Supporting Information

Lithiophilic Three-Dimensional Porous Ti₃C₂T_X-rGO Membrane as a Stable Scaffold for Safe Alkali Metal (Li or Na) Anodes

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reference	0.5 mA cm⁻²	1.0 mA cm⁻²	3.0 mA cm⁻²	5.0 mA cm ⁻²
This work	2400 h	1400 h	800 h	300 h
	(100 days)	(58 days)	(33 days)	(12 days)
1		1400 h		120 h
2		222.2 h	69.4 h	
3	900 h			
4		400 h		
5	1200 h	200 h	91.6 h	
6	852 h	330 h	150 h	
7	500 h			
8	800 h	400 h	133.3 h	
9	800 h	400 h	66.7 h	
9			600 h	
10	2100 h			
11		200 h	66.6 h	40 h
12	2000 h	1000 h	250 h	
13	2480 h (8 mAh cm ⁻²)			650 h
14		216 h	70 h	40 h

Table S1. Cycle times of different current densities for metal Li at 1 mAh cm⁻².

Table S2. Cycling performance at different current densities and capacities for metal

 Na.

reference	Current density (mA cm ⁻²)	Capacity (mAh cm ⁻²)	Cycle number	Cycling Time (h)
This work	0.5	1	500	2000
(NaClO4 III EC/DEC)	1	1	600	1200
	3	1	750	500
15 (porous Al, NaClO4 in EC/DEC)	0.25	0.0625	1200	600
15 (porous Al, NaPF ₆	0.5	0.25	1000	1000
in diglyme)	0.5	1	88	352
16 (Na@rGO, NaPF ₆ in diglyme)	1	1	300	600
16 (Na@rGO, NaCF3SO3 in	3	3	300	300
diglyme)	5	5	300	300
	0.5	1	750	3000
17 (Cu NW-Cu	1	2	350	1400
NaPF ₆ in diglyme)	1	4,8,10,12	172,85,60 ,50	1380,1350,1 190,1170
18 (Na-CF, NaClO ₄ in EC/DEC)	0.5	1	150	300



Figure S1. Determination of surface functional groups by XPS test. ¹⁹⁻²¹The Ti₃C₂T_x after fading reaction written as Ti₃C₂ here. (a) Ti 2p of Ti₃C₂T_x film and (b) C 1s of GO film. After 350 °C reduction (in an Ar-filled glove box), they become (c) Ti 2p of Ti₃C₂ film and (d) C 1s of rGO film. Pie chart of atomic ratio statistics, (e) Ti₃C₂T_x, (f) GO, (g) Ti₃C₂, (h) rGO. From the left side images, we can obvious the surface functional groups on Ti₃C₂T_x and Ti₃C₂are mainly -F, -O and -OH, in addition, F atom slightly reduced and O atom slightly increased due to the formation of less TiO₂ during the high-temperature reduction. Conversely, during the process of GO becoming rGO, the oxygen-containing functional groups are largely lost. Finally, the surface of rGO is mainly C ring, -O and -OH.



Figure S2. The adsorption energy and calculation model of pure rGO and single functional group adsorbing a single Li or Na base on First-principles and Bloch space infinite loop model. (a) The crystal structures of pure rGO, (a') adsorption Li and (a") Na on pure rGO. The absorption energies are the positive number, indicating that graphene repels Li and Na. (b) The crystal structures of rGO adsorption O, (b') adsorption Li and (b") Na on O of rGO. O atoms are bridged to rGO in the form of valence bonds. When Li or Na is close to O, one C-O bond is broken to form C-O-Li/Na. During this process, graphene will form delocalized π bonds to maintain the plane. ²² (c) The crystal structures of rGO adsorption Li and (c") Na on OH (has nothing to do with graphene). Since the absorption energy of C-OH (-0.951 eV) is very small, when Li or Na is close to OH, it will be taken away by Li or Na and form a free Li/Na-OH. The free Li/Na-OH tends to agglomerate together, and when Li or Na is stripped, unstable OH groups may aggregate or accumulate on defects or continue to liberate on graphene. In the process of continuous plating/stripping, the deposition site is not fixed so that the reaction is not uniform and reversible.



