



## Full Length Article

# A study of the most condensed configuration of oxocarbon molecule adsorption on graphene surface: A first-principle investigation

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## ABSTRACT

In our previous study, oxocarbon molecule  $C_6O_6$  was adopted as the active material for the electrode of Li-ion batteries. The cycling performance of organic electrodes could be increased by polymerization or adsorption on backbone materials like graphite or graphene. We choose the second method in our research system and have proven this system has at least 155 mAh/g theoretical capacity. In this research, we systematically investigate 11 different kinds of adsorption densities of  $C_6O_6$  on mono-graphene sheet by density functional theory. Lennard-Jones potential is introduced to calculate the interaction on X-Y plane and adsorption and distortion energy are elucidated separately. A proper graphene layer distance of  $\sim 7.7$  Å is determined. The results imply the maximum theoretical capacity is  $\sim 290$  mAh/g with relative lowest distortion. This combined material possess 2.04 V average voltage and improved conductivity, which can be compared to traditional in-organic materials like  $LiCoO_2$  or  $LiFePO_4$ .

## 1. Introduction

State-of-art Lithium-ion batteries (LIB) is drawing attention widely in recent years. Small size electrical applicants and new energy vehicles (NEV) demand new energy storages with longer cycling performance and higher energy density. Most cathode material of LIB are transition metal oxides in traditional battery industry while in the future organic-based electrodes provide new solutions for cheaper and easier-recycling electrode materials [1–3].

During these years' development, organic-based materials has already obtained high voltage and cycle performance as a competitive contender to traditional Li-ion batteries [2,4–6]. Organic electrode materials contain a functional group of quinone, anhydride, or nitroxide radical. However, most of them perform well at the first cycle, but show remarkable solubility in the electrolyte. Moreover, multiple redox steps due to multiple reaction mechanisms and polarization of active materials have not been well-solved [7]. To improve the cycling performance, polymerization is proved to be an effective method to reduce the solubility of active materials into electrolyte. Another way is to adsorb active materials on some carbon-based 3D scaffold materials like graphite or graphene [8–10].

Recently, oxocarbon  $C_nO_n$  with a high oxygen proportion has been received considerable attention [3,11–17], and in particular, the  $C_6O_6$ -based alkali metal ion electrodes are increasingly favored. In our

previous work, the theoretical capacity and lithiation potential of the material  $C_6O_6$ @graphene nanocompound are calculated by density functional theory (DFT), which are  $\sim 155$  mAh/g and  $\sim 2.6$  V, respectively [18]. After proving the reasonability of this combination as Li-ion battery electrode, further usage potential about the maximum capacity and conductivity is intriguing and necessary for experimental study. Our paper will based on threefold investigations: (i) To clarify the best theoretical density of  $C_6O_6$  molecule on two dimension single graphene layer surface when considering the inter-molecule forces and so-caused distortion of molecule, we introduce Lennard-Jones potential in our DFT framework. (ii) To acquire the best volume density, the distance of graphene layers should be quantitative calculated. (iii) As all know, electrode materials should be conductive and have enough theoretical lithiation voltage, we will prove this  $C_6O_6$ @graphene combination is affordable in these two aspects. In this paper, we focus on the best 3D concentration ratio of  $C_6O_6$  molecule to graphene sheet in order to realize the full usage and acquire the largest capacity of this kind organic molecule based electrode. We will show an extensive method to investigate best density of molecules adsorbing on layered material like graphene and other surface materials. This work give valuable reference for preparation of novel organic molecule based Li-ion battery electrode material.

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## 2. Models and computational details

We used the Perdew-Burke-Ernzerhof (PBE) [19] form (generalized gradient approximation (GGA) [20]) with the projector augmented wave (PAW) [21,22] method for exchange and correlation functions from Vienna Ab-initio Simulation Package (VASP) [23–25]. In previous work, vdW dispersion-corrected DFT have been proved to have great success in organic chemistry or biochemistry [26–28]. Throughout this calculation, ordinary DFT calculation based on PBE and the DFT with van der Waals (vdW) method D2-correction in the VASP scheme [29–31] has been adapted for reference. An energy cutoff of 520 eV is used in the plane wave expansion of wave functions. The maximum Brillouin zones of the  $6 \times 6$  super cell are sampled with  $\Gamma$ -centered k-point grids of  $6 \times 6 \times 1$ . More Brillouin zones for smaller models are chosen with the same cutoff energy and k-point grids. To avoid the spurious coupling effect between periodic graphene layers along the z-direction, the vacuum separation in the model structure is set to 20 Å. All atoms and supercell lattice vectors are relaxed with a force tolerance of 0.01 eV/Å. As AB site is easy to identify and under most conditions has the largest adsorption energy, we choose AB site to build model in this article [32,33].

