Supplementary information

Part I Positions considered in AA, AB and AB-r

AA

B site: Same as on graphene sheet, the Li atom could reside in the middle of C-C bond between the graphene layer and the molecule layer.

H site: Same as on graphene sheet, the Li atom could reside in the center of the C ring of both the C6O6 layer and graphene layer and on z axis in the middle of the two layers.

T site: The Li atom resides both on the top of the C atom of the graphene and beneath the C atom of the C6O6 molecule.

D1 site: The Li atom interact with only one oxygen atom of C6O6 molecule.

D2 site: The Li atom interact with two oxygen atoms of C6O6 molecule.

Far site: The Li atom resides three carbon rings away from the center of C6O6 molecule on the graphene layer.

Far site 2: The Li atom resides average two and a half carbon rings away from the center of C6O6 molecule on the graphene layer.

Out site: The Li atom is set far above graphene and C6O6 molecule to make sure no interaction between Li atom and AB system.

AB

T site: The Li atom resides in the center of the C ring of the C_6O_6 layer and on one C atom of the graphene layer

H site: The Li atom resides both in the middle of graphene ring and beneath one C atom of C_6O_6 ring.

B site: The Li atom resides both in the middle of C-C bond of graphene and in the ring zone of C_6O_6 molecule.

Half hollow site: The Li atom resides in the middle of both ring zone of graphene and C_6O_6 molecule.

B' site: The Li atom resides beneath the C-C bond of C_6O_6 molecule.

D1 site: The Li atom interact with only one oxygen atom of C_6O_6 molecule.

D2 site: The Li atom interact with two oxygen atoms of C_6O_6 molecule.

Out site: The Li atom is set far above graphene and C_6O_6 molecule to make sure no interaction between Li atom and AB system.

AB-r

T site: The Li atom resides in the center of the C ring of the C_6O_6 layer and on one C atom of the graphene layer

T2 site: The Li atom resides on one C atom of the graphene layer but not in the ring range of C_6O_6.

B site: The Li atom resides both in the middle of C-C bond of graphene and in the ring zone of C_6O_6 molecule.

Half hollow site: The Li atom resides in the middle of both ring zone of graphene and C_6O_6 molecule.

B' site: The Li atom resides both in the middle of C-C bond of C_6O_6 molecule and in the middle of ring zone of graphene.

T' site: The Li atom resides beneath one C of the C_6O_6 molecule.

B'2 site: The Li atom resides both in the middle of C-C bond of C6O6 molecule and near the top site of one carbon atom of graphene.

D1 site: The Li atom interact with only one oxygen atom of C_6O_6 molecule.

D2 site: The Li atom interact with two oxygen atoms of C_6O_6 molecule.

D2' site: The Li atom interact with two oxygen atoms of C_6O_6 molecule, while the graphene atom distribution is not totally same with D2 site.

Out site: The Li atom is set far above graphene and C_6O_6 molecule to make sure no interaction between Li atom and AB system.

Part II.1 The Li atom evolution in AA configuration

We have built 128 types of structures containing from 1 to 12 Li atoms in the structure. AA configuration with 1 Li atom has already been discussed in main text. All structures degenerated into three types: D1, D2 and H.

For 2 Li atoms, our consideration starts from the combination of two of these three types. For the notation of our structures, we follow two principles. Firstly, for example, for the combination of D1 and H, we name it D1-H; for the combination of D1 and D2, we name it D2-D1. It has to be noted that we put the more stable structure in the front. Secondly, for a hexangular ring from geometry point of view, if one point is set, another point could have three basic place to be set, that is adjacent point, alternate point and opposite point. Thus, to signify the relative position, we notate ad, al and op as suffix. For example, D2-D1-al means there are two Li atoms in the structure and the two Li atoms are set alternately around the ring. Totally, we got 11 structures of two Li atoms, they are D1-H, D2-H, 2-D1-ad, 2-D1-al, 2-D1-op, 2-D2-ad, 2-D2-al, 2-D2-op, D2-D1-ad, D2-D1-al, D2-D1-op. After our calculations of geometry optimization, we find five of them is unstable under our calculation restriction, they are 2D1-ad, 2D1-al, 2D1-op, D2-D1-ad and D2-D1-op.

