

Supporting Information for “Defective phosphorene as an anode material for high performance Li-, Na- and K-ion batteries: a first-principle study”

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The supporting information contains information on formation of defects and formation energy and geometric structures of defective phosphorene, the absorption energies of Li, Na and K on the defective structures, the highest adsorption energies of Li, Na and K on each defective structure, comparisons of the lowest diffusion barriers between pristine and defective phosphorene not presented in the main paper.

Formation of defects and formation energy

In the formation of defects SW1 and SW2, different P-P bonds in phosphorene are rotated by about 90 degrees and then the structures were optimized. The SV and DV defects are produced by removing the P atom and various P-P bonds from phosphorene and then optimization, respectively. The optimized structure of the point defects in phosphorene is shown in Fig S1 of ESI which are in good agreement with previous studies¹. The DOS and band structure calculations in previous theoretical studies show that the point defects have little effect on phosphorene's electronic properties, still showing semiconducting with similar band gap values to perfect phosphorene, different from graphene and silicene¹⁻³. That is because the occupied and unoccupied states contributed by the defect effaced phosphorus atoms for these defects are respectively close that of other unaffected phosphorus atoms as shown in Fig 4 reference¹.

To check the stability of defects in phosphorene, the formation energy is defined as

$$(S1) \quad E_f = E_{ph} - (N_p \cdot E_p)$$

where E_{ph} represents the total energy of defective phosphorene, E_p is the energy per phosphorus atom in a perfect phosphorene sheet and N_p corresponds to the number of phosphorus atoms in phosphorene. Notice that for perfect phosphorene, E_f is zero. Our calculated stability of defective phosphorene are summarized in Table S1 and compared with phosphorene, graphene and silicene in previous studies.

Table S1 Calculated formation energy E_f (eV) and comparison results of graphene and silicene with corresponding various defects' formation energy E_f (eV).

Model	Phosphorene This work	Phosphorene ref ¹	Graphene ref ²	Silicene ref ³
SW1	1.154	1.012		
SW2	1.189	1.322	4.50	2.09
(5-9)SV	1.725	1.626	7.80	3.77
(5-8-5)DV1	2.093	1.906		
(5-8-5)DV2	3.122	3.041	7.52	3.70
(4-10-4)DV	2.545	2.173	-	-
(555-777)DV1	2.439	2.081		
(555-777)-DV2	2.516	2.350	6.40	2.84

We find that the SW1 defect has smaller formation energy than that of the other defects, indicating that it is more easily generated in phosphorene. The defects in phosphorene are most easily formed among various defects similar to graphene and silicone, indicating that these defects are quite easily formed in phosphorene (Table S1). For DVs, the (5-8-5)DV1 defect is also most stable in phosphorene similar to graphene and silicone. These values agree well with the previous reports¹. The above results show that investigating the effect of defects on AIBs performance is very important.

