Enhanced adsorption of carbonyl molecules on graphene *via* π -Li- π interaction: a first-principle study

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ABSTRACT Carbonyl compounds with elements of C, H, and O and reversible redox-active centers are promising electrode materials in rechargeable batteries owing to their high theoretical capacity, structure flexibility and resources abundance. However, the low conductivity and the dissolution of active molecules in organic electrolyte limit the practical application. Immobilizing the carbonyls on graphene provides a simple approach to address these two issues. However, most reported interaction between carbon-based substrates and carbonyl compounds is weak π - π interaction, which is not strong enough to prohibit the detachment of active materials from carbon surface, and thus leading to undesirable cycling performance. Herein, we applied the first principle calculations to study the carbonyls-graphene interaction and found that the weak π - π interaction can be rationally converted to the strong π -Li- π interaction *via* introducing the groups containing Li atoms. The introduced Li atoms can cooperatively bind with the two aromatic π components through the covalent Li-carbonyl compounds interaction and Li-graphene interaction. The concept of π -Li- π interaction provides a versatile method to suppress the dissolution of active materials and increase the electronic conductivity at the same time, which gains insight into the design of organic electrode materials for rechargeable batteries with high performance.

Keywords: carbonyl compounds, π -Li- π interaction, graphene, density function theory (DFT), organic lithium battery

INTRODUCTION

Carbonyl compounds as active electrode materials in lithium-ion batteries have been gaining more and more attention due to their high theoretical capacities, molecular structure diversities, environmental friendliness and source abundance [1–5]. According to the redox mecha-

nisms, the organic redox-active compounds can be divided into four types: conducting polymers, organic sulfides, organic free radicals, and carbonyl compounds. Among them, carbonyl compounds exhibit high theoretical capacity with lithium inserting in C=O group to form enolates. However, they suffer from poor cycling and sluggish rate performance owing to their high solubility in traditional organic electrolyte and low conductivity [6,7]. Many attempts have been made to suppress the solubility such as polymerization [8–12], electrolyte optimization [13], anchoring on solid substrates [14] and formation of salts [15,16].

Synchronously, the carbon materials such as porous carbon, carbon fibers, carbon nanotubes (CNTs) and graphene have been used as conductive substrates to improve the electronic conductivity of organic electrode [17–20]. Moreover, the immobilization of active carbonyl molecules onto carbon materials especially graphene also offers an effective approach to suppress the dissolution [21–23]. Liang *et al.* [24] proved that introducing anthracene-9,10-dione (AQ) and its derivatives onto graphene is effective to prevent the dissolution. However, how the carbonyl molecules interact with graphene and its influence on electrochemical performance are still ambiguous. Meanwhile, theoretical simulations have also shown great potential in designing organic electrode materials for rechargeable batteries [25–27]. For instance, Yu's group [28,29] performed a dispersion-corrected density functional theory (DFT-D) study on a series of electroactive carbonyl compounds adsorbed on graphene, indicating the importance of the van der Waals (vdW) dispersion-corrected in physical adsorption.

Most previous work ascribed the improved performance

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to the physical π - π interaction between the small electroactive molecules and graphene. This typical π - π interaction is not strong enough to prevent detachment of the small carbonyl molecules from graphene surface [19,24]. The conception of π -metal- π has been proved to enhance the weak interaction between small molecules and graphene *via* doping graphene with metal atoms [30]. It is much stronger than the physical π - π interaction, in which the metal atom is critical to enhance the interaction between the two π parts *via* strong metal- π interaction. Therefore, it is interesting to increase the physical interaction between carbonyl molecules and graphene to strong π -metal- π interaction through introducing functional groups containing lithium atoms such as -OLi and -COOLi.

Herein, DFT calculations were performed to gain insight into the interaction between graphene and carbonyl molecules and their lithium salt derivatives, i.e., benzoquinone ($C_6H_4O_2$, BQ), lithium 3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate) ($Li_2C_6H_2O_4$, BQ-2OLi), lithium 3,6-dioxocyclohexa-1,4-diene-1,4-dicarboxylate ($Li_2C_6H_2O_6$, BQ-2COOLi), anthracene-9,10-dione ($C_{14}H_8O_2$, AQ), lithium 9,10-dioxo-9,10-dihydroanthracene-1,5-bis(olate) ($Li_2C_{14}H_6O_4$, AQ-2OLi) and lithium 9,10-dioxo-9,10-dihydroanthracene-2,6-dicarboxylate ($Li_2C_{16}H_6O_6$, AQ-2COOLi), as shown in Fig. 1a. The adsorption configurations, charge transfer properties and electronic structures were systematically investigated. The results demonstrate that it can be a general approach to introduce -OLi or -COOLi group to enhance the adsorption of organic electrode molecules on graphene *via* π -Li- π interaction. This can significantly prevent dissolution and

increase electronic conductivity of carbonyl molecules.

