Functionalized M₂TiC₂T_x MXenes (M=Cr and Mo; T=O, F, and OH) as High Performance Electrode Materials for Sodium Ion Batteries

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Fig. S1. (a) Side view, (b) Top view of the optimized lattice structures for Mo_2TiC_2 monolayer. The side views of the six possible configurations $Mo_2TiC_2O_2$ monolayers.

In order to study the effects of magnetic arrangements on the stability and sodium adsorption properties of Cr₂TiC₂O₂ and Mo₂TiC₂O₂ systems, the nonmagnetic (NM), ferromagnetic (FM), and anti-ferromagnetism (AFM) states of these systems are considered as shown in Table S1 and Fig. S2. The magnetic arrangements only have neglected effects on the total energy (< 5 m eV for 2×2 supercell) of the $Mo_2TiC_2O_2$ system. However, the relative stability of the $Cr_2TiC_2O_2$ system is greatly affected by the magnetic arrangements. Furthermore, the on-site Coulomb interactions greatly affect the relative stability of Mo₂TiC₂O₂ and Cr₂TiC₂O₂ systems, especially on the Cr₂TiC₂O₂ system as shown in Table S1. Li et al. proved the values of Hubbard U have great influence on magnetic arrangements of the Mo₂TiC₂O₂ system¹, our calculations also show this tendency. The Na_{0.5}Mo₂TiC₂O₂ system shows the FM and NM states under LDA + U and no U corrections calculations, respectively. Fortunately, the Hubbard U and magnetic arrangements both have neglected influence on the relative stability of the Mo₂TiC₂O₂ system. For the Cr₂TiC₂O₂ system, there are large energy difference between NM and other magnetic states under LDA + U calculations, but the total energies of all magnetic states are close without Hubbard U corrections. The energy difference between $Cr_2TiC_2O_2$ and $Na_xCr_2TiC_2O_2$ (x = 0.5, 2, 4) of different magnetic arrangements is relatively close, therefore, it should be a proper approximation use NM state to estimate the electrode performance. Previously, first principles calculations indicate that the Mo₂TiC₂O₂⁻¹ and Cr₂TiC₂O₂⁻² are better to adopt NM state, which will be more consistent with the experimental measurements. Therefore, the NM state is adopted in present study, and the LDA + U approach is used to ensure the accuracy of electronic structures.

Table S1. The total energy of $Cr_2TiC_2O_2$ and $Mo_2TiC_2O_2$ systems with different magnetic arrangements. The most stable system is marked in bold. The AFM configurations are shown in Figure S1.

Systems	LDA+U	NM	FM	AFM-1	AFM-2	AFM-3	AFM-4
Na _{0.5} Mo ₂ TiC ₂ O ₂	Yes	-233.496	-233.500	-233.495	-233.496	-233.496	-233.496
	No	-282.736	-282.734	-282.735	-282.735	-282.736	-282.736
$Cr_2TiC_2O_2$	Yes	-206.997	-211.551	-211.700	-211.620	-210.173	-209.773

	No	-245.031	-244.957	-245.035	-245.032	-245.031	-245.041
N. C. T.C.O.	Yes	-214.683	-218.609	-218.364	-219.480	-219.469	-219.127
$Na_{0.5}C1_2T1C_2O_2$	No	-252.054	-252.072	-252.101	-252.092	-252.072	-252.096
	Yes	-223.405	-226.952	-228.527	-228.750	-225.284	-228.653
$Na_2CI_2IIC_2O_2$	No	-260.338	-260.436	-260.468	-260.473	-260.636	-260.682
	Yes	-230.989	-234.604	-231.805	-231.623	-232.856	-235.249
$\operatorname{Na}_4\operatorname{Cl}_2\operatorname{HC}_2\operatorname{O}_2$	No	-268.127	-268.187	-268.128	-268.127	-268.162	-268.155



Fig. S2. AFM configurations of the $Cr_2TiC_2O_2$ and $Mo_2TiC_2O_2$ systems. (a) AFM-1, (b) AFM-2, (c) AFM-3, (d) AFM-4. The red, brown, light blue, and navy balls denote the oxygen, carbon, Ti, and Cr (Mo) atoms, respectively. The green arrow means the magnetization direction.

The effects of U values on band gaps and distributions of density of states under LDA + U calculations are evaluated as shown in Fig. S3. The studied effective U values of transition metals (Ti, Cr, and Mo) are varied in wide range from 1 to 6 eV. The distributions of valence band of Mo₂TiC₂O₂ are only slightly changed except the small difference on the DOS values. The effective U values have obvious influence on the distributions of conduction band, larger U_{eff} causes larger band gap. However, the band gap difference caused by different U values is smaller than 0.3 eV in studied systems. For the Cr₂TiC₂O₂, larger effects on the distributions of DOS around the Fermi energy level occur comparing the Mo₂TiC₂O₂. The larger U_{eff} (e.g., 5 or 6 eV) will bring sharper peaks just below the Fermi energy level, and the smaller U_{eff} values in Cr₂TiC₂O₂ are only slight affected by the U_{eff} values. Therefore, the U_{eff} values only have small effects on distributions of DOS and band gaps, and the U values of elements are chosen as the same with those in literatures ¹.



