed to 3D conducting, stable, interconnected porous structure of MG aerogels (Figure S23). It should be emphasized that the 3D MG-Li has simultaneously achieved ultrahigh mass capacity of 3560 mAh g^{-1} , ultrahigh cycle rate of 20 mA cm^{-2} and long cycle time of 120 h, which is superior to the reported state-of-the-art composite-Li anodes (Figure 4g, Table S2), such as Ni foam-Li (2061 mAh g^{-1} , 5 mA cm^{-2} , 40 h),³¹ graphitized

carbon fibers-Li (1254 mAh g⁻¹, 4 mA cm⁻², 70 h),⁵⁷ polyimide-Li (2070 mAh g⁻¹, 5 mA cm⁻², 39 h),³³ and carbonized eggplant-Li (3461 mAh g⁻¹, 10 mA cm⁻², 100 h).⁵⁸

To further evaluate the structural stability of MG-Li during galvanostatic cycling, the cells with the same thickness ~500 μm as bare Li anode were subjected to a typical Li-stripping-plating process at current density of 2 mA cm⁻² with a fixed capacity of 10 mAh cm⁻². Notably, the MG-Li cell shows more stable voltage plateau and lower voltage hysteresis (15 mV) than that of bare Li cell (50 mV), indicative of superior stable SEI film during cycling and fast Li deposition process (Figure 5a and Figure S24). To clearly visualize the electrode thickness variation, we further examined the cross-section SEM morphologies of Li stripping-plating process on MG-Li and bare Li electrodes under different stages of cycling (Figure 5b-d). As expected, after extraction 10 mAh cm⁻² capacity of Li, the MG-Li anode exhibits a small volume change, and the thickness slightly changes from 510 μm before cycling to 490 μm after lithium extraction, then back to 530 μm after plating. The overall morphology maintains intact, no observable Li dendrites are found on the electrode (Figure 5c). In a sharp contrast, the shape and thickness of the bare Li anode change dramatically from 480 μm to 210 μm and back to 410 μm upon cycling. The huge thickness/volume fluctuation can be fairly attributed to the lack of a stable scaffold, as well as the formation of massive arrays of Li dendrites observed after cycling (Figure 5d and Figure S25). As previously mentioned, the 3D porous MG framework not only offers a stable flexible scaffold to minimize the volume changes for ultrahigh mass-loading Li, but also efficiently dissipates high current density thanks to the evenly distributed lithiophilic MXene in the whole 3D skeleton. As a result, the Li dendrite growth is greatly inhibited (Figure 5e).⁵⁹

To highlight practical applications, we first paired the MG-Li anode with Li₄Ti₅O₁₂ (LTO) cathode to assemble the MG-Li/LTO full cell, and compared its electrochemical performance with

bare Li/LTO and rGO-Li/LTO cells. All the anodes have a similar thickness ($\sim 500\text{ }\mu\text{m}$). Figure 6a, b indicate that after 450 cycles, the MG-Li/LTO cell maintains 142 mAh g^{-1} with high Coulombic efficiency nearly 100% (Figure S26), while rGO-Li/LTO and Li/LTO decay to 132 mAh g^{-1} and 120 mAh g^{-1} , respectively. Moreover, the MG-Li/LTO cell exhibits superior rate performance to other cells. For example, at 5 C and 10 C, the MG-Li/LTO cell shows 141 mAh g^{-1} and 123 mAh g^{-1} , respectively, much higher than those of rGO-Li/LTO cell (127 mAh g^{-1} , 108 mAh g^{-1}) and bare Li/LTO cell (104 mAh g^{-1} , 81 mAh g^{-1}), as demonstrated in Figure 6c and Figure S26. This is in line with the EIS results, which reveal a much-reduced interfacial charge transfer resistance for the MG-Li/LTO ($32\text{ }\Omega$) compared to rGO-Li/LTO ($61\text{ }\Omega$) and bare Li/LTO ($152\text{ }\Omega$), indicating the MG-Li electrode possesses robust ionic and electronic channels (Figure S28). To demonstrate the advantages of MG-Li anode for potential Li-S application, we also assembled pouch cells by pairing different anodes with the S cathode, the latter composite electrode was simply prepared by mixing sulfur with carbon black and polyvinylidene fluoride without any further modifications. As shown in Figure 6d and Figure S29, the MG-Li/S cell consistently exhibits enhanced rate performance with higher capacities than those of rGO-Li/S and Li/S cells, especially at higher current densities. For instances, the MG-Li/S cell delivers 448 mAh g^{-1} and 400 mAh g^{-1} at 3 C and 5 C, respectively, higher than those of rGO-Li/S (384 and 355 mAh g^{-1}) and bare Li/S (295 and 242 mAh g^{-1}). After cycling at 0.5 C for 300 times, the MG-Li/S cell still delivers larger discharged capacity of 795 mAh g^{-1} with high Coulombic efficiency (Figure S30), and exhibits a higher capacity retention of 54% than those of rGO-Li/S (44%) and bare Li/S cells (only 29%) (Figure 6e, f). In addition, the polarization potential is the lowest in the MG-Li/S cell (188 mV), suggesting improved redox-reaction reversibility benefiting from the lithophilic MXenes and 3D conductive porous scaffold. Nevertheless, all cells showcase rather rapid capacity decay due to the

shuttling effect of lithium polysulfides. We believe the MG-Li/S cell performance can be further improved by modifying the cathode part (*i.e.*, introducing LiPSs chemisorptive sites) and/or the separator (*i.e.*, coating a physical barrier) to suppress the polysulfides diffusion. However, this is beyond the scope of this work.

