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Supporting Information

Theoretical Prediction and Atomic-Scale Investigation of Tetra-VN_2 Monolayer as a High Energy Alkali Ion Storage Material for Rechargeable Batteries

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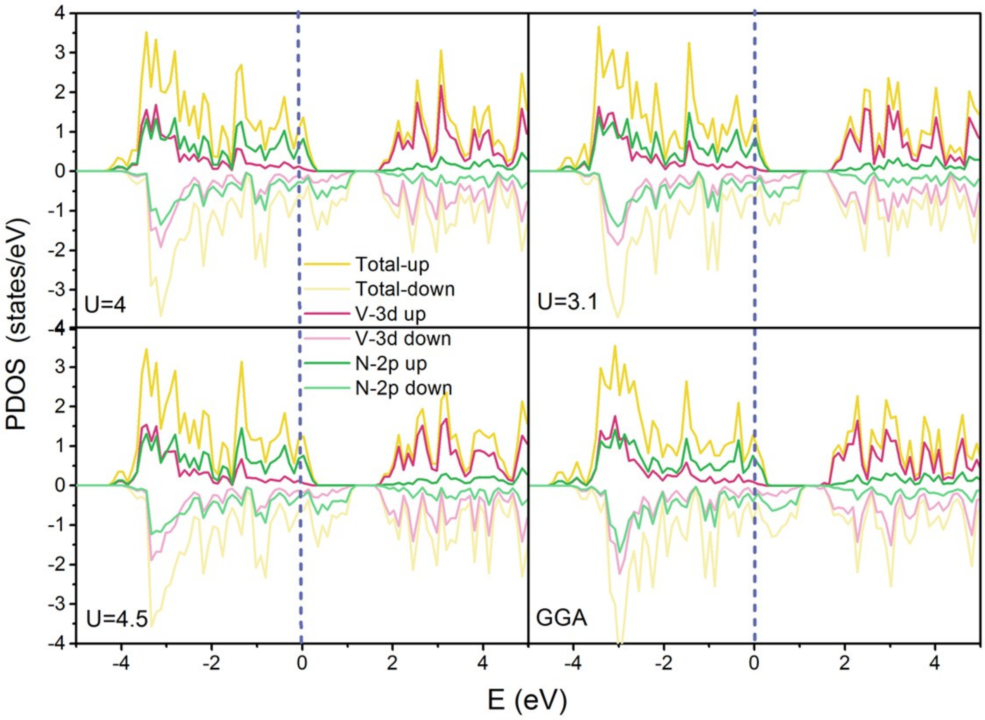

Fig. S1 PDOS for tetra-VN_2 monolayer calculated with different U values, the dash line represents the Fermi level.

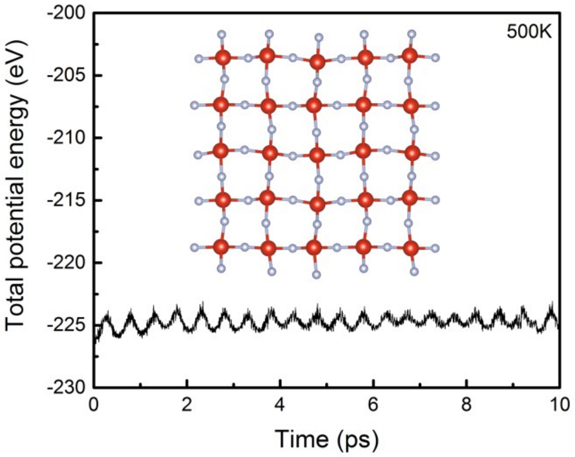

Fig.S2 The variations in total energy versus time for tetra-VN_2 monolayer in AIMD simulations at 500 K. The insets represent the snapshots at the end of AIMD simulations of 10 ps.

