# Supplymentary Information

# Correlated migration of ions in a 2D heterostructure anode: guaranteeing a low barrier for a high site occupancy

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Table S1. POSCAR of a Li intercalated $VS_2/Ti_2CO_2$ heterostructure at Occ.=1.

| VS₂/Ti₂CO₂-Li |
|---|
| VS$_2$/Ti$_2$CO$_2$-Li |
| 1.00000000000000 |
| 3.2388999462000001        0.0000000000000000        0.0000000000000000 |
| -1.6178978150000001        2.8058652002000000        0.0000000000000000 |
| 0.0000000000000000        0.0000000000000000        25.0000000000000000 |
| Ti    C    O    S    V    Li |
| 2    1    2    2    1    1 |
| Direct |
| 0.5616271129020177    0.8886529346160559    0.2240295124594188 |
| 0.2316505026101728    0.2191582673107682    0.1365415021496281 |
| 0.8979722557349076    0.5527547960702942    0.1786265584705758 |
| 0.5639021401114961    0.8838223799415655    0.0820233302126080 |
| 0.2312853023193097    0.2211076735161408    0.2704443959979262 |
| 0.5775761300617931    0.8737569450919271    0.3855990458938140 |
| 0.5782861255458963    0.8729890319350498    0.5004149919375039 |
| 0.2437851236062962    0.2075804841221945    0.4431885949724720 |
| 0.8887703824416248    0.5564356765732144    0.3083840743814751 |

*Adhesion energy.* The adhesion energy, $E_{ad}^{heter}$, of the TMD/MXene heterostructures can be obtained by,

$$E_{ad}^{heter} = \frac{E(Hetero) - E(MXene) - E(TMD)}{N_{hetero}}, \tag{S1}$$

where $E$(MXene), $E$(TMD) and $E$(Hetero) are the free energies of the MXene, TMD and the compositive heterostructure, respectively, and $N_{hetero}$ is the ion number in the heterostructure. Obviously, a lower $E_{ad}^{heter}$ indicates a more stable stacking pattern. Then, the adhesion energies of alkali metals loaded on a heterostructure is shown as,

$$E_{ad}^{ion} = \frac{E(Hetero + N_{ion}alkali) - E(Hetero) - N_{ion}E(alkali)}{N_{ion}}, \tag{S2}$$

where $N_{ion}$ is number of alkali metals on the heterostructure, and $E$(Hetero+ $N_{ion}$alkali) and $N_{ion}E$(alkali) are the free energy of the heterostructure with $N_{ion}$ alkali and the free energy of the $N_{ion}$ alkali in their bulk structures.
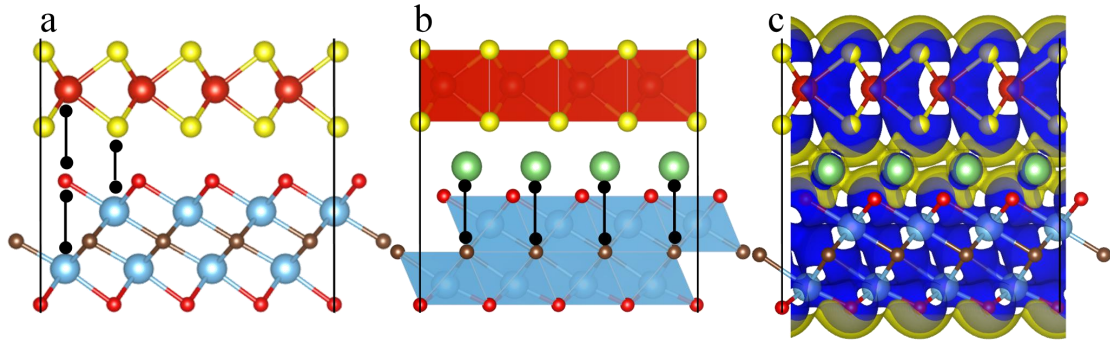
Fgiure S1. (a) Stable stacking pattern of $VS_2$ and $Ti_2CO_2$ used in the present study, (b) intercalated sites of Li ions in the heterojunction after geometry optimization, and (c) charge density isosurfaces of 0.03 (blue) and 0.01 (green) e/bohr$^3$ in the Li intercalated heterojunction are displayed, where the line with two black points indicates the atoms at both ends have same $x$- and $y$-coordinates.
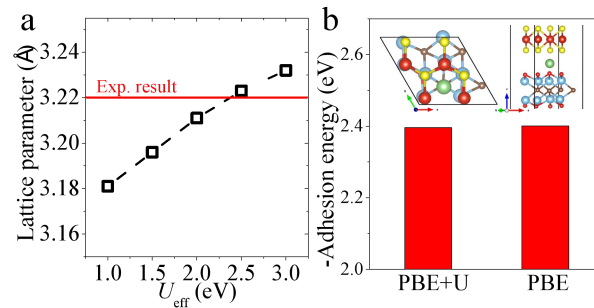


Fgirue S2. (a) Comparison of the lattice parameter of single layer $VS_2$ from PBE+$U$ with experimental value of 3.22 Å in Ref.[1], from which we choose $U_{eff}$=2.5 eV, and (b) comparison of Li adhesion energy obtained from PBE+$U$ and PBE, and almost consistent values are found.