For 3 Li atoms, follow the same principle discussed above, we build totally 22 types of structures. We have to add one suffix “oneside” to modify three adjacent Li atoms. So these notations are 3D2-oneside, 3D1-oneside, 3D2-al, 3D1-al, 2D2-ad-H, 2D2-al-H,2D2-op-H, 2D2-op-D1-al, 2D2-op-D1-ad, 2D2-al-D1-op, 2D2-D2-op, 2D2-D1-op, 2D2-D1-oneside, D2-2D1-oneside, 2D1-D1-op, 2D1-D2-op, 2D1-op-H, 2D1-al-H, 2D1-ad-H, D2-D1-ad-H, D2-D1-al-H and D2-D1-op-H. Also, we find only 10 of them keep unchanged after geometry calculation.

For 4 Li atoms, based on the 10 structures of 3 Li atoms, we build 19 types of structures. They are 3D2-D2, 2D2-2D2-op, 4D2-oneside, 4D1-oneside, 2D2-ad-D2-

op-H, 3D2-oneside-H, 3D2-al-H, 3D1-al-H, 2D2-2D1-oneside, 2D2-D1-op-H, 2D2-D1-oneside-D1-al, 2D2-D1-oneside-D1-op , 2D2-op-2D1-op-al , 2D2-op-D1-al-H , 3D2-oneside-D1-al , 2D2-D1-oneside-D2-al.

For 5 Li atoms, we build 10 types of structures. They are 5D2, 3D2-D2-op-H, 4D2-oneside-H, 2D2-2D2-op-H, 3D2-2D1-oneside, 3D1-D1-op-H, 4D2-oneside-D1-op, 2D2-op-2D1-op-al-H, 3D1-al-D2-al-H, 3D2-oneside-D1-al-H.

For 6 Li atoms, we build 10 types of structures. They are 6-D2, 5D2-H, 5D2-D1-al, 5D2-D1-op, 5D2-oneside-D1-ad, 4D2-oneside-D1-op-H, 2D2-D1-oneside-op, 5D2-down-1D2-up-ad, 5D2-down-1D2-up-al, 5D2-down-1D2-up-op. Here, we test up and down type of stacking because in 7 Li atoms' condition, this type is most stable.

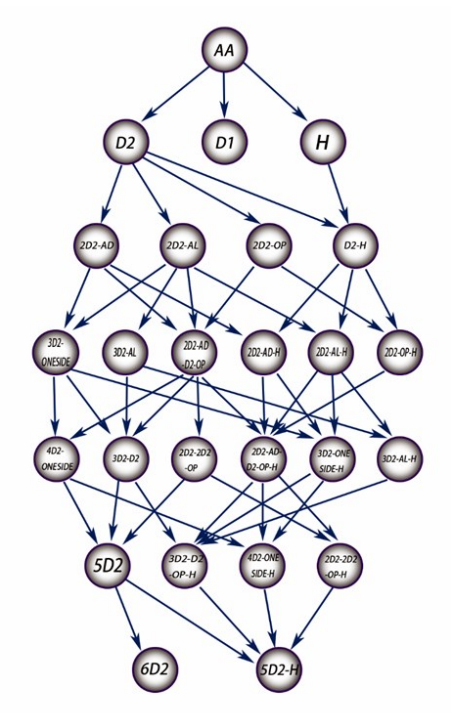


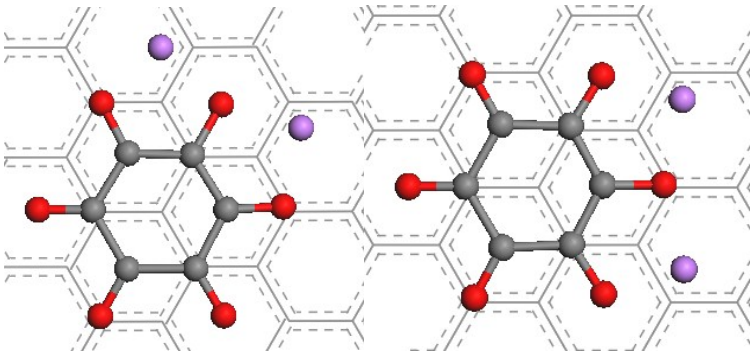
Figure S1. The sketch map of insertion process of Li from 0 to 6 atoms for configuration AA. Note that only D2 and H structures are included in this map.