For the interesting anode performance that endowed by the MG framework, we believe several key factors are playing important roles. First, the 3D lightweight scaffold is suitable for Li-metal melt infusion, increasing the active Li content and minimizing the infinite volume changes of Li anode during stripping and plating process. Second, the interconnected conductive porous structure significantly lowers down the local effective current density to form a uniform Li-ion flux and delays Li dendrites growth rate. Third, the cellular MG scaffold with micrometer scale cavity promotes fast electrolyte uptake and stabilizes the as-formed SEI film. Moreover, the well dispersed lithiophilic MXene nanosheets endow the homogeneous distribution of electric field and Li nucleation sites, thus guarantee the uniform Li plating across the whole framework rather than on the top surface of the electrode. As a result, the formation of Li dendrites and “dead Li” are much suppressed.

CONCLUSIONS

In summary, we successfully develop a 3D highly conductive, chemically lithiophilic, and mechanically robust MG framework as flexible, lightweight and stable Li-molten scaffold for high-performance and dendrite-free Li anode. Owing to the abundant homogeneously dispersed lithiophilic MXene and 3D conductive nanoporous structure in the matrix, the nucleation and growth of metallic Li are well controlled in the 3D MG skeleton. Such a structure design ensures an efficient encapsulation of Li-induced volume change, as well as improves the current density

of the anode electrode. Consequently, the MG achieves 92% of ultrahigh Li content, high Coulombic efficiency of 99%, and a record lifespan of up to 2700 h at high capacity of 5 mA h cm⁻². Impressively, ultrahigh current density of 20 mA cm⁻² and large capacity of 5 mAh cm⁻² are obtained, coupled with long-term cycling stability free of Li dendrite growth. Furthermore, MG-Li anode based full cells exhibit substantially improved cycling stability and rate performance. This strategy sheds light on the reasonable design of ultrahigh capacity and exceptionally stable metallic Li anodes, and is expected to develop of next-generation high-safety and high-energy-density Li metal batteries, such as Li-S, Li-O₂, and solid-state batteries.

METHODS

Preparation of 3D MGO Aerogels. Ti₃C₂T_x MXene was prepared from Ti₃AlC₂ by LiF/HCl etchants previously reported,⁶⁰ and GO was synthesized by the modified Hummer's method.⁶¹ After that, the homogenous solution was obtained by mixing GO (5 mg mL⁻¹) and MXene (10 mg mL⁻¹) solution by sonication for 10 min under the argon flow. The MXene amount was optimized by tuning the mass ratio of GO and MXene from 1:1 to 3:1 and 5:1. Finally, the resulting suspension was freeze-dried for 3 days to obtain 3D MGO aerogels. For comparison, GO aerogels were also prepared without adding MXene while other steps kept unchanged.

Fabrication of MG-Li Anode. First, 3D MGO aerogels were pressed at 10 MPa to form 3D MGO films. Then, MGO films were cut and put into contact with the molten Li in an Ar-filled glovebox with O₂ and H₂O content below 0.1 ppm. The spark reaction occurs within seconds to partially reduce the MGO films into MG films. Subsequently, the MG film was put on the top of the molten Li. Molten Li can steadily climb up and infiltrate the whole inner MG film to afford

the MG-Li electrode (See Movie S1). For comparison, rGO-Li anode was prepared following the above steps except only replacing the MGO film with a GO film.

Material Characterization. The morphology and structure of materials were characterized by SEM (JEOL JSM-7800F), TEM (JEM-2100), AFM (Veeco nanoscope multimode II-D), XPS (Thermo ESCALAB 250Xi equipped with monochromatic Al K α source of 1486.5eV), FTIR (Bruker, Hyperion 3000), XRD (Empyrean with Cu K α radiation in the 2 θ range from 5 to 90°), thermogravimetric analysis (TGA, SDT Q600 V20.9 Build 20), Raman spectroscopy (LabRAM HR 800 Raman spectrometer, 632 nm), Mastersizer 2000 (Malvern Instruments, UK). Nitrogen adsorption and desorption isotherm was carried out to investigate the specific surface area and pore size distribution of the products. Electrical conductivity was measured by a standard four-point probe system (RTS-9).

