Electronic Supplementary Material (ESI)

Lattice Matching and Halogen Regulation for Synergistically Induced large Li and Na storage by Halogenated MXene $V_3C_2Cl_2$

Min Zhou,[1,#] Yanqing Shen,[1,2,#],* LingLing Lv,[1] Yu Zhang,[1] Xianghui Meng,[1] Xin Yang,[1] Qirui He,[1] Bing Zhang,[1] Long Pang,[1,3],* Peng E,[1,3],* Zhongxiang Zhou[1,2]

1 School of Physics, Harbin Institute of Technology, Harbin 150001, PR China

2 Heilongjiang Provincial Key Laboratory of Plasma Physics and Application Technology, Harbin Institute of Technology, Harbin 150001, PR China

3 Laboratory for Space Environment and Physical Sciences, Harbin Institute of Technology, Harbin, 150001, China

#These authors contributed equally to this work.

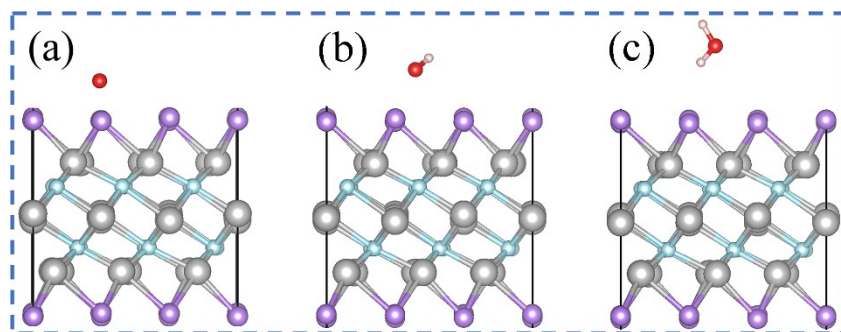* Corresponding author: Yanqing Shen. E-mail: shenyanqing2004@163.com

Figure S1. Optimized structures of O, OH, and H_2O on the $V_3C_2Cl_2$ monolayer. (a) O-adsorption; (b) OH-adsorption; (c) H_2O-adsorption.
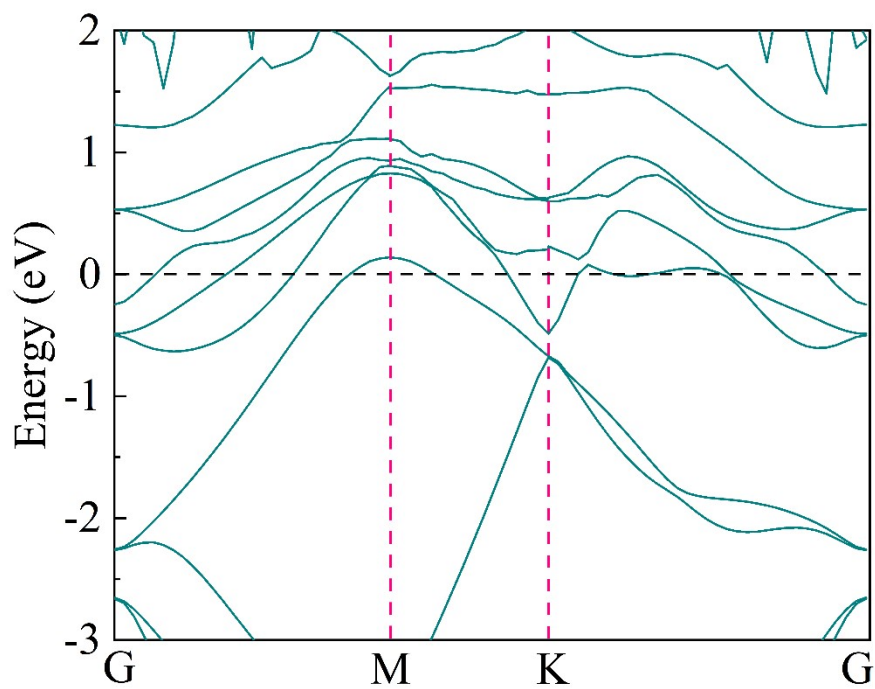