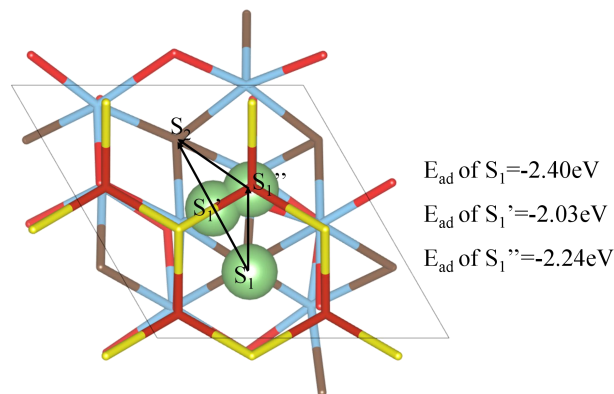$E_{ad}$ of $S_1$=-2.40eV

$E_{ad}$ of $S_1$'=-2.03eV

$E_{ad}$ of $S_1$''=-2.24eV

Figure S3. Comparison of adhesion energies, $E_{ad}$, for Li ion in the stable site ($S_1$) and in two unstable sites ($S_1$', $S_1$'') in diffusion path. $S_1$' is in the middle of $S_1$ and $S_2$, and $S_1$'' is directly facing (has same x- and y-coordinates with) an O atom in the $Ti_2CO_2$.
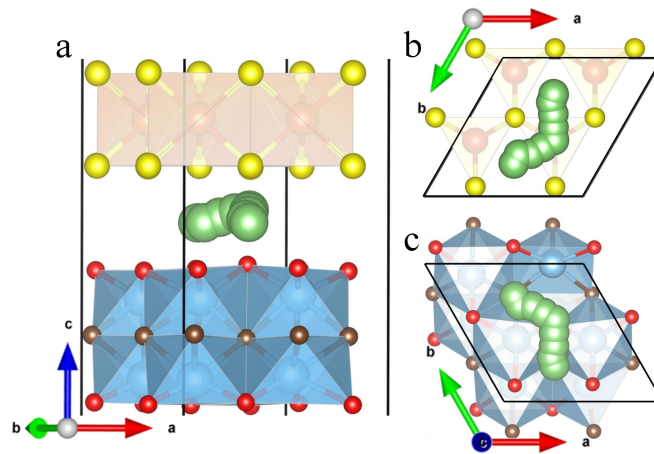
Figure S4. Polyhedral plots for the (a) heterostructure, (b) only $VS_2$ and (c) only $Ti_2CO_2$ with Li diffusion path.
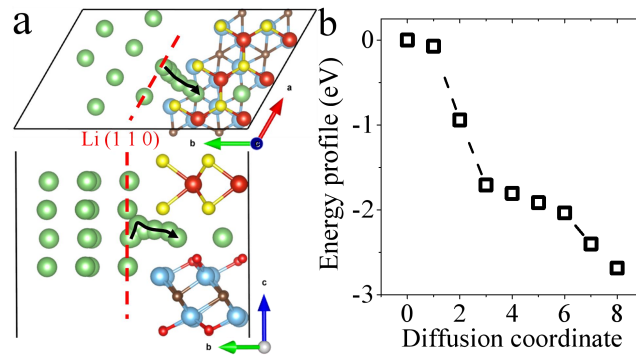


Figure S5. (a) Interface of Li (1 1 0) face and $VS_2/Ti_2CO_2$ heterostructure and the intercalating path for a Li atom from the Li crystal to an intercalation site, and (b) the corresponding energy profile. When preforming the CI-NEB calculation, other atoms (except the mobile ion) are fixed.
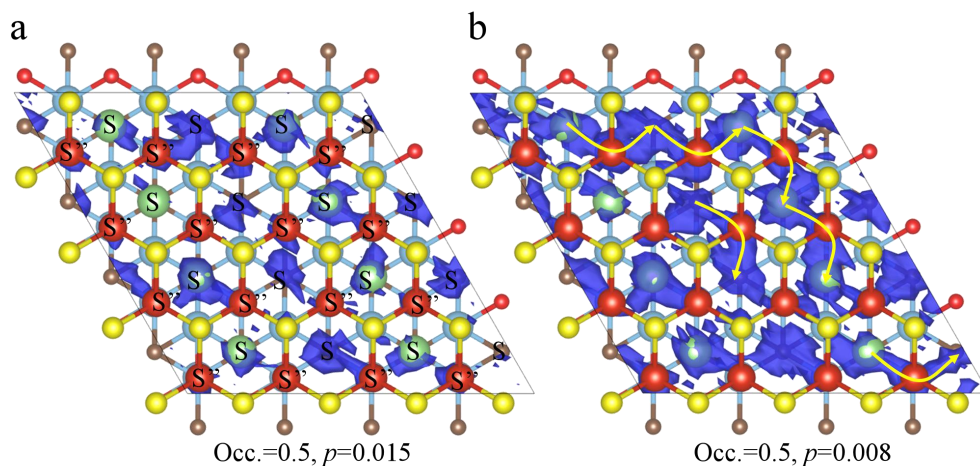