Electrochemical Measurement. All the cells were assembled with standard CR2025 coin-type cells in an Ar-filled glovebox with O₂ and H₂O content below 0.5 ppm. The electrolytes employed were either 1.0 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in a mixture solution of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, vol. ratio) with 1 wt% LiNO₃ as additive or 1 M lithium hexafluorophosphate (LiPF₆) in 1:1 ethylene carbonate (EC)/diethyl carbonate (DEC), about 40 μ L electrolyte was dropped into each cell, and the polypropylene membrane (Celgard 2700) is used as the separator. MG film, rGO film or planar Cu as the working electrode, Li foil as the counter/reference electrode to evaluate the Coulombic efficiencies. The assembled cells were pre-cycled between 0.01 and 3 V at 100 μ A for five times to stabilize the SEI formation and remove surface contaminations. After that, a certain capacity of Li was deposited onto the current collector and then charged to 1 V (*versus* Li⁺/Li) to strip the Li at certain current density for each cycle on a LAND CT2001A battery system. And symmetric cell

configurations were assembled with MG-Li, rGO-Li or bare Li anodes to evaluate the long-time cycling stability. For the full cells, the working electrode contains 80 wt% of active materials (LTO or S), 10 wt% of carbon black, and 10 wt% of polyvinylidene fluoride with N-methyl-2-pyrrolidone as the solvent, the well-mixed slurry was cast onto carbon-coated Al foil using the doctor blade technique. The cast electrodes were dried under vacuum at 120 °C (LTO) and 55 °C (S) for 12 h. The cathode with LTO loading of $\sim 2.0 \text{ mg cm}^{-2}$ were employed in MG-Li//LTO full cells, using 1.0 M LiPF₆ in EC/DEC (v/v = 1:1) as the electrolyte. The sulfur cathode with sulfur loading of $\sim 1.0 \text{ mg cm}^{-2}$ were employed in Li-S cells, using LiTFSI in DOL/DME (v/v = 1:1) with 2.0% LiNO₃ as electrolyte in Li-S cells, about 20 μL electrolyte was added into each cell. CV curves were carried out on a CHI 760E electrochemical workstation at a scan rate of 0.1 mV s^{-1} . EIS were carried out using a CHI 760E workstation by applying an ac amplitude of 5 mV over the frequency range of 100 kHz to 0.01 Hz.

Computational Simulation. All calculations have been performed with DMol3 package.⁶³ In the framework of DFT, the generalized gradient approximation (GGA) combined with the Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the exchange and correlation potential.⁶⁴ All the atoms of the calculated systems are allowed to fully relax in order to optimize the adsorption geometries. A double-numerical basis with polarization functions (DNP) is utilized to expand the valence electron functions into a set of numerical atomic orbitals, and the DFT semi-core pseudopotential (DSPP) is used when tackling the electron-ion interactions. The k-points mesh in the Monkhorst Pack sampling scheme was set as $1 \times 1 \times 1$.⁶⁵ The Fermi smearing is set to $5.0 \times 10^{-3} \text{ Ha}$ (1 Ha = 27.21 eV). For the convergence criteria, the SCF tolerance used was $1.0 \times 10^{-5} \text{ eV atom}^{-1}$, the maximum force and displacement were set as $5.0 \times 10^{-2} \text{ eV \AA}^{-1}$ and $2.0 \times 10^{-3} \text{ \AA}$, respectively. For the Li ion combined with graphene and MXene, the binding energy (E_a) is

defined as the energy difference between the substrate with Li ion (E_t) and the summation of Li ion (E_1) and substrate system (E_2): $E_a = E_1 + E_2 - E_t$. The migration energy is defined as the change of binding energy when the Li ion migrates along the diffusion path on the substrate surface.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at <http://pubs.acs.org>. Materials characterization, electrochemical characterization, and additional figures, and the table used to performance comparison of our MG-Li anode with the state-of-the-art Li metal composite anodes. (PDF)

AUTHOR INFORMATION

Author Contributions

Z.-S.W. proposed and supervised the overall project. H.D.S. did the fabrication and electrochemical measurement of MG-Li. H.D.S. and Z.S.W. analyzed the data. C.F.Z. prepared the MXene nanosheets. Y.F.D. and P.C.W. participated in the structural characterization of the related materials. P.F.L. did the DFT calculation. H.D.S., C.F.Z. and Z.-S.W. co-wrote this paper. All authors commented and have given approval to the final version of the manuscript. H.D.S. and C.F.Z. contributed equally to this work.

Corresponding Author

*E-mail (Z.-S.Wu): wuzs@dicp.ac.cn

ACKNOWLEDGMENT

This work was financially supported by the National Key R&D Program of China (Grants 2016YBF0100100, and 2016YFA0200200), National Natural Science Foundation of China (Grants 51572259, 51872283, and 21805273), LiaoNing Revitalization Talents Program (Grant XLYC1807153), Natural Science Foundation of Liaoning Province (Grant 20180510038), DICP (DICP ZZBS201708, DICP ZZBS201802), DICP&QIBEBT (Grant DICP&QIBEBT UN201702), Dalian National Laboratory For Clean Energy (DNL), CAS, DNL Cooperation Fund, CAS (DNL180310, DNL180308, DNL201912, and DNL201915), China Postdoctoral Science Foundation (Grant 2018M631831, 2018M633497), and the Fundamental Research Funds for the Central Universities of China (Grant N180503012). Dedicated to the 70th anniversary of Dalian Institute of Chemical Physics, CAS.