Figure S3. The adsorption energy and calculation model of many functional groups adsorbing a single Li or Na base on First-principles and Bloch space infinite loop model. (a) The crystal structures of $Ti_3C_2T_x$ adsorption many F atoms, (a') adsorption Li and (a") Na on many F atoms of $Ti_3C_2T_x$. Different from Figure 2 (b"), the F-Na bonds is become mixed covalent/ionic bonds from electrostatic adsorption. (b) The crystal structures of $Ti_3C_2T_x$ adsorption Li and (b") Na on many O atoms of $Ti_3C_2T_x$. (c) The crystal structures of $Ti_3C_2T_x$ adsorption OH groups, (c') adsorption Li and (c") Na on many OH groups of $Ti_3C_2T_x$. The same thing with Figure 2 (d") is that OH groups are repellent to Na and cannot form a bond chain. However, in the adsorption of OH on Li, due to the strong adsorption capacity of multiple O atoms, OH-Li bonds can be formed, but the energy deficiency is positive, which means the system is unstable and still has no adsorption.



Figure S4. (a) Statistics on the atom mass (non-material quality) fraction of each part in the Ti₃C₂T_x-rGO composite material (the striped part is rGO), and (b) the adsorption energy statistics of the main components in the Ti₃C₂T_x-rGO composite film. In the Ti₃C₂T_x-GO film, the mass ratio of Ti₃C₂T_x is 70 %. Combined with the atomic ratio in Fig. S1 and the atomic mass, we can calculate the mass ratio of each part in the Ti₃C₂T_x-rGO film. It can be seen from the pie chart that the beneficial functional groups (O and F of Ti₃C₂T_x) account for most of the surface functional groups. It is worth noting that although a small amount of TiO₂ is present, it is capable of intercalating Li or Na, which is also very advantageous for inducing uniform deposition. In contrast, the proportion of O of rGO is 3 %, which contains a lot of useless and harmful OH functional groups, and there is a large amount of pure graphene surface, which is no adsorption energy for Li or Na. Combined with the adsorption energy and contents of each part, it can be seen that Ti₃C₂T_x in the Ti₃C₂T_x-rGO film



Figure S5. Schematic diagram of MXene-Ti₃C₂T_x preparation from MAX-Ti₃AlC₂.



Figure S6. XRD of the transformation from Ti_3AlC_2 to multilayer $Ti_3C_2T_x$ to less-layer $Ti_3C_2T_x$.



Figure S7. The changes of pure $Ti_3C_2T_x$ films in the experiment. The fade reaction occurred when the $Ti_3C_2T_x$ films touched the hot table. The $Ti_3C_2T_x$ films still maintained the complete shape and better mechanical properties but some blisters. The layer spacing had no change before and after fade reaction from the SEM. When one side of the $Ti_3C_2T_x$ films touched molten metal lithium, metallic lithium could quickly blend into the surface of the $Ti_3C_2T_x$ films, but it was difficult to wet the entire film, after ~2 mins, the color of $Ti_3C_2T_x$ film became darker and a small amount of Li was wrapped on each layer $Ti_3C_2T_x$.



Figure S8. The changes of pure GO films in the experiment. The spark reaction occurred when the GO films touched the hot table. The rGO films could not maintain a good film shape and had poor mechanical properties.



Figure S9. The characteristic of Ti₃C₂T_x-rGO film (9:1 for Ti₃C₂T_x: GO). (a) SEM; (b) specific capacity.



Figure S10. The mechanical stability of $Ti_3C_2T_x$ -rGO films of different ratios. For 5:5, 3:7 and 1:9 ($Ti_3C_2T_x$: GO), the violent spark reaction during the interlayer would make the $Ti_3C_2T_x$ -rGO membranes fragile. When the films contact the molten metal in a lateral manner, it was difficult to separate therefrom due to the intimate bonding force from Li and Li.



Figure S11. The low-magnification cross-section SEM images of the complex film before and after the fade reaction. (a) Ti₃C₂T_x-GO film of tightly stacked. (b) Ti₃C₂T_x-rGO film of multi-aperture.



Figure S12. The surface SEM image of the complex Li-Ti₃C₂T_x-rGO film.



Figure S13. The surface SEM image of the complex Na-Ti₃C₂T_x-rGO film.



Figure S14. The cycling stability comparison of Li-Ti₃C₂T_x-rGO film and bare-Li at a current density of 0.5 mA cm⁻² (1 mAh cm⁻²). The initial average overvoltage of the Li-Ti₃C₂T_x-rGO electrode is 35 mV and the average overvoltage drops to 28 mV after 1200 h and after 2000 h the average overvoltage is just 36 mV. The initial overvoltage of the bare-Li electrode is over 200 mV and the overvoltage over 1.5 V at less than 1200 h.