Figure S2: Band structures of $V_3C_2Cl_2$ monolayer with HSE06 method.
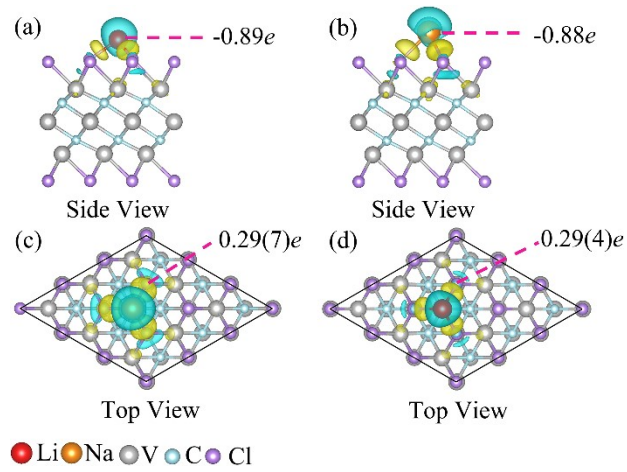
Figure S3: Charge density difference (CDD) maps of Li and Na on site S_V in $V_3C_2Cl_2$ monolayer, respectively. The green areas represent electron depletion, and the yellow areas represent electron gains.
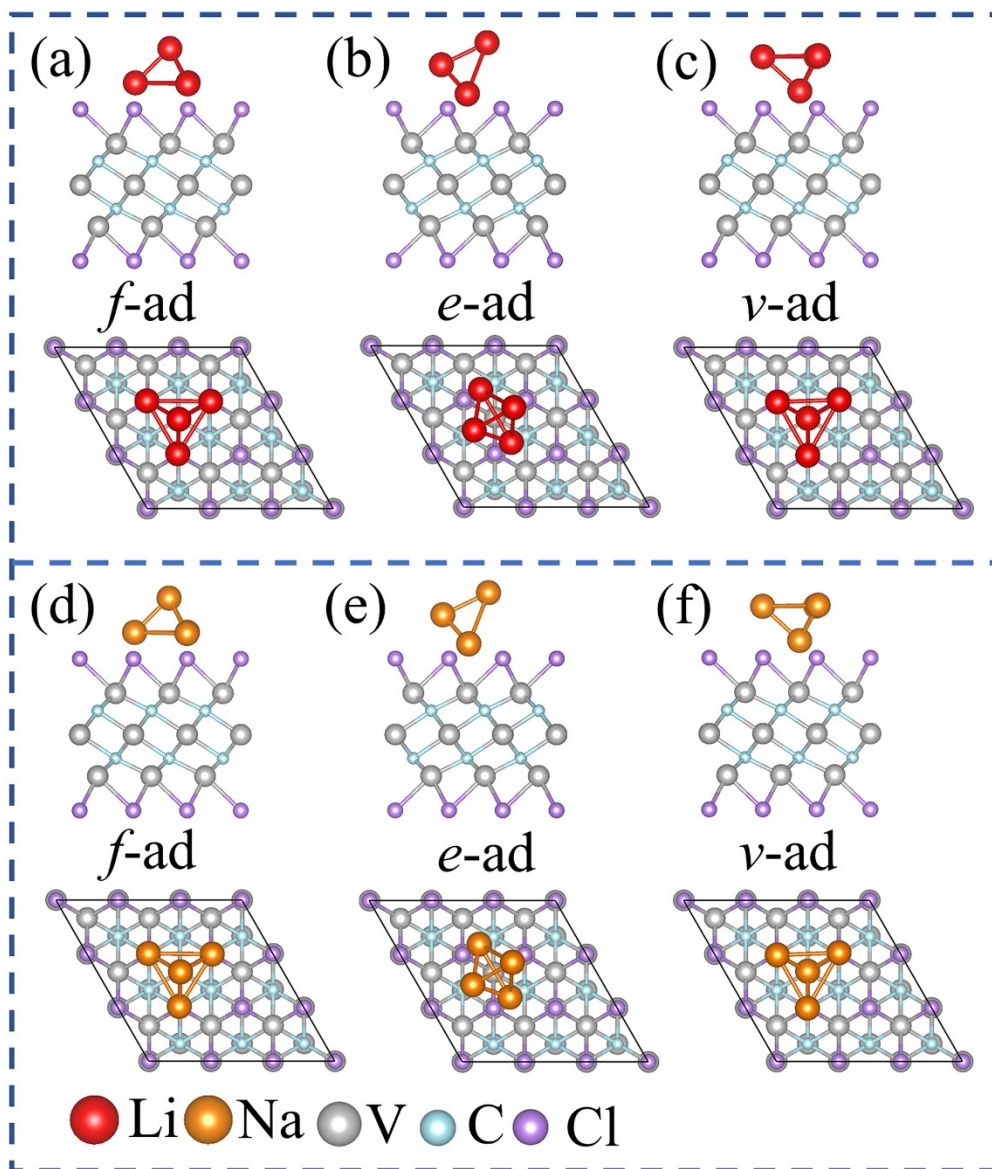
Figure S4: Before structural optimization of Li_4/Na_4 cluster adsorb on the $V_3C_2Cl_2$ monolayer. (a), (b) and (c) are the structures with Li_4 cluster adsorption; (d), (e) and (f) are the structures with Na_4 cluster adsorption; The *f*-ad, *e*-ad, and *v*-ad represent Li_4/Na_4 clusters adhere to the surface in the form of monolayer-parallel arrangements, with each cluster oriented parallel to the surface along its face, edge, or vertex.
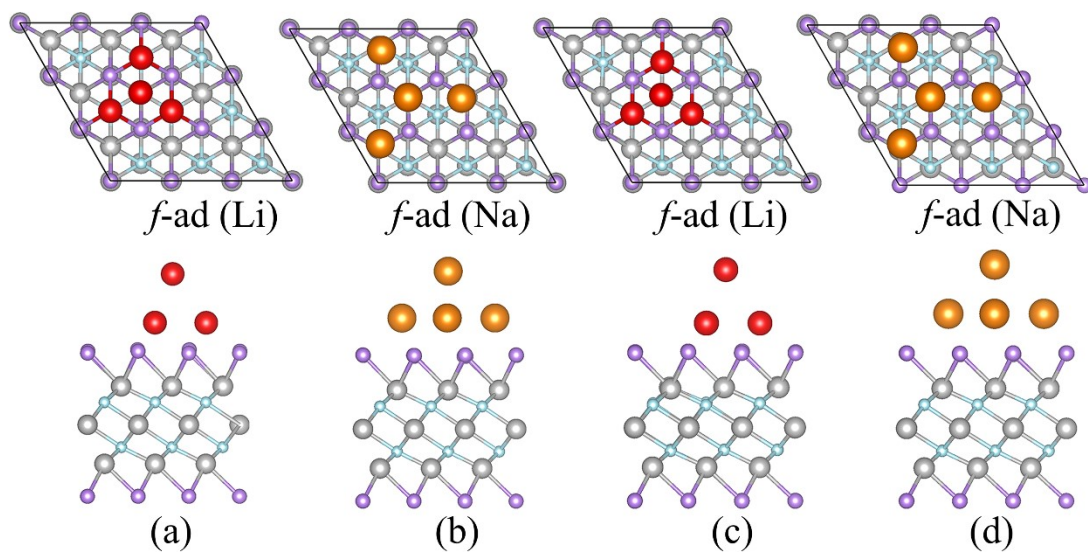
f-ad (Li) f-ad (Na) f-ad (Li) f-ad (Na)