Occ.=0.5, $p$=0.015

Occ.=0.5, $p$=0.008

Figure S6. Li probability density isosurfaces for the Li intercalated 4×4 supercell of $VS_2/Ti_2CO_2$ at 900 K, where density value $p$ is set as 0.015 and 0.008 for a and b. In a, we found Li ions mainly stay around the stable sites S and sometimes around the metastable site S'', which is consistent with the geometry optimization result. Then, when decreasing the density value, the main

diffusion path, from S to S'' then to S, is clearly shown in b, which verifies the lowest barrier path from CI-NEB calculations.

**Discussions for Fig. S7.** Fig. S7a shows that unoccupied Li sites are the mediums for ion migration. If Occ.~1 (i.e. there are very few unoccupied sites), the lack of diffusion medium may hinder the correlated migrations. However, in a practical 2D heterostructure anode, the adhesion energy, $E_{ad}$, of Li ion can gradually increase with site occupancy, as shown in Fig. S7b. Such as in reference[2], the authors found that Li average adhesion energy (they called binding energy) in $Sc_2C(OH)_2$/graphene heterostructure increases from ~-0.9 eV at ~0.11 Occ. (they called concentration) to ~0 eV at ~0.75 Occ., which means new Li ions will not continue to intercalate in the heterostructure when Occ.>0.75 due to the weak adhesion. Similarly, reference[3] shows that the adhesion energies of Na, Ca and K ions in $Ti_2CO_2$/graphene also significantly increase with Occ. and become very close to 0 eV, indicating weak adhesions at high ion site occupancy.

In Fig. S7b, the gap between Occ. of $E_{ad}$~0 to 1 is we mentioned "gap to 1". When $E_{ad}$>0, ions trend to form the Li crystal due to the lower energy other than entering the heterostructure, as shown in Fig. S7c. Because of the "gap to 1", there should be some unoccupied sites for the correlated migrations of Li in most cases.
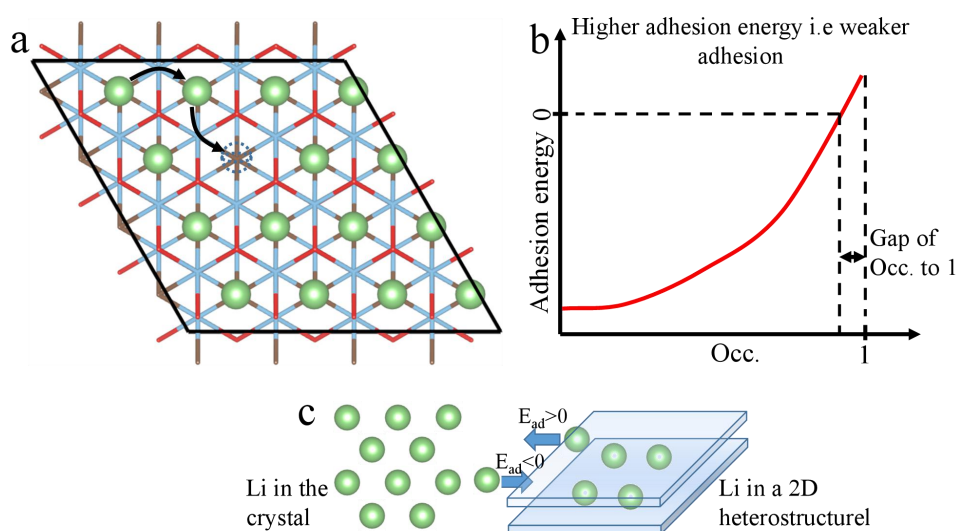


Figure S7. (a) Unoccupied Li sites as the mediums for ion migration. (b) Adhesion energy, $E_{ad}$, of intercalated ions gradually increasing with site occupancy and when when $E_{ad}$ reaches to 0, the gap between Occ. to 1 is we mentioned "gap to 1". (c) Effect of $E_{ad}$ on the intercaltion of ions, where if $E_{ad}$<0 ions trend to be intercalated into the heterostructure, and if $E_{ad}$>0 ions trend to form the Li crystal due to the lower energy other than entering the heterostructure.

**References**

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