Part II.2 The Li atom evolution in AB and AB-r configuration

In these two configurations, very similar to AA configuration, Li atom could settle at D2 and D1 position. However, H site in AA will transfer to T site in AB and AB-r.

We built 44 types of structures for AB configuration.

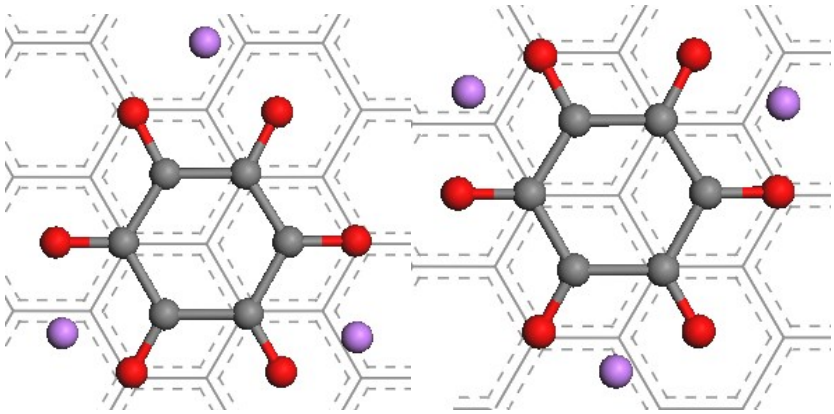
For 2 Li atoms, we build 6 types of structures. They are 2D2-ad, 2D2-ad-II, 2D2-al, 2D2-op, D2-T and D1-T. Here 2D2-ad has two types shown below in Figure S2. The result shows very little difference between them.



(a) (b)

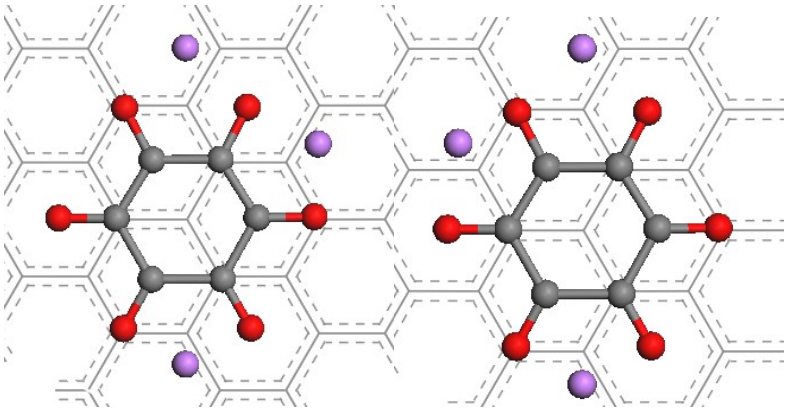
Figure S2. 2D2-ad and 2D2-ad' are shown in (a) and (b), respectively.

For 3 Li atoms, we build 8 types of structures. They are 3D2-al-and-al, 3D2-al-and-al-2, 3D2-oneside, 2D2-ad-T, 2D2-al-T, 2D2-op-T, 2D2-1-two-I and 2D2-1-two-II. Here 3D2-al-and-al and 2D2-D2-op has two types shown in Figure S3 and Figure S4.



(a) (b)

Figure S3. 3D2-al-and-al-I and 3D2-al-and-al-II are shown in (a) and (b), respectively.



(a) (b)

Figure S4. 2D2-D2-op-I and 2D2-D2-op--II are shown in (a) and (b), respectively.

For 4 Li atoms, we build 8 types of structures. They are 3D2-D2, 4D2-oneside, 2D2-2D2-op, 3D2-al-and-al-T, 3D2-al-and-al-2-T, 3D2-oneside-T, 2D2-D2-op-I-T and 2D2-D2-op-II-T.

For 5 Li atoms, we build 7 types of structures. They are 5D2, 3D2-D2-T-I, 2D2-2D2-T-I, 2D2-2D2-T-II, 3D2-1D1-T-II, 4D2-oneside-T-I, 4D2-oneside-T-II.

For more than 5 Li atoms, we build 7 types of structures. They are 6D2, 6-D2-down-1-D2-up, 6-D2-down-2-D2-up-op, 6-D2-down-3-D2-up-al, 6-D2-down-2-D2-op-up, 6-D2-down-5-D2-up, 6-D2-down-6-D2-up.

We built 28 types of structures for AB-r configuration.