COMPUTATIONAL METHODS

The spin-polarized DFT calculations were performed by using Vienna *ab initio* Simulation Package (VASP) [31]. The projector augmented wave (PAW) method and generalized gradient approximation (GGA) with the function of Perdew-Burke-Ernzerhof (PBE) [32,33] were employed. The cut-off energy for plane-wave basis was set to 400 eV. The total energy and the residual Hellmann-Feynman force were converged to 10^{-5} eV/atom and 0.01 eV $\text{\AA}^{-1}$, respectively. The vacuum layers of 20 $\text{\AA}$ along z direction were adopted to avoid interacting between graphene repetitiveness. All the adsorbate molecules were individually put in a $15 \text{ \AA} \times 16 \text{ \AA} \times 17 \text{ \AA}$ box and then relaxed with Gamma point. The organic molecules/graphene model was implemented through anchoring the molecules on graphene surface with a distance about 2.5 $\text{\AA}$. Then, the geometry relaxation was performed using a $3 \times 3 \times 1$ k -point mesh. Since the PBE-D2 has been demonstrated as a powerful method to study the organic electrode material of lithium battery [34,35]. Thus, the DFT-D2 method of Grimme [36] was employed to consider the inter-molecular and intra-molecular dispersion interactions. The default values of the atomic dispersion coefficients, atomic radii, and scaling parameters were used.

The adsorption energy (E_{ads}) was applied to describe the relative thermodynamic stability of each configuration. The E_{ads} was defined as:

$$E_{\text{ads}} = E(\text{graphene-M}) - E(\text{graphene}) - E(M), \quad (1)$$

where $E(\text{graphene-M})$, $E(\text{graphene})$ and $E(M)$ represent the energy of electrode molecules adsorbed on graphene, graphene and isolated electrode molecules, respectively. The negative value of E_{ads} means the configuration is thermodynamically stable. The more negative value of E_{ads} corresponds to the more stable configuration.

Charge density difference is a useful tool to investigate the charge transfer as well as the binding nature of the adsorbed system. It is defined as following:

$$\nabla \rho = \rho(\text{graphene-M}) - \rho(\text{graphene}) - \rho(M), \quad (2)$$

where $\rho(\text{graphene-M})$, $\rho(\text{graphene})$ and $\rho(M)$ represent the charge densities of electrode molecules adsorbed on graphene, graphene and isolated electrode molecules, respectively.

RESULTS AND DISCUSSION

Fig. 1b shows the five possible adsorption sites of a BQ molecule containing C_6 ring (BQ) adsorbed on graphene. They are assigned to AA stacking (AA), AB stacking (AB),

Figure 1 (a) Molecular structures of BQ, AQ and their derivatives. (b) Five possible adsorption configurations of BQ adsorbed on graphene.

Bridge-Parallel stacking (BP), Bridge-Slant stacking (BS) and Cross stacking (C), respectively. AA stacking indicates the central C₆ ring of BQ coincides well with in the C₆ ring of graphene. AB stacking corresponds to three carbon atoms in C₆ ring of BQ locating in the middle of C₆ ring of graphene while the other three carbon atoms on the top of graphene C₆ ring. BP stacking means four C–C bonds in the C₆ ring of BQ across the C–C bonds of graphene while the other two C–C bonds parallel to the central C–C bond of graphene. BS describes four carbon atoms in C₆ ring of BQ locating in the middle of C–C bonds of graphene while the other two are in the hollow site of adjacent C₆ ring of graphene. Cross (C) represents all the 6 atoms of central C₆ ring in the middle of the C–C bond of graphene. The adsorption geometry is crucial to the interaction between adsorbate and adsorbent [37]. Thus, all the five possible adsorption sites are taken in account for every designed molecule in Fig. 1a.