Figure S15. Schematic diagram of Li-Li bonds (a) on the $Ti_3C_2T_x$ and (b) bare metal Li.



Figure S16. The EIS curves of the Li-Ti₃C₂T_x-rGO film in different states.



Figure S17. The cycling stability comparison of Li-Ti₃C₂T_x-rGO film and bare-Li at a current density of 3.0 mA cm⁻² (1 mAh cm⁻²). The initial average overvoltage of the Li-Ti₃C₂T_x-rGO electrode is 65 mV and the average overvoltage drops to 60 mV after 500 h. The initial overvoltage of the bare-Li electrode is over 200 mV and the overvoltage is over 2 V at less than 300 h.



Figure S18. Cycling performance of Li-Ti₃C₂T_x symmetrical cell at 5 mA



cm⁻² (1 mA h cm⁻²).

Figure S19. (a) Cycling performance of Li-rGO symmetrical cell at 5 mA cm⁻² (1 mA h cm⁻²); (b) and (c) SEM of Li-rGO.

Note, in order to ensure mechanical properties and unify the experimental conditions as much as possible, a mild reduction process was performed as shown in Experimental Section.



Figure S20. The initial voltage curves and surface morphologies of the Li-Ti₃C₂T_x-rGO film and bare-Li after 3 cycles at different current densities (0.5, 1.0, and 3.0 mA·cm⁻²) and after different cycles (1, 3, and 10 cycles) at 1 mA·cm⁻².



Figure S21. The surface SEM image of the Li-Ti₃C₂T_x-rGO film after cycling for 800 h at a current density of 1.0 mA cm⁻² (1 mAh cm⁻²). There is very smooth and no lithium dendrite.



Figure S22. The SEM images of Li-Ti₃C₂T_x-rGO film after cycling for 100 h at a current density of 5.0 mA cm⁻² (1 mAh cm⁻²). (a) SEI generate on the surface, (b) a low-magnification cross-section SEM image and (c) a high-magnification cross-section SEM image. The layer spacing has been filled by SEI but still can see the layered structure.



Figure S23. The SEM images of Li-Ti₃C₂T_x-rGO film after cycling for 200 h at a current density of 5.0 mA cm⁻² (1 mAh cm⁻²). (a) SEI broke on the surface. (b) A low-magnification cross-section SEM image and (c) a high-magnification cross-section SEM image. Compared to the surface, SEI is more likely to be born between layers (the layer spacing has been filled by SEI without any layered structure).



Figure S24. XPS tests for SEI layers of (a) Li-Ti₃C₂T_x-rGO and (b) bare Li.



Figure S25. The specific capacity test of the Li-Ti₃C₂T_x-rGO film. Constant current charging to 1.5 V at 1 mA cm⁻².



Figure 26. Rate performance of Li-Ti₃C₂T_x-rGO films with different thicknesses. (a) 2.0 mg cm⁻², (b) 1.6 mg cm⁻², and (c) 1.2 mg cm⁻² for Ti₃C₂T_x-GO films.



Figure 27. SEM images of Ti₃C₂T_x-rGO films with different thicknesses. Ti₃C₂T_x-rGO of 124, 49, and 20 μ m corresponding to Ti₃C₂T_x-GO of 2.0 mg cm⁻², 1.6 mg cm⁻², and 1.2 mg cm⁻², respectively.



Figure S28. The charge-discharge curves of LFP|Li-Ti₃C₂T_x-rGO film and LFP|bare-Li at the current density of 0.2, 0.5, 1.0, 2.0, 5.0, 10 C.



Figure S29. EIS test for LFP full cells after cycling.



Figure S30. Cycling stability of various Li metal anodes//LTO full cells, with 0.2 C (1 C= 170 mAh g⁻¹) for the first 3 cycles and 0.5 C for later cycles. LTO of High areal capacity (~3 mAh cm⁻²) corresponded to metal Li electrodes of ~10 mAh cm⁻². Since $Ti_3C_2T_x$ could not accommodate a large amount of metal Li, LTO of ~0.8 mAh cm⁻² corresponded to Li-Ti₃C₂T_x electrode of ~3 mAh cm⁻². Cell with Li-Ti₃C₂T_x-rGO electrode started to decay at 59 cycles, Li-rGO at 39 cycles, 50 µm bare-Li at 9 cycles, and Li-Ti₃C₂T_x at 5 cycles.