REFERENCES

- (1) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, *117*, 10403-10473.
- (2) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J.-M. Li-O₂ and Li-S Batteries with High Energy Storage. *Nat. Mater.* **2012**, *11*, 19.
- (3) Kang, K.; Meng, Y. S.; Bréger, J.; Grey, C. P.; Ceder, G. Electrodes with High Power and High Capacity for Rechargeable Lithium Batteries. *Science* **2006**, *311*, 977-980.
- (4) Albertus, P.; Babinec, S.; Litzelman, S.; Newman, A. Status and Challenges in Enabling the Lithium Metal Electrode for High-Energy and Low-Cost Rechargeable Batteries. *Nat. Energy*

2018, 3, 16.

(5) Lin, D.; Liu, Y.; Cui, Y. Reviving the Lithium Metal Anode for High-Energy Batteries. *Nat. Nanotechnol.* **2017**, *12*, 194.

(6) Shen, X.; Liu, H.; Cheng, X.-B.; Yan, C.; Huang, J.-Q. Beyond Lithium Ion Batteries: Higher Energy Density Battery Systems Based on Lithium Metal Anodes. *Energy Storage Mater.* **2018**, *12*, 161-175.

(7) Xu, W.; Wang, J. L.; Ding, F.; Chen, X. L.; Nasybutin, E.; Zhang, Y. H.; Zhang, J. G. Lithium Metal Anodes for Rechargeable Batteries. *Energy Environ. Sci.* **2014**, *7*, 513-537.

(8) Pang, Q.; Liang, X.; Kwok, C. Y.; Nazar, L. F. Advances in Lithium-Sulfur Batteries Based on Multifunctional Cathodes and Electrolytes. *Nat. Energy* **2016**, *1*, 16132.

(9) Peng, H.-J.; Huang, J.-Q.; Zhang, Q. A Review of Flexible Lithium-Sulfur and Analogous Alkali Metal-Chalcogen Rechargeable Batteries. *Chem. Soc. Rev.* **2017**, *46*, 5237-5288.

(10) Agostini, M.; Scrosati, B.; Hassoun, J. An Advanced Lithium-Ion Sulfur Battery for High Energy Storage. *Adv. Energy Mater.* **2015**, *5*, 1500481.

(11) Peng, Z.; Freunberger, S. A.; Chen, Y.; Peter, G. B. A Reversible and Higher-Rate Li-O₂ Battery. *Science* **2012**, *337*, 563-566.

(12) Cheng, X.-B.; Yan, C.; Chen, X.; Guan, C.; Huang, J.-Q.; Peng, H.-J.; Zhang, R.; Yang, S.-T.; Zhang, Q. Implantable Solid Electrolyte Interphase in Lithium-Metal Batteries. *Chem* **2017**, *2*, 258-270.

(13) Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, *117*, 10403-10473.

(14) Peng, L.; Zhu, Y.; Chen, D.; Ruoff, R. S.; Yu, G. Two-Dimensional Materials for Beyond-Lithium-Ion Batteries. *Adv. Energy Mater.* **2016**, *6*, 1600025.

- (15) Ding, F.; Xu, W.; Graff, G. L.; Zhang, J.; Sushko, M. L.; Chen, X.; Shao, Y.; Engelhard, M. H.; Nie, Z.; Xiao, J.; Liu, X.; Sushko, P. V.; Liu, J.; Zhang, J. G. Dendrite-Free Lithium Deposition via Self-Healing Electrostatic Shield Mechanism. *J. Am. Chem. Soc.* **2013**, *135*, 4450-4456.
- (16) Lu, D.; Shao, Y.; Lozano, T.; Bennett, W. D.; Graff, G. L.; Polzin, B.; Zhang, J.; Engelhard, M. H.; Saenz, N. T.; Henderson, W. A.; Bhattacharya, P.; Liu, J.; Xiao, J. Failure Mechanism for Fast-Charged Lithium Metal Batteries with Liquid Electrolytes. *Adv. Energy Mater.* **2015**, *5*, 1400993.
- (17) Qiu, F.; Li, X.; Deng, H.; Wang, D.; Mu, X.; He, P.; Zhou, H. A Concentrated Ternary-Salts Electrolyte for High Reversible Li Metal Battery with Slight Excess Li. *Adv. Energy Mater.* **2019**, *9*, 1803372.
- (18) Zheng, J.; Engelhard, M. H.; Mei, D.; Jiao, S.; Polzin, B. J.; Zhang, J.-G.; Xu, W. Electrolyte Additive Enabled Fast Charging and Stable Cycling Lithium Metal Batteries. *Nat. Energy* **2017**, *2*, 17012.
- (19) Li, W. Y.; Yao, H. B.; Yan, K.; Zheng, G. Y.; Liang, Z.; Chiang, Y. M.; Cui, Y. The Synergetic Effect of Lithium Polysulfide and Lithium Nitrate to Prevent Lithium Dendrite Growth. *Nat. Commun.* **2015**, *6*, 7436.
- (20) Zhang, X. Q.; Cheng, X. B.; Chen, X.; Yan, C.; Zhang, Q. Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Lithium Metal Batteries. *Adv. Funct. Mater.* **2017**, *27*, 1605989.
- (21) Liang, X.; Pang, Q.; Kochetkov, I. R.; Sempere, M. S.; Huang, H.; Sun, X.; Nazar, L. F. A Facile Surface Chemistry Route to a Stabilized Lithium Metal Anode. *Nat. Energy* **2017**, *2*, 17119.
- (22) Yan, K.; Lu, Z. D.; Lee, H. W.; Xiong, F.; Hsu, P. C.; Li, Y. Z.; Zhao, J.; Chu, S.; Cui, Y. Selective Deposition and Stable Encapsulation of Lithium through Heterogeneous Seeded Growth. *Nat. Energy* **2016**, *1*, 16010.