(a)   (b)   (c)   (d)

Figure S5: After structural optimization of Li_4/Na_4 cluster adsorb on the $V_3C_2Cl_2$ monolayer. (a) and (b) are the structures with Li_4/Na_4 cluster adsorption with fixed the $V_3C_2Cl_2$ monolayer; (c) and (d) are the structures with Li_4/Na_4 cluster adsorption without fixed the $V_3C_2Cl_2$ monolayer.
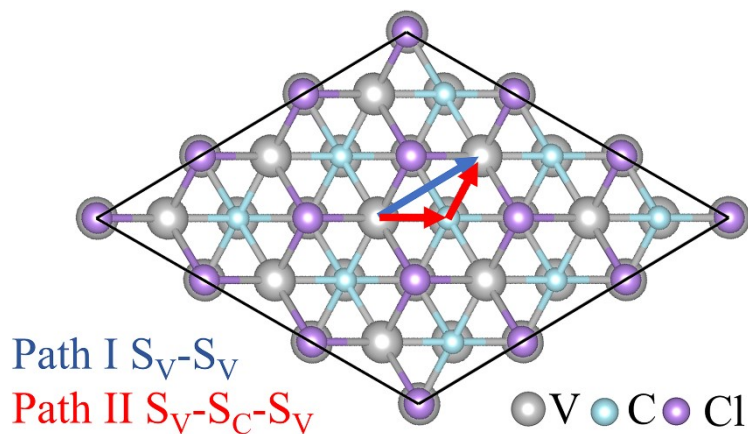

Path I S_V-S_V
Path II S_V-S_C-S_V

V C Cl

Figure S6: Li/Na migration path on the $V_3C_2Cl_2$ monolayer. Path I is the path that the Li/Na diffuse from the S_V site to S_V site directly; Path II is the path that the Li/Na diffuse from the S_V site to S_C site and then diffuse from the S_C site to S_V site.
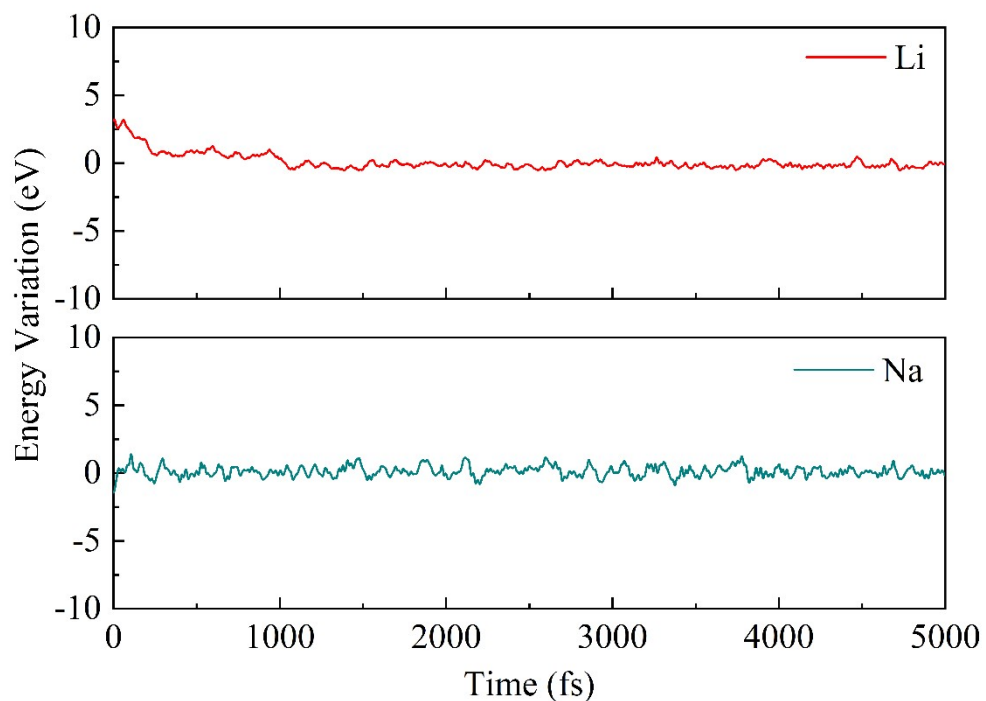
Figure S7: Variation in free energy over 5 ps during the AIMD simulation at 300 K of $V_3C_2Cl_2$ monolayer with maximum Li/Na adsorption concentration.
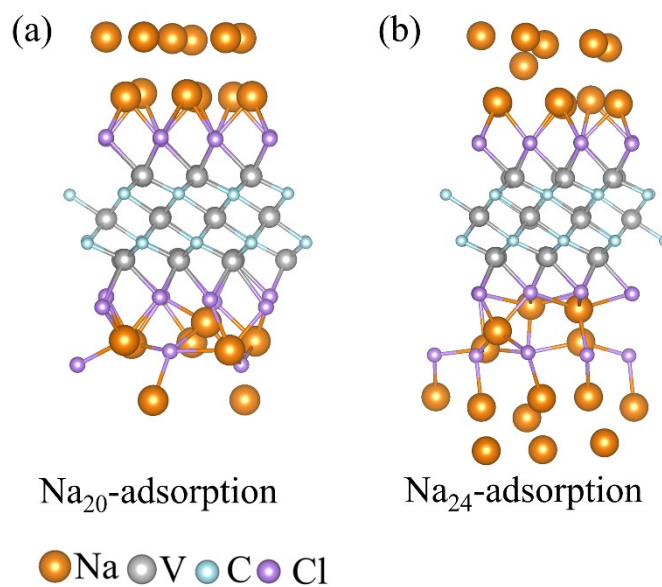