Fig. 2 displays the relaxed structures of the adsorption configurations of the six selected molecules adsorbed on graphene. The other relaxed configurations and corresponding adsorption energies are shown in Figs S1–S6 and Tables S1–S6. The most stable configurations of BQ, BQ-2OLi, BQ-2COOLi, AQ, AQ-2OLi and AQ-2COOLi adsorbed on graphene are AB, AA, AA, AB, C and C stacking, respectively. As shown in Fig. S7, the initial adsorbate molecules are quasi-planar. When BQ (Fig. S8a) is adsorbed on a graphene sheet, it presents the quasi-planar structure with little deformation, which suggests the weak interaction between BQ and graphene. The little deformation of structure, low adsorption energy (−0.546 eV), long adsorption distance (3.474 Å) and small transferred charge (0.122 |e|) indicates the noncovalent π - π interaction between BQ and graphene, which coincides with the previous study [30]. This physical π - π interaction is too weak to maintain the adsorbate molecules anchoring on

Figure 2 Top view of the most stable geometries of BQ/graphene, BQ-2OLi/graphene, BQ-2COOLi/graphene, AQ/graphene, AQ-2OLi/graphene and AQ-2COOLi/graphene, respectively.

the graphene sheet during the repeated charge-discharge process, resulting in the unsatisfactory cycling performance [24]. In contrast, upon the introduction of Li-containing functional groups (−OLi and −COOLi), the quasi-planar adsorbate molecules (Fig. S8b, c) form a bent structure with Li atoms tilted close to the graphene sheet. This deformation of BQ-2OLi and BQ-2COOLi makes the Li atoms be the nearest atoms to the graphene sheet, suggesting the strong interaction between Li atoms and graphene. As shown in Table S7, the adsorption distances of BQ-2OLi (2.838 Å) and BQ-2COOLi (2.572 Å) are shorter than that of BQ (3.474 Å), indicating that a stronger interaction is achieved. As shown in Fig. 3, compared with BQ (−0.546 eV), the increased adsorption energies are also obtained in BQ-2OLi (−0.981 eV) and BQ-2COOLi (−1.188 eV), as well as in AQ (−0.959 eV) and its derivatives, i.e., AQ-2OLi (−1.483 eV) and AQ-2COOLi (−1.765 eV).

Charge density difference isosurfaces are shown in Fig. 4 to show the charge transfer between adsorbate molecules and graphene. The BQ molecule (Fig. 4a, b) is in the electron accumulation area (yellow) with graphene in the electron depletion area (cyan). This indicates that the charge transfers from graphene to BQ, resulting in the p doping of graphene. Based on the Bader charge analysis, the transferred charge from graphene to BQ is 0.122 |e|. After the introduction of Li atoms, most of the carbon atoms in graphene are in electron accumulation area, while the graphene carbon atoms beneath the Li atoms are in the electron depletion area (Fig. 4c–f). Meanwhile, the Li atoms are in the electron depletion area, suggesting the role of electron donor of Li atoms. Therefore, the net transferred charges of BQ-2OLi (0.004 |e|) and BQ-2COOLi

Figure 3 The E_{ads} of BQ, BQ-2OLi, BQ-2COOLi, AQ, AQ-2OLi and AQ-2COOLi adsorbed on graphene.

(0.023 |e|) are smaller than that of BQ (0.122 |e|) (Table S7) due to the electro-donating property of Li atoms. No obvious interfacial charge is observed, confirming the noncovalent π - π interaction between BQ and graphene. For comparison, there exists unnegligible interfacial charge transfer upon BQ-2OLi and BQ-2COOLi adsorbed on graphene, suggesting the strong π -Li- π interaction. The enhanced adsorption of BQ-2OLi and BQ-2COOLi on graphene is attributed to the much stronger π -Li- π interaction rather than the π - π interaction between BQ and graphene.

The traditional π -Li- π interaction is achieved *via* external Li atoms doping of graphene, leading to the noncovalent π -Li- π bridging interaction between Li and graphene [30], which can be seen from Scheme 1. Comparatively, we achieve this interaction *via* internal functionalization of the adsorbate molecules with groups containing Li atoms. In addition, the reported π -Li- π interaction through the external metals doping can be divided into two individual noncovalent Li- π interaction (Scheme 1). However, the π -Li- π interaction *via* functional group substitution can be divided into two parts: the ionic bond interaction between Li and adsorbate molecules and the noncovalent Li- π interaction between Li and graphene, leading to the strong interaction between the adsorbate molecules and graphene.