- (23) Sun, J.; Zeng, Q.; Lv, R.; Lv, W.; Yang, Q.-H.; Amal, R.; Wang, D.-W. A Li-Ion Sulfur Full Cell with Ambient Resistant Al-Li Alloy Anode. *Energy Storage Mater.* **2018**, *15*, 209-217.
- (24) Ye, H.; Zheng, Z. J.; Yao, H. R.; Liu, S. C.; Zuo, T. T.; Wu, X. W.; Yin, Y. X.; Li, N. W.; Gu, J. J.; Cao, F. F.; Guo, Y. G. Guiding Uniform Li Plating/Stripping *via* Lithium Aluminum Alloying Medium for Long-Life Li Metal Batteries. *Angew. Chem. Int. Ed.* **2019**, *58*, 1094-1099.
- (25) Liang, Z.; Lin, D.; Zhao, J.; Lu, Z.; Liu, Y.; Liu, C.; Lu, Y.; Wang, H.; Yan, K.; Tao, X.; Cui, Y. Composite Lithium Metal Anode by Melt Infusion of Lithium into a 3D Conducting Scaffold with Lithiophilic Coating. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 2862-2867.
- (26) Yan, C.; Cheng, X. B.; Yao, Y. X.; Shen, X.; Li, B. Q.; Li, W. J.; Zhang, R.; Huang, J. Q.; Li, H.; Zhang, Q. An Armored Mixed Conductor Interphase on a Dendrite-Free Lithium-Metal Anode. *Adv. Mater.* **2018**, *30*, 1804461.
- (27) Cha, E.; Patel, M. D.; Park, J.; Hwang, J.; Prasad, V.; Cho, K.; Choi, W. 2D MoS₂ as an Efficient Protective Layer for Lithium Metal Anodes in High-Performance Li-S Batteries. *Nat. Nanotechnol.* **2018**, *13*, 337-344.
- (28) Ye, H.; Xin, S.; Yin, Y. X.; Li, J. Y.; Guo, Y. G.; Wan, L. J. Stable Li Plating/Stripping Electrochemistry Realized by a Hybrid Li Reservoir in Spherical Carbon Granules with 3D Conducting Skeletons. *J. Am. Chem. Soc.* **2017**, *139*, 5916-5922.
- (29) Kong, L.; Zhang, Q. Three-Dimensional Matrix for Lithium Metal Anode for Next-Generation Rechargeable Batteries: Structure Design and Interface Engineering. *J. Energy Chem.* **2019**, *33*, 167-168.
- (30) Yang, C. P.; Yin, Y. X.; Zhang, S. F.; Li, N. W.; Guo, Y. G. Accommodating Lithium into 3D Current Collectors with a Submicron Skeleton Towards Long-Life Lithium Metal Anodes. *Nat. Commun.* **2015**, *6*, 8058.

- (31) Chi, S.-S.; Liu, Y.; Song, W.-L.; Fan, L.-Z.; Zhang, Q. Prestoring Lithium into Stable 3D Nickel Foam Host as Dendrite-Free Lithium Metal Anode. *Adv. Funct. Mater.* **2017**, *27*, 1700348.
- (32) Xu, Y.; Menon, A. S.; Harks, P. P. R. M. L.; Hermes, D. C.; Haverkate, L. A.; Unnikrishnan, S.; Mulder, F. M. Honeycomb-Like Porous 3D Nickel Electrodeposition for Stable Li and Na Metal Anodes. *Energy Storage Mater.* **2018**, *12*, 69-78.
- (33) Liu, Y. Y.; Lin, D. C.; Liang, Z.; Zhao, J.; Yan, K.; Cui, Y. Lithium-Coated Polymeric Matrix as a Minimum Volume-Change and Dendrite-Free Lithium Metal Anode. *Nat. Commun.* **2016**, *7*, 10992.
- (34) Lin, D. C.; Liu, Y. Y.; Liang, Z.; Lee, H. W.; Sun, J.; Wang, H. T.; Yan, K.; Xie, J.; Cui, Y. Layered Reduced Graphene Oxide with Nanoscale Interlayer Gaps as a Stable Host for Lithium Metal Anodes. *Nat. Commun.* **2016**, *11*, 626-632.
- (35) Sun, Z.; Jin, S.; Jin, H.; Du, Z.; Zhu, Y.; Cao, A.; Ji, H.; Wan, L.-J. Robust Expandable Carbon Nanotube Scaffold for Ultrahigh-Capacity Lithium-Metal Anodes. *Adv. Mater.* **2018**, *30*, 1800884.
- (36) Zhang, R.; Li, N. W.; Cheng, X. B.; Yin, Y. X.; Zhang, Q.; Guo, Y.-G. Advanced Micro/Nanostructures for Lithium Metal Anodes. *Adv. Sci.* **2017**, *4*, 1600445.
- (37) Zhu, M.; Li, B.; Li, S.; Du, Z.; Gong, Y.; Yang, S. Dendrite-Free Metallic Lithium in Lithiophilic Carbonized Metal-Organic Frameworks. *Adv. Energy Mater.* **2018**, *8*, 1703505.
- (38) Yu, B.; Tao, T.; Mateti, S.; Lu, S.; Chen, Y. Nanoflake Arrays of Lithiophilic Metal Oxides for the Ultra-Stable Anodes of Lithium-Metal Batteries. *Adv. Funct. Mater.* **2018**, *28*, 1803023.
- (39) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2 . *Adv. Mater.* **2011**, *23*, 4248-4253.
- (40) Dong, Y.; Wu, Z.-S.; Zheng, S.; Wang, X.; Qin, J.; Wang, S.; Shi, X.; Bao, X. Ti_3C_2 MXene-