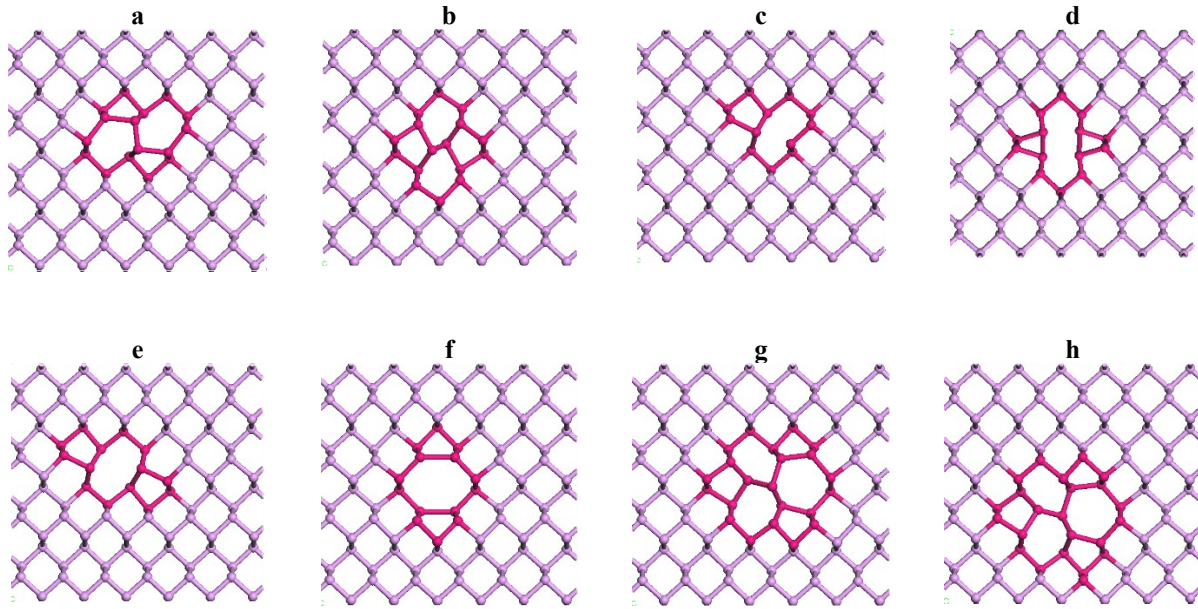


Figure S1. Geometric structures of defective phosphorene in the 4×5 supercell, including the (a) SW1, (b) SW2, (c) (5-9)SV, (d) (4-10-4)DV, (e) (5-8-5)DV1, (f) (5-8-5)DV2, (g) (555-777)DV1, (h) (555-777)DV2, defects. The violet and red balls denote unaffected and affected phosphorus atoms, respectively.

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>
SW1-1	-1.74	-0.91	-2.24
SW1-2	-	-	-2.16
SW1-3	-1.82	-0.94	-
SW1-4	-	-0.97	-
SW1-5	-2.02	-	-2.19
SW1-6	-2.04	-1.03	-
SW1-7	-2.05	-1.05	-2.17
SW1-8	-1.63	-0.78	-2.16

Table S2. The absorption energies of Li, Na and K on SW1 structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>
SW2-1	-1.58	-0.57	-2.27
SW2-2	-2.01	-0.79	-2.10
SW2-3	-	-1.42	-2.18
SW2-4	-2.11	-0.99	-2.12
SW2-5	-1.89	-	-

Table S3. The absorption energies of Li, Na and K on SW2 structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>
SV-1	-2.414	-1.036	-2.602
SV-2	-2.302	-1.762	-2.833
SV-3	-	-1.627	-
SV-4	-2.752	-1.807	-2.736
SV-5	-2.009	-1.386	-
SV-6	-	-	-2.753
SV-7	-2.468	-1.742	-
SV-8	-2.888	-1.990	-2.735
SV-9	-2.083	-	-

Table S4. The absorption energies of Li, Na and K on SV structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>
(4-10-4)DV-1	-2.130	-1.395	-2.388
(4-10-4)DV-2	-1.867	-1.565	-2.313
(4-10-4)DV-3	-2.457	-1.569	-2.396
(4-10-4)DV-4	-1.916	-1.570	-2.397
(4-10-4)DV-5	-1.913	-1.591	-2.384

Table S5. The absorption energies of Li, Na and K on (4-10-4)DV structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>

(5-8-5)DV1-1	-2.490	-2.033	-2.649
(5-8-5)DV1-2	-2.774	1.500	-2.650
(5-8-5)DV1-3	-1.922	-1.040	-2.367
(5-8-5)DV1-4	-2.377	-1.363	-2.367

Table S6. The absorption energies of Li, Na and K on (5-8-5)DV1 structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>
(5-8-5)DV2-1	-2.148	-2.719	-3.055
(5-8-5)DV2-2	-2.292	-2.036	-2.773
(5-8-5)DV2-3	-2.211	-2.046	-2.797
(5-8-5)DV2-4	-2.086	-1.918	-2.751

