Supporting Information for "Adsorption and migration of alkali metals (Li, Na, and K) on pristine and defective graphene surface"

Emilia Olsson^{1,2}, Guoliang Chai³, Martin Dove², and Qiong Cai¹

¹Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2
7XH, United Kingdom
² School of Physics and Astronomy, Queen Mary University London, London, E1 4NS, United Kingdom
³ State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure

of Matter, Chinese Academy of Sciences, Fuzhou City, Fujian Province, China, 350002.

The supporting information contains information on dispersion correction selection, charge density plot of pristine graphene, wider range PDOS for metals on pristine graphene, structural distortions of defective graphene, and metal migration paths and their associated energy barriers together with a discussion of the metal migration of the defects not presented in the main paper.

Dispersion Correction Selection

Table S1. Lattice parameters (a and c) in Å of graphene and two-layer graphite, together with binding energy in meV/atom between graphene sheets in graphite, and the carbon vacancy formation energy in eV on graphene and in graphite for different vdW functionals.

	Grap	hene	AA C	Graphit	e		AB C	Graphit	e	
Functional	a	d _{C-C}	a	c	d _{C-C}	E _b	a	c	d _{C-C}	E _b
Experimental	2.46	1.42	2.46	3.35	1.42	~-50	2.46	3.35	1.42	~-50
PBE	2.47	1.424	2.47	6.64	1.42	-0.41	2.47	4.08	1.42	2.68
D2G	2.47	1.424	2.47	3.43	1.42	-41.06	2.46	3.21	1.42	-54.94
D3BJ	2.47	1.424	2.47	3.59	1.42	-44.78	2.47	3.35	1.42	-51.42
D3G	2.47	1.424	2.47	3.66	1.42	-42.58	2.47	3.43	1.42	-45.95
DF2	2.47	1.429	2.47	3.66	1.43	-47.19	2.48	3.51	1.43	-50.68
optB86D	2.47	1.423	2.47	3.50	1.42	-58.38	2.47	3.30	1.42	-69.74
optB88	2.46	1.423	2.46	3.52	1.42	-59.33	2.46	3.34	1.42	-69.14
optPBE	2.47	1.426	2.47	3.60	1.43	-56.34	2.47	3.42	1.43	-63.23
revDF2	2.46	1.423	2.46	3.54	1.42	-49.41	2.46	3.30	1.42	-59.75

Charge Density of Pristine Carbon Surface



Figure S1. Charge density for graphene with iso-value 0.2.



Figure S2. Projected density of states for a) Li, b) Na, and c) K adsorbed on hole site on carbon surface. d) PDOS for pristine carbon surface. $E-E_F=0$ eV is the Fermi level, where negative $E-E_F$ values represent the occupied bands and positive values represent the virtual bands. Please note that the Li, Na, and K PDOS have been multiplied as indicated in the legends for the benefit of the reader.

Structural Distortion in Defective Carbon Layer

	N _C	V _C	N _C V _C	N_CV_C -pass	V _C -pass	3O _C	2O _C	N _C 2O _C	O _C N _C
C-C (Å)	1.42	1.38-1.48	1.39-1.52	1.40-1.46	1.40-1.46	1.40-1.46	1.38-1.47	1.40-1.45	1.38-1.46
C-O (Å)	N/A	N/A	N/A	N/A	N/A	1.38	1.34	1.37-1.38	1.33
C-N (Å)	1.41	N/A	1.33	1.35	N/A	N/A	N/A	1.34	1.31
C-H (Å)	N/A	N/A	N/A	1.08	1.07-1.08	N/A	N/A	N/A	N/A
C-Ĉ-C (°)	120	113-126	110-127	119-123	115-125	117-125	118-125	118-124	116-126
C-Ĉ-O (°)	N/A	N/A	N/A	N/A	N/A	118-120	115-120	119-120	113-121
C-Ô-C (°)	N/A	N/A	N/A	N/A	N/A	122	133	123	135
C-Ñ-C (°)	120	N/A	122	123	N/A	N/A	N/A	121	132
C-Ĉ-N (°)	120	N/A	121	120-121	N/A	N/A	N/A	119-122	116-122
C-Ĉ-H (°)	N/A	N/A	N/A	117-119	114-121	N/A	N/A	N/A	N/A

Table S2. Range of bond distances (Å), and bond angles (°) for defect structures presented in figure 4. C-C in pristine graphene is 1.42 Å, and C-Ĉ-C is 120°.