Fig. S3. The total DOS of $Mo_2TiC_2O_2$ and $Cr_2TiC_2O_2$ systems. The effects of U values on total density of states of $Mo_2TiC_2O_2$ and $Cr_2TiC_2O_2$ (color version).

The densities of states (DOS) of non-magnetic (NM) M_2TiC_2 (M=Cr, Mo) and $M_2TiC_2T_2$ (T=F, O) were analyzed and shown in Fig. S4. The M_2TiC_2 and $M_2TiC_2T_2$ exhibit metallic-like character. However, the antiferromagnetic (AFM) $M_2TiC_2F_2$ and $M_2TiC_2(OH)_2$ were found to be semiconductors^{2, 3}. The ferromagnetic (FM) Cr₂TiC₂ is discovered to be intrinsic semiconducting material with a band gap of 0.4 eV⁴. The $Mo_2TiC_2O_2$ and $Cr_2TiC_2O_2$ exhibit metallic-like character, which is consistent with previous research conclusions^{1, 2}.



Fig. S4. The total densities of states of (a) Cr_2TiC_2 and $Cr_2TiC_2T_2$, (b) Mo_2TiC_2 and $Mo_2TiC_2T_2$.

Fig. S5 shows the effects of vacuum thickness on the stability of Cr₂TiC₂O₂ and Mo₂TiC₂O₂ systems, which will help us to understand the reactions between slabs. For none sodium adsorbed systems, the total energy will be decrease sharply when the lattice parameter of c is shorter than 1 nm due to the repulsive interactions between oxygen terminations. The Na₂Cr₈Ti₄C₈O₈ and Na₂Mo₈Ti₄C₈O₈ systems show similar characteristics due to the few coverage of sodium, and the oxygen terminations repulsions are still strong. However, when the both surfaces are covered by sodium atoms, e.g., Na₂Cr₂TiC₂O₂ and Na₄Cr₂TiC₂O₂ systems, the slabs will prefer to approach each other due to the attractions between sodium atoms. Therefore, the 2D configurations may transform to 3D configurations under high coverage of sodium ions and the large interval between the 2D slabs (the *c*-lattice parameters of MXenes ≥ 25 Å), the 2D→3D transformations are not considered in present work, they will be studied in further study.



Fig. S5. The relationship between total energy and the length of lattice parameters of *c*. (a) $Cr_2TiC_2O_2$ and $Mo_2TiC_2O_2$, (b) $Na_2Cr_8Ti_4C_8O_8$ and $Na_2Mo_8Ti_4C_8O_8$, (c) $Na_2Cr_2TiC_2O_2$ and $Na_2Mo_2TiC_2O_2$, (d) $Na_4Cr_2TiC_2O_2$ and $Na_4Mo_2TiC_2O_2$.

Table S2. The structure parameters (Å) of the six possible configurations of $M_2 TiC_2 T_2$ (M= Cr/Mo, T = O/F/OH).

materials	Ι	II	III	IV	V	VI
$Cr_2TiC_2F_2$	2.97	2.94	2.92	2.94	3.07	3.05
Cr ₂ TiC ₂ O ₂	2.92	2.88	2.84	2.92	3.11	3.01
Cr ₂ TiC ₂ (OH) ₂	2.99	2.96	2.94	2.97	3.09	3.07
$Mo_2TiC_2F_2$	3.02	3.02	3.00	3.03	3.15	3.18
Mo ₂ TiC ₂ O ₂	3.06	3.01	2.97	3.04	3.23	3.13
Mo ₂ TiC ₂ (OH) ₂	3.05	3.06	3.03	3.05	3.12	3.05

Table S3. The lattice parameters (a-LP in (Å)) of magnetic and non-magnetic MXenes materials.

material	a-LP (non-magnetic)	a-LP (magnetic)
Cr ₂ TiC ₂	2.96	3.13
$Cr_2TiC_2F_2$	2.92	3.05

Cr ₂ TiC ₂ O ₂	2.84	2.98
Cr ₂ TiC ₂ (OH) ₂	2.94	3.07
Mo ₂ TiC ₂	2.99	2.99
Mo ₂ TiC ₂ F ₂	3.01	3.06
Mo ₂ TiC ₂ O ₂	2.97	2.97
Mo ₂ TiC ₂ (OH) ₂	3.03	3.05



Fig. S6. The most stable structures for (a) $Mo_4Ti_2C_4F_4$, (b) $Mo_4Ti_2C_4O_4$ and (c) $Mo_4Ti_2C_4(OH)_4$, and the definition of interlayer spacing (d) used in this work.