Table S7. The absorption energies of Li, Na and K on (5-8-5)DV2 structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>
(555-777)DV1-1	-1.633	-0.869	-2.357
(555-777)DV1-2	-1.633	-1.426	-2.357
(555-777)DV1-3	-2.346	-1.655	-2.428
(555-777)DV1-4	-1.840	-1.651	-2.372
(555-777)DV1-5	-2.022	-1.337	-2.208

Table S8. The absorption energies of Li, Na and K on (555-777)DV1 structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

<i>sites</i>	<i>E int(eV)</i>		
	<i>Li</i>	<i>Na</i>	<i>K</i>
(555-777)DV2-1	-2.139	-1.493	-2.442
(555-777)DV2-2	-1.645	-1.632	-2.430
(555-777)DV2-3	-1.691	-1.574	-2.441
(555-777)DV2-4	-1.786	-1.571	-2.445
(555-777)DV2-5	-2.409	-1.440	-2.319

Table S9. The absorption energies of Li, Na and K on (555-777)DV2 structure with its site number. The highest adsorption energies are indicated in yellow(Li), green(Na) and blue(K).

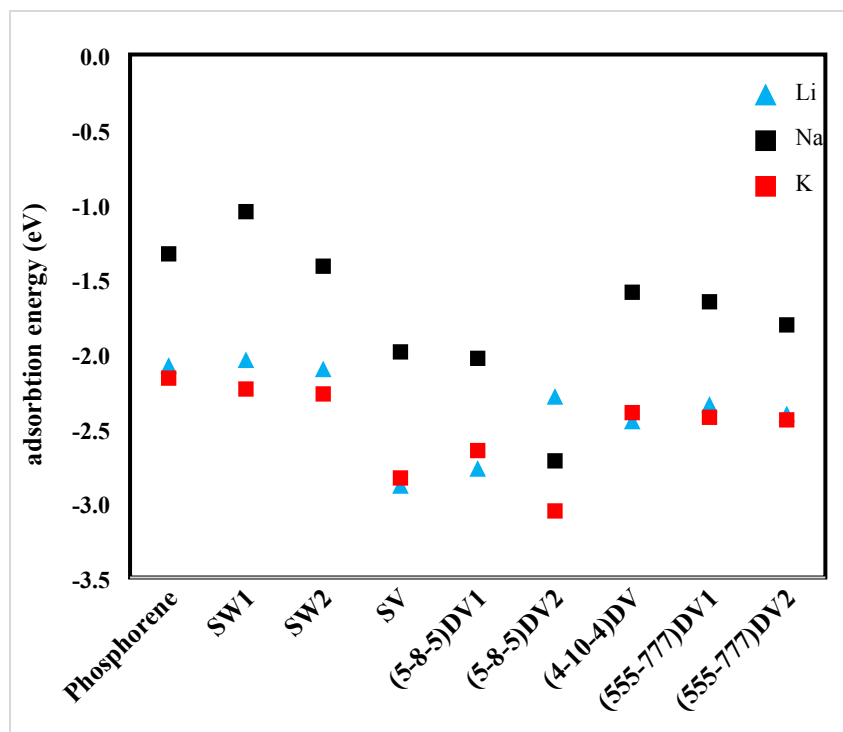


Figure S2. The highest adsorption energies of Li, Na and K on each defective structure.