Projected Density of States for Defective Graphene

Figure S3. Projected density of states for a) nitrogen substituted carbon site, b) carbon vacancy, c) combination of carbon vacancy and nitrogen substituted carbon site, d) passivated c), e) passivated carbon vacancy, f) graphene with carbon vacancy, and oxygen substitutions around the vacancy site, g) oxygen substituted carbon, h) carbon vacancy with NN carbon sites substituted with oxygen and nitrogen, respectively, and i) one oxygen, and one nitrogen substituted carbon.. ×2, ×3, and ×4 indicates that PDOS has been multiplied by a factor of 2, 3, or 4, respectively, for ease of viewing.

Metal Adsorption Energy on Defective Graphene

	Li	Na	K
Non-defective	-1.22	-0.62	-1.05
N _C	-0.85	-0.40	-0.85
V _C	-2.72	-2.03	-2.14
N _C V _C	-3.08	-2.30	-2.43
N _C V _C -pass	-2.50	-1.76	-1.97
V _C -pass	-2.07	-1.45	-1.80
3O _C	-2.28	-1.35	-1.48
2O _C	-1.64	-0.67	-1.15
N _C 2O _C	-2.79	-1.68	-1.74
O _C N _C	-3.63	-2.90	-3.06

Table S3. Metal adsorption energy(in eV) on defective carbon surface.

Metal Migration Paths on Defective Surfaces



Figure S4. End and starting points for metal migration for graphene sheet with N_{C} defect.

Table S4.	Barrier	for metal	migration	from 1	N _C defect.
14010 0 1.	Darrer	ioi iiiotai	moration		

		E	_b (eV)	
Metal	Path 1-2	Path 1-3	Path 1-4	Path 1-5
Li	0.22	0.24	0.28	0.26
Na	0.12	0.12	0.13	0.13
K	0.07	0.09	0.10	0.10



Figure S5. End and starting points for metal migration for graphene sheet with $N_{\rm C}V_{\rm C}$ defect.

Table S5. Barrier for metal migration from $N_{C}V_{C}$ defect.

E _b (eV)									
Metal	Path 1-3	Path 1-4	Path 1-5	Path 1-6	Path 2-3	Path 2-4	Path 6-7		
Li	0.86	1.02	1.20	0.76	0.41	0.53	0.46		
Na	0.001	0.001	0.81	0.0006	0.01	0.0005	0.68		
Κ	0.0009	0.002	0.49	0.002	0.15	0.16	0.42		



Figure S6. End and starting points for metal migration for graphene sheet with $N_C V_C$ -pass defect.

Tabla	86	Dorrior	for motal	migration	from	N-V-no	an defeat
Table	50.	Darrier	101 metal	Ingration	nom	INC V C-pa	ss ucicci.

E _b (eV)								
Metal	Path 1-2	Path 1-3	Path 1-4	Path 2-6	Path 5-4	Path 7-8		
Li	0.72	0.78	0.67	0.22	0.68	0.85		
Na	0.45	0.49	0.00	0.17	0.01	0.54		
K	1.02	0.56	0.18	0.17	0.17	0.39		



Figure S7. End and starting points for metal migration for graphene sheet with $N_C 2O_C$ defect.

Table S7. Barrier for metal migration from $N_C 2O_C$ defect.

E _b (eV)								
Metal	Path 1-2	Path 1-3	Path 1-4	Path 1-5	Path 1-6			
Li	1.74	1.62	1.42	1.62	1.73			
Na	1.07	0.001	0.002	0.86	0.99			
K	0.64	0.06	0.001	0.04	0.61			



Figure S8. End and starting points for metal migration for graphene sheet with V_C defect. Table S8. Barrier for metal migration from V_C defect.

E	E _b (eV)					
Metal	Path 1-2					
Li	0.77					
Na	0.27					
K	0.49					



Figure S9. End and starting points for metal migration for graphene sheet with passivated V_C defect.

Table S9. Barrier for metal migration from passivated V_C defect.

E _b (eV)					
Metal	Path 1-2				
Li	0.36				
Na	0.27				
K	0.09				



Figure S10. End and starting points for metal migration for graphene sheet with $O_C N_C$ defect.

Table S10. Barrier for metal migration from $O_C N_C$ defect.

	E _b (eV)	
Metal	Path 1-2	Path 1-3
Li	2.22	0.63
Na	2.28	2.12
K	1.80	1.51



Figure S11. End and starting points for metal migration for graphene sheet with $2O_C$ defect.