Materials	d (monolayer)	<i>d</i> (bilayer)
Cr ₂ TiC ₂	19.97	2.21
$Cr_2TiC_2F_2$	18.90	3.31
Cr ₂ TiC ₂ O ₂	18.89	3.12
Cr ₂ TiC ₂ (OH) ₂	16.59	2.50
Mo ₂ TiC ₂	20.56	2.59
$Mo_2TiC_2F_2$	17.94	3.03
Mo ₂ TiC ₂ O ₂	16.70	3.27
Mo ₂ TiC ₂ (OH) ₂	15.51	2.38

Table S4. The interlayer spacing (d(Å)) of monolayer and bilayer M₂TiC₂T_x.

The adsorption energy (E_{ad}) of T-groups on bare Mxenes was estimated via the definition as below⁵:

$$E_{ad} = \frac{1}{x} \left[E_{M_2 T i C_2 T_x} - \left(E_{M_2 T i C_2} + \frac{x}{2} E_{T_2} \right) \right]$$
(S1)

where T represents F, O or OH groups, and E_{F_2} and E_{O_2} are the energy of F₂ and O₂ in the gas phase, respectively. The $E_{(OH)_2}$ means the energy of two OH group. The $E_{M_2TiC_2T_x}$ and $E_{M_2TiC_2}$ are the total energy of the M₂TiC₂T_x and M₂TiC₂, respectively.

Table S5. The adsorption energy (E_{ad} (eV)) of T-groups on M₂TiC₂ monolayer and M₄Ti₂C₄ bilayer.

Materials	$M_2 TiC_2 (E_{ad})$	$M_4Ti_2C_4$ (E_{ad})
$Cr_2TiC_2F_2$	-3.704	-3.214
Cr ₂ TiC ₂ O ₂	-3.240	-2.800
Cr ₂ TiC ₂ (OH) ₂	-3.353	-2.930
$Mo_2TiC_2F_2$	-3.684	-3.305
Mo ₂ TiC ₂ O ₂	-3.910	-3.526
Mo ₂ TiC ₂ (OH) ₂	-3.363	-3.028



Fig. S7. Three possible adsorption sites for single sodium atom adsorbed on $Mo_2TiC_2O_2$ monolayer. (a) M1 site, (b) M2 site, (c) M3 site.



Fig. S8. The adsorption configurations for Na adsorbed on (a) $Mo_4Ti_2C_4$, (b) $Mo_4Ti_2C_4F_4$, (c) $Mo_4Ti_2C_4O_4$ and (d) $Mo_4Ti_2C_4(OH)_4$.



Fig. S9. (a) The diffusion pathways and (b) diffusion barriers of Na between the bilayer $Cr_4Ti_2C_4O_4$ and $Mo_4Ti_2C_4O_4$ layers.



Fig. S10 the diffusion pathway and diffusion barrier of one sodium atom on $Na_8Cr_{18}Ti_9C_{18}O_{18}$ monolayer surface.

The calculation consumption on estimations of convex-hull of Na on $M_2TiC_2T_x$ MXenes are really huge due to the large adsorption ability of MXenes on Na ions. In present study, we firstly tried all possible adsorption sites to find the most stable adsorption site for single Na ion. As the adsorption energy of the sodium atom at the M1 sites is lowest, the 1st and 2nd sodium atoms are more likely to be adsorbed at the M1 sites on the both sides of $Cr_2TiC_2O_2$ monolayer. When the 3rd and 4th sodium atoms are adsorbed at the M1 sites (Fig. S11 (a)), the average adsorption energy is - 1.32 eV, which is lower than that at the M2 sites (Fig. S11 (d)). When the 1st to 4th sodium atoms are adsorbed at the M1 sites, the 5th to 6th sodium atoms cannot be stably adsorbed at the M2 sites, but can be adsorbed at the M1 sites. This is due to the repulsion of sodium atoms. Meanwhile, the average adsorption energy of the eight sodium atoms at the M1 sites (Fig. S11 (b)) is smaller than that at the M2 sites (Fig. S11 (e)). As shown in Fig. S11 (c) and (f), the difference between the average adsorption energy of sodium atoms adsorbed at M2 and M3 sites is very small after all M1 sites are occupied by Na atoms.



Fig. S11. The top views of the different configurations of $Na_xCr_8Ti_4C_8O_8$ monolayer. (a, d) $Na_4Cr_8Ti_4C_8O_8$, (b, e) $Na_8Cr_8Ti_4C_8O_8$, (c, f) $Na_{16}Cr_8Ti_4C_8O_8$.

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