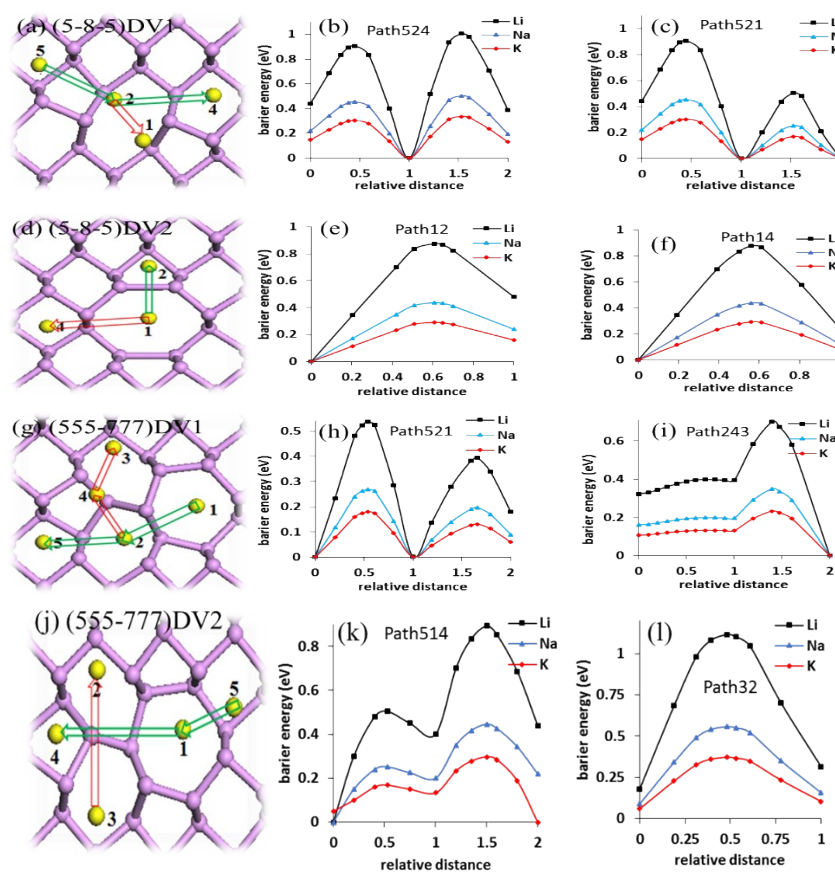


Fig S3. Schematic of the considered metal diffusion paths on (5-8-5)DV1 (a), (5-8-5)DV2 (d), (555-777)DV1 (g) and (555-777)DV2 (j) and respective migration barriers for Li, Na, and K on (5-8-5)DV1 (b,c), (5-8-5)DV2 (e,f), (555-777)DV1 (h,i) and (555-777)DV2 (k,l) using the CI-NEB method.

	<i>Li</i>	<i>Na</i>	<i>K</i>
Phosphorene	0.100	0.027	0.022
Graphene	0.300	0.140	0.120
Silicene	0.230	0.250	0.097
SW1-Ph	0.309	0.207	0.092
SW2-Ph	0.231	0.115	0.077
SV-Ph	0.165	0.082	0.055
(5-8-5)DV1-Ph	0.468	0.234	0.156
(5-8-5)DV2-Ph	0.396	0.263	0.132
(4-10-4)DV-Ph	0.108	0.065	0.036
(555-777)DV1-Ph	0.306	0.153	0.102
(555-777)DV2-Ph	0.104	0.042	0.025

Table S10. Comparisons of the lowest diffusion barriers between pristine and defective phosphorene and other typical 2D electrode materials, such as graphene⁴, silicene⁵⁻⁷.