Na_{20}-adsorption Na_{24}-adsorption

● Na ● V ● C ● Cl

Figure S8: Adsorption structures of 20th and 24th Na atoms on the $V_3C_2Cl_2$ monolayer. (a) 20th Na atoms adsorption; (b) 24th Na atoms adsorption.

Table S1. The Bader charge of $V_3C_2Cl_2$, V_1 represents the V atom on the surface of MXenes, and V_2 is the central one.

MXenes	V_1	V_2	C	Cl
V_3C_2	-1.00 e	-1.41 e	1.71 e	-
$V_3C_2Cl_2$	-1.48 e	-1.39 e	1.61 e	0.57 e

Table S2. Calculated the adsorption energies of Li and Na on the $V_3C_2Cl_2$ monolayer. The negative value represents exothermic adsorption.

Energy	E_V (eV)	E_C (eV)	E_{Cl} (eV)
Li	-0.88	-0.86	-
Na	-0.78	-0.78	-

Supplementary Discussion I

The energies of gas molecules adsorb on the $V_3C_2Cl_2$ monolayer are defined as,[1-2]

$$E_{ads} = E_{L + M} - E_L - E_M \qquad (1)$$

where E_{ads} is the adsorption energies, E_L represent the energy of $V_3C_2Cl_2$ monolayer, and E_M are the energies of O, OH, and H_2O energies. The energy of O is expressed as half of the binding energy of the oxygen molecule. The adsorption configuration is deemed spontaneous and exothermic when the adsorption energy is negative. Nonetheless, the optimized structures reveal that O, OH, and H_2O molecules have not undergone adsorption on the monolayer. In light of the aforementioned observations, one can infer that the $V_3C_2Cl_2$ monolayer exhibits both corrosion resistance and hydrophobicity.

References

[1] M. Li, X.L. Li, G.F. Qin, K. Luo, J. Lu, Y.B. Li, G.J. Liang, Z.D. Huang, J. Zhou, L. Hultman, P. Eklund, P. Persson, S.Y. Du, Z.F. Chai, C.Y. Zhi, Q. Huang Halogenated Ti_3C_2 MXenes with Electrochemically Active Terminals for High-Performance Zinc Ion Batteries, ACS Nano 2021, 15, 1077-1085.

[2] J. Zhao, N.G. Ma, T.R. Wang, N. Li, Y.H. Wang, J. Fan, Theoretical Design of High-Performance Halogen Anion Batteries with MXene Electrodes: Influence of Functional Groups, Metals, and Anions, J. Mater. Chem. A, 2022, 10, 21611-21621.