Table S11. Barrier for metal migration from $2O_C$ defect.

E _b (eV)		
Metal	Path 1-2	
Li	0.93	
Na	0.18	
K	0.40	



Figure S12. End and starting points for metal migration for graphene sheet with $3O_C$ defect.

Table S12. Barrier for metal migration from 3O_C defect.

E _b (eV)		
Metal	Path 1-2	
Li	1.11	
Na	0.34	
Κ	0.32	

Metal Migration on Defective Surfaces for Less Probable Defects



Figure S13. Migration paths for Li, Na, and K following migration path a) 1-5, b) 2-3, and c) 6-7 for defective surface with N_CV_C defect.

Figure S13 shows the metal migration on the carbon surface with a carbon vacancy in conjunction with a substitutional nitrogen defect (N_CV_C). The migration of a Li atom away from the defect site has a minimum energy barrier of 0.76 eV (Table S5), and migration over the defect have migration barriers of 0.53 eV (Table S5). Hence, even if this defect is not directly binding the Li atom, it does hinder its mobility. Similarly, the migration energy barriers of a Na atom are increased by approximately 0.5 eV. K migration from the five-membered ring to the adjacent hole site (path 2-3 Figure S13) have slightly larger migration energy barriers

(0.15 eV Figure S13) than on the pristine surface, but no significant difference that would alter K migration behavior. Moving a K atom between two hole sites either side of the defect (path 6-7 Figure S13c), and likewise from the middle of the defect to a hole site next nearest neighbor to the nitrogen site (path 1-5 Figure S13a) face a ~0.3 eV higher barrier, similar to the situation found for Na. Hence, it is likely that the dominating K ion migration pathway is the one shown in Figure S13b. The presence of the N_CV_C defect on the surface is, as expected from the defect formation energy, very unlikely, and if it does exist, it will be in very small concentrations. Hence, the N_eV_C defect could be detrimental for LIBs and SIBs if the metals encounter this defect. For PIBs on the other hand, the lower energy migration paths available for this defect should be dominating over the higher energy ones, and trapping in terms of metal migration should hence be limited.



Figure S14. Migration paths for metals on graphene sheet with N_CV_C -pass defect, and migration paths a) 1-2, b) 1-3, c) 7-8.

Passivating the carbon vacancy in the defect discussed in the previous section (N_CV_C -pass), lowers the metal migration energy barriers (Figure S14) as compared to N_CV_C . However, E_b compared to the pristine carbon surface is still higher for all metals, and the centre of the defect acts as a metal ion trapping site. From a practical point of view, these high migration barriers should not be detrimental to anode performance, as the concentration of this defect is calculated to be very low, indeed the probability for Li, Na, or K to encounter a N_CV_C -pass defect is much lower than for any of the other defects.



Figure S15. a) End and starting points for metal migration for graphene sheet with V_c defect, and b) 1-2 migration path.

Figure S15 shows the metal migration on carbon surface with a single carbon vacancy (V_C) . The diffusion of metals adsorbed on a V_C site would be slower than on the pristine surface, and an increase of migration activation barriers of ~0.4 eV are observed for all metal ions. As seen for other defects above, Li ion has the highest energy barrier, but Na ion migration has a lower barrier than K ion migration.

Passivation of the carbon vacancy (Figure S16), lowers the metal migration barriers, offering a similar situation to the N_CV_C and the passivated N_CV_C defects. Hence, it can be construed that passivating the surface carbon vacancies in anode materials could reduce the trapping effect of vacancies and increase metal mobility to values close to those at the pristine carbon surface.



Figure S16. a) End and starting points for metal migration for graphene sheet with passivated V_C defect, and b) 1-2 migration path.

Substitution of three carbons with oxygen ions (Figure S17) leads to strong adsorption of Li, but weaker adsorption of Na and K. This difference in adsorption strength could be used to explain the difference in metal migration barriers seen for the $3O_C$ defect in Figure S17, where the barrier for Li migration is 0.7 eV higher than for Na or K migration. The Na and K diffusion around this defect will be energetically more expensive than on pristine surface, but should still be quick at NIB and PIB operating temperatures. Fortunately, the formation energy of the $3O_C$ defect is very high, and hence its influence on LIB anode cycling should be limited.



Figure S17. a) End and starting points for metal migration for graphene sheet with $3O_C$ defect with b) 1-2 migration path.