Note, since LTO itself does not supply Li for cell and it has high Coulombic efficiency, the consumption of Li and the attenuation of battery capacity can be attributed to the loss of the metal Li electrode. The stable cycling cycles presents the Coulombic efficiency of metal Li. Such as, if the Coulombic efficiency of metal Li is 90%, 0.3 mAh cm⁻² (3 mAh cm⁻² × 10 %) Li will be lost every cycle. Therefore, the cell will start to decay at ~23 cycles (0.3 mAh cm⁻² × 23=10–3 mAh cm⁻²).



Figure S31. The cycling stability comparison of Na-Ti₃C₂T_x-rGO film and bare-Li at a current density of 0.5 mA cm⁻² (1 mAh cm⁻²). The initial average overvoltage of the Na-Ti₃C₂T_x-rGO electrode is 38 mV and the average overvoltage drops to 26 mV after 1000 h and after 2000 h the average overvoltage is just 36 mV. The initial overvoltage of the bare-Na electrode is over 200 mV and the bare Na electrode is short-circuited after 200 h of cycling.



Figure S32. The EIS curves of the Na-Ti $_3C_2T_x$ -rGO film at initial and after cycling.



Figure S33. The surface SEM image of the Na-Ti₃C₂T_x-rGO film after cycling for 300 h at a current density of 0.5 mA cm⁻² (1 mAh cm⁻²). There is very smooth and no sodium dendrite.



Figure S34. The SEM images of Na-Ti₃C₂T_x-GO film after cycling for 100 h at a current density of 3.0 mA cm⁻² (1 mAh cm⁻²). (a) A smooth surface, (b) a low-magnification cross-section SEM images and (c) a high-magnification cross-section SEM images. There is no sodium dendrite on the surface but a little dendrite on the interlayer.



Figure S35. The SEM images of Na-Ti₃C₂T_x-rGO film after cycling for 200 h at a current density of 3.0 mA cm⁻² (1 mAh cm⁻²). (a) surface image, (b) a low-magnification cross-section SEM images and (c) a high-magnification cross-section SEM images. Most of the surface of the Na-Ti₃C₂T_x-rGO film remains smooth with a little sodium dendrite. Fortunately, there is a lot of dendrite on the interlayer. This is different from the large number of SEI between the layers of Li-Ti₃C₂T_x-rGO film.

Computational Methods

First-principles calculations were performed in the DFT framework using the Vienna *Ab Initio* simulation package (VASP) ^{23, 24} with the Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA). ^{25, 26} The projector-augmented wave (PAW) ²⁷ voltage was used to describe the interaction between ions and electrons, and its cutoff energy is set to 500 eV. In this model, all atomic movements were allowed until their respective forces were <0.01 eV / and the total energy converges to 10-6 eV. Moreover, the DFT-D2 method was combined to accurately simulate Van der Waals correction.

Experimental Section

Preparation of less-layer $Ti_3C_2T_x$ dispersion liquid and GO nanosheets

Ti₃C₂T_x was obtained by synthetic HF solution. Specifically, 1.5 g of LiF (Alfa Aesar, 98.5%) was dissolved in 20 mL of 9 M HCl. Then 1.0 g of Ti₃AlC₂ (200 mesh, purchased from 11 Technology Co., Ltd.) powders was slowly added into the above mixture solution and kept at 35 °C for 30 h while stirring. The above product was washed with distilled water until neutral, then added 30 ml water, sonicated for 5 min. The upper dispersion was collected and the precipitate was further added 30 ml water and sonicated for 5 min. Repeat 3 times to obtain more Ti₃C₂T_x dispersion liquid. Finally, the less-layer Ti₃C₂T_x dispersion was obtained by a low speed centrifugation process (3000r, 10 mins). The GO nanosheets were obtained by ultrasonic stripping the graphite oxide synthesized by the modified Hummers method. ²⁸

Preparation of the Li- $Ti_3C_2T_x$ films, and Li-rGO films.

Since the compact layer of $Ti_3C_2T_x$ structure could not absorb the molten metal lithium quickly, the Li-Ti₃C₂T_x film was obtained by absorbing it in parallel for 2 mins. For Li-rGO, in order to ensure mechanical properties and unify the experimental conditions as much as possible, we prepared the rGO films through a mild reduction process. First, the GO films touched a hypothermal hot table of 200 °C, with a mild spark reaction occurred, and then, the temperature of hot table was increased to 400 °C slowly. Finally, the Li-rGO film was synthetized by a vertical absorption process for molten Li.

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