For 2 Li atoms, we build 5 types of structures. They are 2-Li-2D2-al, 2D2-ad, 2D2-op, D2-T-I and D2-T-II.

For 3 Li atoms, we build 4 types of structures. They are 3D2-al-I, 3D2-al-II, 3D2-oneside-1 and 3D2-oneside-2.

For more than 3 Li atoms, we build 9 types of structures. They are D2-D2-op, 5D2, 6D2, 6-D2-down-1-D2-up, 6-D2-down-2-D2-up-al, 6-D2-down-3-D2-up-al, 6-D2-down-4-D2-up-op, 6-D2-down-5-D2-up and 6-D2-down-6-D2-up.

Part III The method used in calculating the possibility of multi-Li atoms insertion

As discussed in main article, the D2 site is the most stable of all sites. It was hypothesized that each newly-added Li preferred the D2 site to the D1 and others. Note that only 6 D2 sites are always available in each structure. The maximum number of D1 sites is also 6, however, according the calculations, D1 cannot exist itself independently in most circumstances. According to this principle, a total of 129 kinds of configuration AA, 44 kinds of configuration AB, 29 kinds of configuration AB-r are calculated.

The formation energy of each structure corresponds to one circle in this network, and the formation energies are listed in Table S1 including those structures with D1 bonds. The unstable sites are grey in color. If a designed structure is not stable, such as the T site, it will degenerate into a D1, and its derivatives will not be considered in the following Li-adding process. To distinguish the position relation between the existing Li atoms and those newly added, the suffixes for adjacent, alternate and opposite, i.e. ad, al and op are used. Table S1 in the supplementary material shows the corresponding relations of notation and binding energy of Li atoms for configuration AA.

Table S1. Adsorption energy of each Li atoms for all possible structures of configuration AA. Those structures in grey are unstable in this calculation frame.