Derived Sodium/Potassium Titanate Nanoribbons for High-Performance Sodium/Potassium Ion Batteries with Enhanced Capacities. *ACS Nano* **2017**, 11, 4792-4800.

(41) Zhang, X.; Lv, R.; Wang, A.; Guo, W.; Liu, X.; Luo, J. MXene Aerogel Scaffolds for High Rate Lithium Metal Anodes. *Angew. Chem. Int. Ed.* **2018**, 57, 15028-15033.

(42) Li, B.; Zhang, D.; Liu, Y.; Yu, Y.; Li, S.; Yang, S. Flexible Ti_3C_2 MXene-Lithium Film with Lamellar Structure for Ultrastable Metallic Lithium Anodes. *Nano Energy* **2017**, 39, 654-661.

(43) Zhang, C. J.; Kremer, M. P.; Seral-Ascaso, A.; Park, S.-H.; McEvoy, N.; Anasori, B.; Gogotsi, Y.; Nicolosi, V. Stamping of Flexible, Coplanar Micro-Supercapacitors Using MXene Inks. *Adv. Funct. Mater.* **2018**, 28, 1705506.

(44) Zhang, C. J.; McKeon, L.; Kremer, M. P.; Park, S. H.; Ronan, O.; Seral-Ascaso, A.; Barwich, S.; Coileain, C. O.; McEvoy, N.; Nerl, H. C.; Anasori, B.; Coleman, J. N.; Gogotsi, Y.; Nicolosi, V. Additive-Free MXene Inks and Direct Printing of Micro-Supercapacitors. *Nat. Commun.* **2019**, 10, 1795.

(45) Yue, Y.; Liu, N.; Ma, Y.; Wang, S.; Liu, W.; Luo, C.; Zhang, H.; Cheng, F.; Rao, J.; Hu, X.; Su, J.; Gao, Y. Highly Self-Healable 3D Microsupercapacitor with MXene-Graphene Composite Aerogel. *ACS Nano* **2018**, 12, 4224-4232.

(46) Yan, J.; Ren, C. E.; Maleski, K.; Hatter, C. B.; Anasori, B.; Urbankowski, P.; Sarycheva, A.; Gogotsi, Y. Flexible MXene/Graphene Films for Ultrafast Supercapacitors with Outstanding Volumetric Capacitance. *Adv. Funct. Mater.* **2017**, 27, 1701264.

(47) Huang, G.; Han, J.; Zhang, F.; Wang, Z.; Kashani, H.; Watanabe, K.; Chen, M. Lithiophilic 3D Nanoporous Nitrogen-Doped Graphene for Dendrite-Free and Ultrahigh-Rate Lithium-Metal Anodes. *Adv. Mater.* **2019**, 31, 1805334.

(48) Deng, W.; Zhou, X.; Fang, Q.; Liu, Z. Microscale Lithium Metal Stored inside Cellular

Graphene Scaffold toward Advanced Metallic Lithium Anodes. *Adv. Energy Mater.* **2018**, *8*, 1703152.

(49) Ma, Y.; Yue, Y.; Zhang, H.; Cheng, F.; Zhao, W.; Rao, J.; Luo, S.; Wang, J.; Jiang, X.; Liu, Z.; Liu, N.; Gao, Y. 3D Synergistical MXene/Reduced Graphene Oxide Aerogel for a Piezoresistive Sensor. *ACS Nano* **2018**, *12*, 3209-3216.

(50) Shang, T.; Lin, Z.; Qi, C.; Liu, X.; Li, P.; Tao, Y.; Wu, Z.; Li, D.; Simon, P.; Yang, Q. H. 3D Macroscopic Architectures from Self-Assembled MXene Hydrogels. *Adv. Funct. Mater.* **2019**, *29*, 1903960.