The total density of states (TDOS) and partial density of states (PDOS) of the three adsorbed systems are shown in

Scheme 1 The difference between the π -Li- π interaction *via* external metals doping of graphene and *via* internal functionalization of the adsorbate molecules with groups containing Li atoms.

Figure 4 Side and top view of charge density difference isosurfaces of BQ/graphene (a, b), BQ-2OLi/graphene (c, d) and BQ-2COOLi/graphene (e, f), respectively. The yellow/cyan color represents the accumulation/depletion of electron.

Fig. 5a–c to understand the effect of π -Li- π interaction on the electronic structure. The TDOS of BQ-graphene in Fig. 5a shows little discrete molecular levels near the Fermi level with the pristine graphene in Fig. S9, and indicates the relatively weak π - π interaction between BQ and graphene. No obvious orbital hybridization is observed near the Fermi level, implying the noncovalent π - π interaction between BQ and graphene. Comparatively, the BQ-2OLi/graphene (Fig. 5b) and BQ-2COOLi/graphene (Fig. 5c) show significant states near the Fermi level, presenting the strong adsorption of adsorbate molecules on graphene. It is notable that the states near the Fermi level mainly originate from the adsorbate molecules and the approximate band gaps of three adsorbed systems are 0.6, 0.2 and 0.1 eV, respectively. This implies that the introduction of groups containing Li atoms also improves the electronic conductivity and would be beneficial for the rate capability of carbonyl compounds based electrode materials.

In the π -Li- π interaction, the Li atoms act as a ‘glue’ to bind with both the two π components firmly, which can prevent the detachment of active materials from the graphene substrate and hence improve the cycling performance. Thus, it is supposed that the Li can be replaced by other alkali metals (such as Na and K) to form a versatile π -metal- π interaction between electroactive molecules and graphene, which can be also extended from organic Li batteries to Na and K batteries.

CONCLUSIONS

In summary, a comprehensive DFT calculation was performed to gain insights into the adsorption of functionalized carbonyl compounds on graphene. It is revealed that the introduction of Li atoms can effectively enhance the adsorption of organic carbonyl molecules on graphene *via* the

Figure 5 TDOS and PDOS of BQ (a), BQ-2OLi (b) and BQ-2COOLi (c) adsorbed on graphene, respectively. The Fermi level is set to zero.

strong π -Li- π interaction. It is derived from the synergistic effect between the covalent Li-adsorbate molecules interaction and the Li-graphene interaction, which is much stronger than the π - π interaction. This strong π -Li- π interaction is beneficial to improve the stability and rate capability of carbonyl organic compounds. It will pave a new pathway to design graphene-based organic electrode materials for rechargeable batteries with high performance.

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- Conflict of interest** The authors declare that they have no conflict of interest.
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π -Li- π 作用增强羰基分子在石墨烯上吸附的第一性原理研究

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摘要 具有氧化还原活性位点的羰基化合物仅含碳、氢、氧,具有高理论容量、结构多变、来源丰富等优点,有望成为二次电池的新型电极材料。但是,这类材料的电子导电率较低,同时在有机电解液中具有高的溶解性,限制了其实际应用。将这类活性材料与石墨烯负载复合,可一箭双雕地解决这两大难题。目前报道的羰基化合物和碳材料之间的相互作用力为较弱的 π - π 作用力,无法阻止活性材料从碳材料表面脱落,从而造成电池循环性能衰退。为获得更好的电池性能,必须要提高活性材料和石墨烯之间的相互作用力。本文通过第一性原理计算系统研究了羰基分子和石墨烯的相互作用力。研究结果表明,通过在羰基化合物中引入带有锂金属原子的官能团,可以有效地将较弱的 π - π 作用力转换为较强的 π -Li- π 相互作用力。引入的锂原子通过锂原子-羰基化合物和锂原子-石墨烯之间的协同作用将两个芳香性的 π 组分结合起来。 π -Li- π 相互作用的概念提供了一个通用的方法来提高电子导电率,并抑制活性材料的溶解,可为高性能二次电池有机电极材料的设计提供支撑。