Type	Adsorption energy of average Li (eV)	Type	Adsorption energy of average Li (eV)	Type	Adsorption energy of average Li (eV)	Type	Adsorption energy of average Li (eV)
1- Li- H	0.695	3- Li- 2D2- D2- op	2.240	4- Li- 2D2- D1- oneside- D2- ad	2.067	8- Li- 6D2- D1- H	1.439
1- Li- T	1.961	3- Li- 2D2- D1- op	2.246	4- Li- 2D2- D1- oneside- H	1.646	8- Li- 6D2- 2D1- ad	1.401
1- Li- B	2.588	3- Li- 2D2- D1- oneside	1.490	5- Li- D2	1.975	8- Li- 6D2- 2D1- al	1.309
1- Li- D1	1.954	3- Li- 2D1- D1- op	2.083	5- Li- 3D2- D2- op- H	1.659	8- Li- 6D2- 2D1- op	1.319
1- Li- D2	2.581	3- Li- 2D1- D2- op	2.276	5- Li- 4D2- oneside- H	1.662	8- Li- 6D2- down- 2D2- ad	1.501
1- Li- far	0.474	3- Li- 2D1- op- H	1.556	5- Li- 2D2- 2D2- op- H	1.697	8- Li- 6D2- down- 2D2- al	1.550
1- Li- far2	2.585	3- Li- 2D1- al- H	1.232	5- Li- 3D2- 2D1- oneside	1.953	8- Li- 6D2- down- 2D2- op	1.555
1- Li- Out	0.160	3- Li- 2D1- ad- H	1.674	5- Li- 3D1- D1- op- H	1.423	8- Li- 6D2- down- 1D2- 1D1- ad	1.413
2- Li- D2- H	1.534	3- Li- D2- 2D1- oneside	2.198	5- Li- 4D2- oneside- D1- op	1.840	8- Li- 6D2- down- 1D2- 1D1- al	1.549
2- Li- D1- H	1.178	3- Li- D2- D1- op- H	1.665	5- Li- 2D2- op- 2D1- op- al- H	1.426	8- Li- 6D2- down- 1D2- 1D1- op	1.531
2- Li- 2D2- al	2.513	3- Li- D2- D1- al- H	1.661	5- Li- 3D1- al- D2- al- H	1.661	9- Li- 6D2- 3D1- oneside	1.169
2- Li- 2D2- ad	2.465	3- Li- D2- D1- ad- H	1.659	5- Li- 3D2- oneside- D1- al- H	1.521	9- Li- 6D2- 3D1- al	1.297
2- Li- 2D2- op	2.463	4- Li- 3D2- D2- op	2.071	6- Li- D2	1.909	9- 6D2- 2D1- ad- 1D1- op	1.208
2- Li- 2D1- al	2.400	4- Li- 2D2- 2D2- op	2.105	6- Li- 5D2- H	1.682	9- Li- 6D2- 2D1- op- H	1.099
2- Li- 2D1- ad	2.510	4- Li- 4D2- oneside	2.057	6- Li- 5D2- D1- al	1.564	9- Li- 6D2- down- 3D2- up- al	1.289
2- Li- 2D1- op	2.523	4- Li- 4D1- oneside	2.082	6- Li- 5D2- D1- op	1.655	10- Li- 6D2- 4D1- oneside	1.025
2- Li- D2- D1- al	2.216	4- Li- 2D2- ad- D2- op- H	1.681	6- Li- 5D2- oneside- D1- ad	1.910	10- Li- 6D2- 3D1- al- H	1.060
2- Li- D2- D1- ad	2.482	4- Li- 2D2- ad- D1- op- H	1.659	6- Li- 4D2- oneside- D1- op- H	1.559	10- Li- 6D2- 2D1- ad- 1D1- op- H	1.093
2- Li- D2- D1- op	2.527	4- Li- 3D2- oneside- H	1.645	6- Li- 2D2- D1- oneside- op	1.265	10- Li- 6D2- 4D1- op	1.036
3- Li- 3D2- oneside	2.200	4- Li- 3D2- al- H	1.678	6- Li- 5D2- down- 1D2- up- ad	1.694	10- Li- 6D2- down- 2D2- 2D2- up- op	1.041
3- Li- 3D2- al	2.275	4- Li- 3D1- al- H	1.139	6- Li- 5D2- down- 1D2- up- al	1.651	11- Li- 6D2- 5D1	0.862
3- Li- 3D1- al	1.629	4- Li- 2D2- 2D1- oneside	2.063	6- Li- 5D2- down- 1D2- up- op	1.628	11- Li- 6D2- 5D1- ba	0.975
3- Li- 3D1- oneside	2.090	4- Li- 2D2- al- D1- op- H	1.600	7- Li- 6D2- H	1.706	11- Li- 6D2- up- 5D2- down	0.875
3- Li- 2D2- op- H	1.635	4- Li- 2D2- 1D1- oneside- D1- al	1.955	7- Li- 6D2- D1	1.577	11- Li- 5D2- up- 6D2- down	0.879
3- Li- 2D2- op- D1- al	2.068	4- Li- D2D2- D1- oneside- D1- op	1.908	7- Li- 6D2- D1- ba	1.706	11- Li- 6D2- 4D1- oneside- H	0.939
3- Li- 2D2- op- D1- ad	2.244	4- Li- 2D2- op- 2D1- op- al	1.811	7- Li- 5D2- 2D1- al	1.250	11- Li- 6D2- 4D1- oneside- H- ba	0.989
3- Li- 2D2- al- H	1.666	4- Li- 2D2- op- D1- al- H	1.506	7- Li- 5D2- 2D1- op	1.279	11- Li- 6D2- 4D1- op- H	0.958
3- Li- 2D2- ad- H	1.656	4- Li- 3D2- oneside- D1- al	1.918	7- Li- 5D2- 2D1- ad	1.229	12- Li- 6D2- up- 6- D2- down	0.881
3- Li- 2D2- al- D1- op	2.083	4- Li- 2D2- D1- oneside- D2- al	2.066	7- Li- 5D2- oneside- D1- ad- H	1.707	12- Li- 6D1- 5- D2- H	0.866

To simulate the real voltage process accurately, all possible processes from AA to 6-

D2 or 5-D2-H are investigated. For a total of 639 types of process, the probability of each small step is defined as:

$$P_{i,j} = \Delta E_{i,j} = -(E_{i,j} - E_{i-1,j}) .$$

where $P_{i,j}$ is the absolute probability of j steps and i represents the number of Li atoms. The corresponding voltage for each step is:

$$V_{i,j} = -(E_{i,j} - E_{Li} - E_{i-1,j}) .$$

The reduced voltage for different i of configurations AA is obtained thus:

$$V_i = \frac{\prod_j P_{i,j} \cdot V_{i,j}}{\sum_j P_{i,j}} .$$