(51) Li, H. Y.; Hou, Y.; Wang, F. X.; Lohe, M. R.; Zhuang, X. D.; Niu, L.; Feng, X. L. Flexible All-Solid-State Supercapacitors with High Volumetric Capacitances Boosted by Solution Processable MXene and Electrochemically Exfoliated Graphene. *Adv. Energy Mater.* **2017**, *7*, 1601847.

(52) Ghidui, M.; Halim, J.; Kota, S.; Bish, D.; Gogotsi, Y.; Barsoum, M. W. Ion-Exchange and Cation Solvation Reactions in Ti_3C_2 MXene. *Chem. Mater.* **2016**, *28*, 3507-3514.

(53) Peng, H. J.; Huang, J. Q.; Zhang, Q. A Review of Flexible Lithium-Sulfur and Analogous Alkali Metal-Chalcogen Rechargeable Batteries. *Chem. Soc. Rev.* **2017**, *46*, 5237-5288.

(54) Pu, J.; Li, J.; Shen, Z.; Zhong, C.; Liu, J.; Ma, H.; Zhu, J.; Zhang, H.; Braun, P. V. Interlayer Lithium Plating in Au Nanoparticles Pillared Reduced Graphene Oxide for Lithium Metal Anodes. *Adv. Funct. Mater.* **2018**, *28*, 1804133.

(55) Hafez, A. M.; Jiao, Y.; Shi, J.; Ma, Y.; Cao, D.; Liu, Y.; Zhu, H. Stable Metal Anode Enabled by Porous Lithium Foam with Superior Ion Accessibility. *Adv. Mater.* **2018**, *30*, 1802156.

(56) Shi, H.; Dong, Y.; Zhou, F.; Chen, J.; Wu, Z.-S. 2D Hybrid Interlayer of Electrochemically Exfoliated Graphene and $\text{Co}(\text{OH})_2$ Nanosheet as a Bi-Functionalized Polysulfide Barrier for High-

Performance Lithium-Sulfur Batteries. *J. Phys.: Energy* **2018**, *1*, 015002.

(57) Zuo, T. T.; Wu, X. W.; Yang, C. P.; Yin, Y. X.; Ye, H.; Li, N. W.; Guo, Y. G. Graphitized Carbon Fibers as Multifunctional 3D Current Collectors for High Areal Capacity Li Anodes. *Adv. Mater.* **2017**, *29*, 1700389.

(58) Wang, H.; Lin, D.; Xie, J.; Liu, Y.; Chen, H.; Li, Y.; Xu, J.; Zhou, G.; Zhang, Z.; Pei, A.; Zhu, Y.; Liu, K.; Wang, K.; Cui, Y. An Interconnected Channel-Like Framework as Host for Lithium Metal Composite Anodes. *Adv. Energy Mater.* **2019**, *9*, 1802720.

(59) Tikekar, M. D.; Choudhury, S.; Tu, Z. Y.; Archer, L. A. Design Principles for Electrolytes and Interfaces for Stable Lithium-Metal Batteries. *Nat. Energy* **2016**, *1*, 1-7.

(60) Zhao, M. Q.; Ren, C. E.; Ling, Z.; Lukatskaya, M. R.; Zhang, C.; Van Aken, K. L.; Barsoum, M. W.; Gogotsi, Y. Flexible MXene/Carbon Nanotube Composite Paper with High Volumetric Capacitance. *Adv. Mater.* **2015**, *27*, 339-345.

(61) Eda, G.; Fanchini, G.; Chhowalla, M. Large-Area Ultrathin Films of Reduced Graphene Oxide as a Transparent and Flexible Electronic Material. *Nat. Nanotechnol.* **2008**, *3*, 270-274.

(62) Delley, B. From Molecules to Solids with the DMol³ Approach. *J. Chem. Phys.* **2000**, *113*, 7756-7764.

(63) White, J. A.; Bird, D. M. Implementation of Gradient-Corrected Exchange-Correlation Potentials in Car-Parrinello Total-Energy Calculations. *Phys. Rev. B* **1994**, *50*, 4954.

(64) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(65) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188.

Figures and Figure Captions

Figure 1. Fabrication and characterization of 3D MG-Li anode. (a) Schematic illustration of the fabrication process of 3D MG-Li anode and corresponding photographs of MGO film, MG film and MG-Li anode. (b, c) AFM images and height profiles of (b) MXene and (c) GO nanosheets. (d) SEM image of MG film. Inset is the photograph of the bent MG film. (e) EDX elemental mapping of carbon (red), titanium (green) and fluorine (blue). (f, g) Raman spectra of (f) MXene film, MG aerogels and (g) rGO, MG aerogels. (h) XPS full spectra of MXene and MG aerogels. (i) N₂ adsorption-desorption isotherm of MG film. Inset is the plot of pore size distribution. (j) Photographs (top) and corresponding cross-section SEM image (bottom) of MG-Li anode.