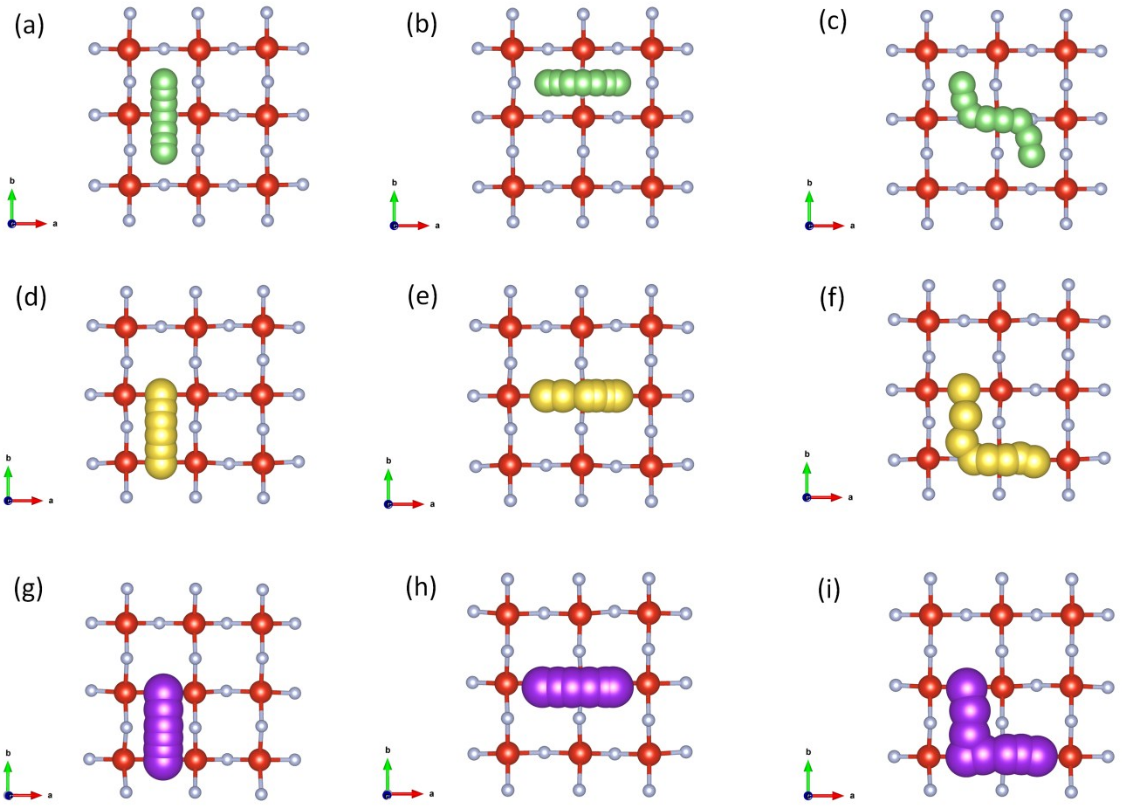

Fig. S3 The alkali ion migration pathways after full structure relaxation. (a, b, c) path-1 (T_h-T_b-T_h), path-2 (T_h-T_a-T_h) and path-3 (T_h-T_v-T_h) for Li^+, respectively. (d, e, f) path-I (T_b-T_h-T_b), path-II (T_b-T_v-T_b) and path-III (T_b-T_a-T_b) for Na^+, respectively. (g, h, i) path-I (T_b-T_h-T_b), path-II (T_b-T_v-T_b) and path-III (T_b-T_a-T_b) for K^+, respectively.

Conventional DFT calculations fails for the materials with strongly correlated electrons, which contain many electrons in partially filled 3d or 4f shells. The electrons in conventional DFT calculations experience strong correlations with a incorrect delocalization, resulting underestimated band gap[1] and the inaccuracy of redox potential[2]. The DFT+U method provides a means through empirical U parameters to correct these errors. However, it is a big challenge to find an absolutely correct U value for newly designed materials (such as the VN_2 in this work) due to lack of experimental and empirical U values. What we can do at present is to study the effect of U values on the electronic and electrochemical properties of the material. Generally, the U values used for 3d transitional metals (T, V, Cr, Mn, Fe) can be chosen in the range of 2.0-4.0, while the U values for rare earth metals can be 4.0-7.0. **Fig. S1** demonstrated that the electron state density of VN_2 did not change much at different U values. Here, in order to find the effect of different U values on electrochemical properties, we carefully calculated the convex hull (**Fig. S4**) and voltage profiles (**Fig. S5**) of VN_2 using different U values, including U = 1, 4, and 7 (extra U = 2.5 and 3.1 were used for Li_xVN_2). Calculation results indicated that the formation energy and the shape of the convex hull, as well as the voltage profiles at different U values were very similar, except for U = 7 which showed slightly larger deviation. However, as mentioned above, U = 7 is not commonly used for 3d systems. In addition, the maximum adsorption capacities have been calculated as Li_2VN_2, Na_4VN_2 and K_4VN_2 at above U values. No larger adsorption contents can be obtained due to the positive adsorption energies. As a result, the capacity of different U values does not change.