In our previous work, we ignored the interaction of neighbouring  $C_6O_6$  molecules in X-Y plane [18], thus the adsorption energy between a single  $C_6O_6$  molecule and graphene layer is:

$$E_{adsorption} = E_{graphene} + E_{C_6O_6} - E_{xxy} \quad (1)$$

If the interaction energy between  $C_6O_6$  molecules is considered in this work, the energy is named as “condensed energy”  $E_{condensed}$ . Then we could rewrite the formula into:

$$E_{adsorption} = E_{graphene} + E_{C_6O_6} - E_{xxy} + E_{condensed} \quad (2)$$

And further, the condensed energy contains two parts, one part is the energy caused by the distortion of the molecule (the distortion of graphene is small and can be ignored), another part is caused by the attractive and repulsive force interaction, which should obey the Lennard-Jones potential [34,35] and only change with distance of two molecule. Thus,

$$E_{condensed} = E_{distortion} + E(r) = E_{distortion} + \sum_i \left( \frac{A}{r_i^6} + \frac{B}{r_i^{12}} \right) \quad (3)$$

A and B represent the attractive and repulsive constant respectively. For the first part  $E_{distortion}$ , we sketchily consider it only depends on whether the molecule has distortion, and the distortion depends on the force from neighbour molecules, namely the distance of neighbour molecules. For the second part, seen from Fig. 1, it should be mentioned we just consider the neighbour eight molecules, namely four site centres  $r_i$ s (one is along X axis, one is along Y axis, and two along diagonals) for each molecule. Thus, aiming to evaluate the distortion and adsorption energy of molecules and graphene depend on the  $E_{condensed}$ , the less condensed it is, the larger  $E_{adsorption}$  is and the tighter physisorption is.

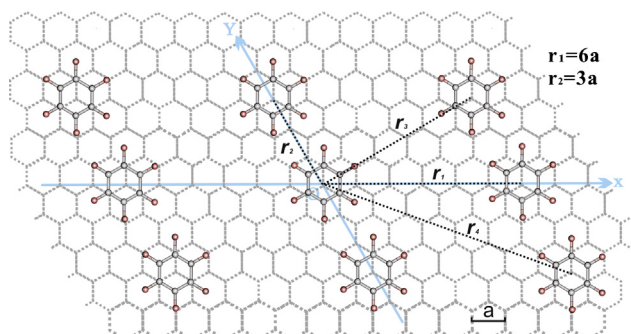


Fig. 1. The sketch picture of distance  $r_1$  to  $r_4$  of neighbouring 8 molecules for 3a-6a configuration from top view.

Finally, the equations are like this:

$$E_{distortion} + 2 \left( \sum_{i=1,2,3,4} \frac{A}{r_i^6} + \frac{B}{r_i^{12}} \right) = E_{adsorption} + E_{xxy} - E_{C_6O_6} - E_{graphene} \quad (4)$$

## 3. Results and discussion

### 3.1. Density on X-Y plane

Based on the group theory, graphene belongs to complex lattice and has two sets of grids. For each grid, the included angle of X axis and Y axis is  $60^\circ$  or  $120^\circ$ . Therefore, we could definite the distance of neighbour  $C_6O_6$  molecules in an  $x \times y$  grid with unit distance  $a$  as one carbon ring. In order to investigate the maximum capacity, we could either insert more  $C_6O_6$  molecules, which leads more lithium atoms adsorbed into fixed supercell, or keep the number of molecules within smaller volume of supercell, which means reduce the area of graphene layer meanwhile keep one  $C_6O_6$  molecule in the supercell. The core scientific issue is the mass ratio  $\eta$  of  $C_6O_6$  molecule to certain area of monolayer graphene in the supercell. From this aspect, these two method are theoretical the same while the latter one has less calculation amount than the former one due to less atoms in supercell, then less computational resource is needed. Here in this work, we adopt the method of reducing the supercell to study the relationship of the maximum capacity and the percentage of  $C_6O_6$  molecule.

Based on above, adsorption calculation of system without Li atoms are performed firstly. As X axis and Y axis is in mirror symmetry, there is no need to distinguish their sequential order in multiplication. For example, one couldn't tell the difference of  $4a \times 5a$  from  $5a \times 4a$ . From our calculation 3 carbon ring's distance is the minimum distance of two neighbour  $C_6O_6$  molecules. Furthermore, we choose the AB configuration in previous work due to its high adsorption energy. Finally, we build 11 types of X by Y and the results of the binding energies between graphene and  $C_6O_6$  molecule are listed in Table 1. The x and y in notation xa-ya denotes  $r_1$  and  $r_2$  in Fig. 1.

For the value of  $E_{adsorption}$ , it could be calculated in the following way. Do the geometry optimization after fully relaxation, then the most stable configurations under different ratios are found. After this, the free energy of  $C_6O_6$  molecules and graphene are calculated separately with each of the atoms fixed. Thus, the  $E_{condensed}$  energy is included inside of the free energy of  $C_6O_6$  molecules and the real adsorption energy  $E_{adsorption}$  could be calculated with Eq. (1).

By doing this, we could list a system of ten equations from 3a-3a to 6a-6a with twelve unknowns namely A, B and ten  $E_{distortion}$  values. It is supposed that within larger supercell, the smaller  $E_{distortion}$  would be. And after some certain scale, the value of distortion is zero. By introducing 7a-7a configuration, and making  $E_{distortion7 \times 7}$  equals to zero, we could solve the value of A, B and nine values of  $E_{distortion}$ .

For the condition without D2-DFT, a groups of parameters are obtained. The results were listed in Table 1. For condition with D2-DFT, as the vdW-correction has already contained, no need for the existence of

Table 1  
The distortion energy and value of A, B parameter of the system with and without vdW-correction.

value/distortion energy (eV)	A	B	3a-3a	3a-4a	3a-5a	3a-6a	4a-4a
With vdW	–	2.46	5.24	–9.75	–6.94	–6.79	–3.19
Without vdW	–36.82	18.35	3.31	8.65	–1.03	–4.31	–2.15
value/distortion energy (eV)	4a-5a	4a-6a	5a-5a	5a-6a	6a-6a	7a-7a	
With vdW	8.25	9.71	5.42	2.74	2.25	0	
Without vdW	7.37	6.22	5.02	4.17	0	0	

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