Figure 2. Mechanism illustration of MG film for Li deposition. (a) Binding energy of a Li atom with graphene and MXene. (b) The deformation charge density at a Li atom adsorption site of graphene and MXene. (c) Migration paths and (d) corresponding diffusion barrier profile for Li diffusion on MXene. (e) Electrical conductivity of MG and pure rGO electrode. (f) Photograph and (g) top SEM images showing nonuniform Li deposition on rGO and MXene guided uniform plating on MG electrode (1 mAh cm^{-2}). MXene layer is deposited on the upper half rGO electrode. (h) Schematic illustrating the mechanism for MG and pure rGO electrodes during Li plating/stripping process. (i) Schematics of Li adatom on Li surface with and without electrolytes. The white and yellow areas represent vacuum and electrolyte, respectively. (j, k) Contact angle of an organic electrolyte drop on (j) MG-Li anode and (k) bare Li anode at initial state (top) or 1 min later (bottom).

Figure 3. Coulombic efficiencies of MG, rGO and Cu electrodes. (a) Coulombic efficiencies of the MG electrodes with different mass ratio of GO and MXene, and pure GO electrode under deposition capacity of 0.5 mAh cm⁻² at 0.5 mA cm⁻². (b, c) Coulombic efficiencies of MG, rGO, and Cu foil at current density of (b) 0.5 mA cm⁻² and (c) 1 mA cm⁻² with the capacity of 2 mAh cm⁻². (d) Coulombic efficiencies of MG and Cu electrodes with increasing current densities from 0.25 to 2.5 mA cm⁻². Li was plated for 1 h at each cycle with a certain current density and then stripped away up to 1.0 V. (e) Long-life Coulombic efficiencies of MG electrode at current density of 0.5 mA cm⁻² with Li deposition amount of 5 mAh cm⁻² for 2700 h. (f) Enlarged plating-stripping curves of MG, rGO, and Cu foil electrodes at 0.5 mA cm⁻² for 2 mAh cm⁻². (g) Nyquist plots of MG, rGO, and Cu foil electrodes at pristine cycles. Inset is the relationship between Z' and square root of the frequency ($\omega^{-1/2}$) in the low-frequency region.

Figure 4. Electrochemical performance of symmetric cells based on MG-Li, rGO-Li and bare Li electrodes, respectively. (a) Galvanostatic cycling of symmetric cells based on MG-Li, rGO-Li and bare Li electrodes with current density of 3 mA cm^{-2} under stripping/plating capacity of 1 mAh cm^{-2} . Inset is corresponding detailed voltage profiles of the 100th, 300th and 700th cycles, respectively. (b) High current density cycling of symmetric cells based on MG-Li, rGO-Li and bare Li electrodes with a stripping/plating capacity of 1 mAh cm^{-2} . (c) Galvanostatic cycling of MG-Li symmetric cell obtained at ultrahigh current density of 20 mA cm^{-2} under higher capacity of 5 mAh cm^{-2} . (d) Rate performance of symmetric cells based on the MG-Li, rGO-Li and bare Li electrodes, respectively. (e) Nyquist plots of the symmetric cells before cycles. (f) Full Li stripping curve of the MG-Li electrode to 0.5 V versus Li^+/Li . (g) Comparison of gravimetric capacity vs current density and cycle time of the MG-Li anode with currently reported high gravimetric capacity Li composite anodes.

Figure 5. Morphologies of Li electrodeposition on MG-Li and bare Li anodes under different stages. (a) Voltage profiles of a typical Li-stripping-plating process at current density of 2 mA cm⁻² with the capacity of 10 mAh cm⁻² for MG-Li and Li anodes, and (b) corresponding thickness at various stages of cycling. #1 corresponds to the stage before cycling, #2 stands for the stage after 50% Li extraction, and #3 represents the stage after Li plating back. (c, d) Cross-section SEM images showing the volume fluctuation and shape change of (c) MG-Li and (d) bare Li anode at various stages of cycling #1, #2 and #3. Insets are top-view SEM images. (e) Schematic illustration of the microscale Li plating and stripping in 3D MG-Li (top) and bulk Li anode (bottom).

Figure 6. Electrochemical performance of full cells based on MG-Li, rGO-Li and bare Li anode paired with LTO or pure S cathode. (a) Galvanostatic charge and discharge curves obtained at different cycles, (b) cycling stability for 450 cycles tested at 1.0 C (1.0 C = 175 mAh g⁻¹ for LTO anode), and (c) rate performance of MG-Li/LTO, rGO-Li/LTO and bare Li/LTO full cells. (d) Rate capability, (e) galvanostatic charge and discharge curves obtained at first and 300th cycles, and (f) cycling stability for 300 cycles tested at 0.5 C (1.0 C = 1675 mAh g⁻¹ for S cathode) of MG-Li/S, rGO-Li/S and bare Li/S full cells.

Table of Contents

A conductive and lithiophilic 3D MXene/graphene framework is demonstrated for dendrite-free Li scaffold. The 3D MXene/graphene scaffold showcases an ultrahigh Li content, high Coulombic efficiency, and a record lifespan of up to 2700 h. The as-formed MXene/graphene-Li anode demonstrates improved rate capability and cyclability in the as-assembled full cells, showing promising applications for long lifetime, high-energy-density batteries.