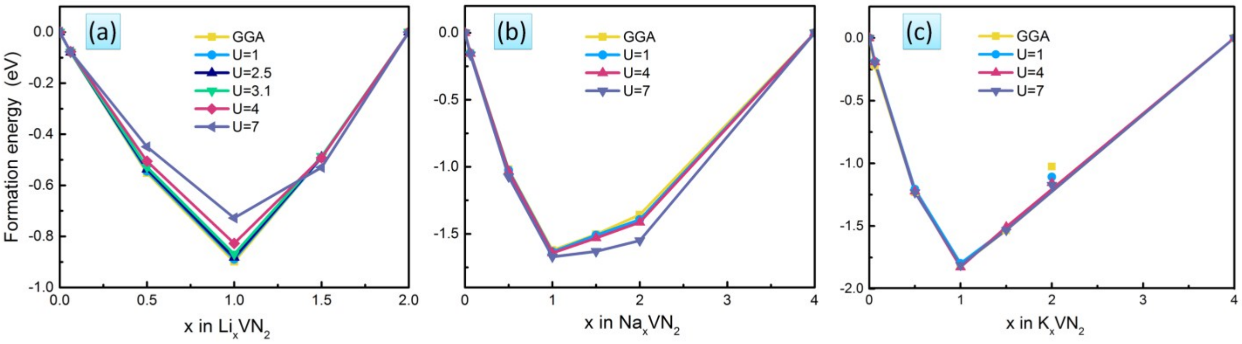

Fig. S4 Convex hull profiles for the tetra-VN_2 monolayer obtained with GGA and GGA+U at different U values. (a, b, c, for Li-, Na-, K-ion batteries, respectively).

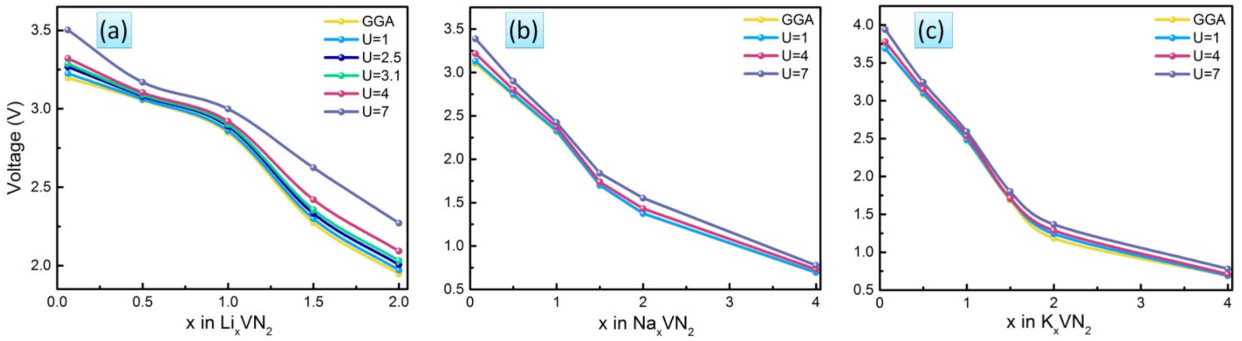

Fig. S5 Calculated voltage profiles for the tetra-VN_2 monolayer obtained with GGA and GGA+U at different U values. (a, b, c, for Li-, Na-, K-ion batteries, respectively).

Table S1 The adsorption energies (eV) of alkali atoms at different adsorption sites.

site	Li	Na	K
T_h	-3.24	-3.08	-3.61
T_b	-3.00	-3.10	-3.69
T_a	-2.71	-2.73	-3.42
T_v	-2.98	-2.83	-3.52

Table S2 The transferred charges (*e*) of N and M for M-N bond at different adsorption sites. "-" respects lost electrons.

site	Li	Na	K
N(T_h)	0.61	0.39	0.32
N(T_b)	0.29	0.49	0.46
N(T_a)	0.34	0.21	0.18
N(T_v)	0.48	0.34	0.29
M(favorite site)	-0.88	-0.87	-0.90

Reference

1 M. Cococcioni and S. de Gironcoli, *Phys. Rev. B*, 2005, **71**, 035105.

2 F. Zhou, M. Cococcioni, C. A. Marianetti, D. Morgan and G. Ceder, *Phys. Rev. B*, 2004, **70**, 235121.