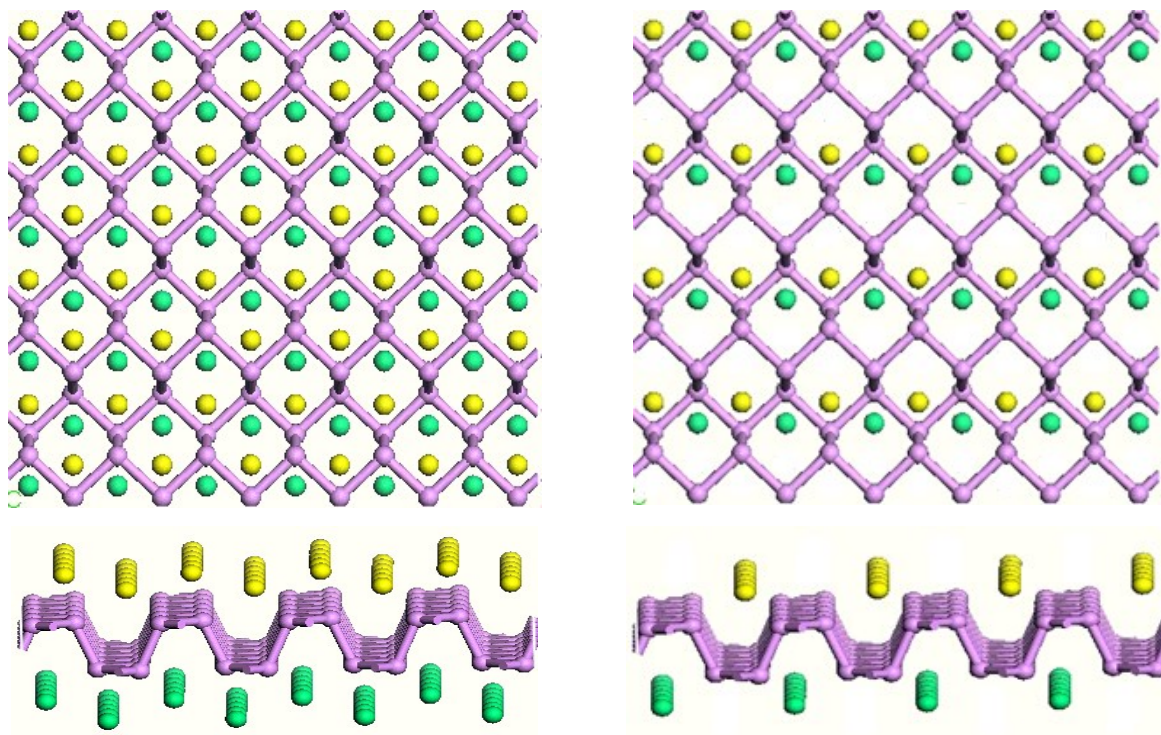


Figure S4. The top view (a) and side view (b) of optimized structure of the $M_{96}P_{16}$. The metal atoms are yellow and green and phosphorus atoms are purple color. Atoms in different layers are depicted in yellow and green, respectively.

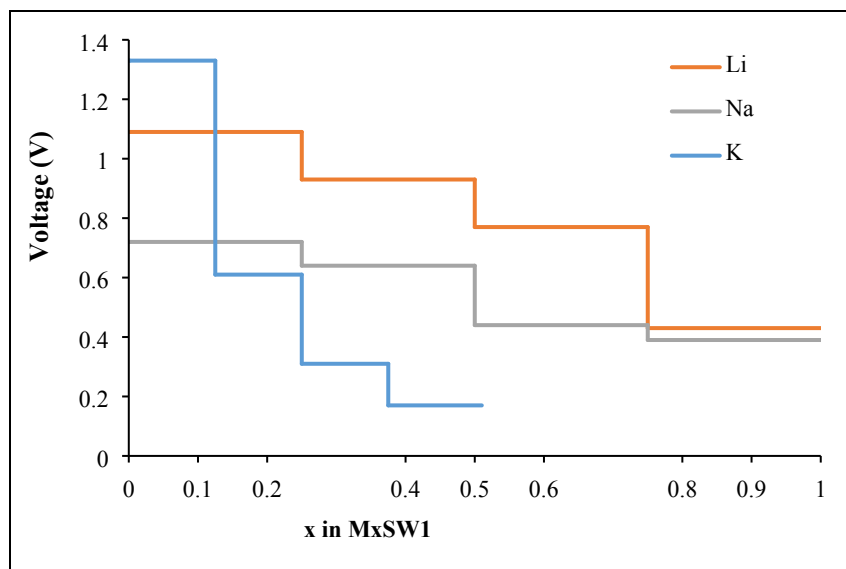


Figure S5. The calculated voltage profiles along with the Li/Na/K increasing on the SW1 defective phosphorene

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