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Computational electrochemistry of Pillar[5]quinone cathode material for lithium-ion batteries

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ABSTRACT

Multi-carbonyl macrocyclic compounds have recently attracted much attention due to their high performance relative to some short chain carbonyl compounds as the cathode active constituents for lithium-ion batteries (LIBs). However, little is known about the evolution mechanism of their electrochemical properties during charging and discharging processes. In this paper, the application of density functional calculations at the M06-2X/6-31G(d,p) level of theory is presented to study systematically the electrochemical properties of pillar[5]quinone (P5Q) as a cathode active material for LIBs. The optimized structures of P5Q accepting different number of electrons and binding different number of lithium atoms are obtained, respectively. The geometry structure, thermodynamics property, electronic structural property, solvent effect and redox potential are discussed in detail. The uneven-distribution of extra electrons in several $P5Q^{n-}$ anions can minimize the repulsive interactions as far as possible. The macrocyclic skeletons in $P5QLi_n$ structures are distorted to different extents by the binding interactions between Li atoms and P5Q. More than eight intercalated lithium atoms into per P5Q molecule are confirmed in this work, indicating a high utilization ratio of carbonyl groups of P5Q as a cathode material. Compared with pillar[4]quinone and pillar[6]quinone, P5Q is predicted to have better cycling performance due to its higher structural stability.

1. Introduction

In recent years, the application fields of lithium-ion batteries (LIBs) have been widely expanded, especially in portable electronics devices [1,2]. To meet the requirements of the further application in large-capacity and high-power electronics, one of the critical issues is to find some of the redox-active materials with high electrochemical performance, environmental sustainability, and low cost [3–5]. Some quinone-containing compounds have been considered as electrode active materials for LIBs [6–10]. Recently, macrocyclic compounds with several quinone units were chosen as the promising cathode materials of LIBs due to their high electrochemical performances and low solubility in organic electrolyte relative to short chain quinone compounds. Chen et al. [11] have reported the quasi-solid-state LIBs with calix[4]quinone (C4Q, $C_{theo} = 446\ mAh\ g^{-1}$) as the cathode active constituent, which delivered a reversible capacity of $379\ mAh\ g^{-1}$ after 100 cycles at 0.2 C rate. Most recently, a novel pillar[5]arene derivative, pillar[5]quinone (P5Q, $C_{theo} = 446\ mAh\ g^{-1}$) was selected as the cathode active material for an all-solid-state LIB by Chen's group [12]. The chemical structure and proposed electrochemical redox mechanism of P5Q was given in Scheme 1. P5Q cathode delivered an initial capacity of $418\ mAh\ g^{-1}$ and showed a stable cyclability with 94.7% capacity retention after 50 cycles, suggesting a possible use for high capacity LIBs. To further understand the electrochemical behavior of P5Q, a four-step mechanism of the electron uptake sequence was presented by Kaifer et al. [13] using experimental methods.

Based on the working principle of lithium ion rechargeable batteries, the alternative cathode materials must be able to accept and release lithium ions and electrons repeatedly and quickly. Therefore, the cathode performance critically depends on the structural variation during charging and discharging processes. To characterize the micro-structure of the cathode materials, the combination of theoretical and experimental approaches is very necessary [14]. However, for macrocyclic quinone-containing cathode materials, the theoretical studies are relatively lagging behind. In the past few decades, Density Functional Theory (DFT) calculations have emerged as a powerful tool in complementing experiments, identifying and characterizing a large variety of molecular systems.

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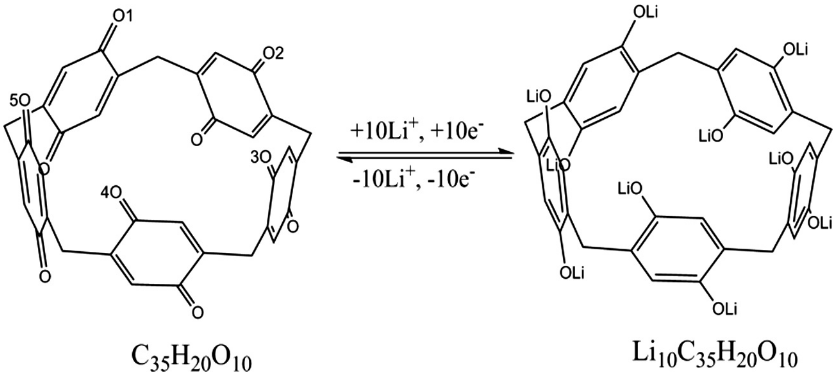

Scheme 1. Chemical structure and proposed electrochemical redox mechanism of P5Q.

Our previous theoretical work has predicted the possibility of pillar[4]quinone as a cathode active material for LIBs [15]. Due to the inherent structural instability, no such experimental research to verify the applicability of pillar[4]quinone cathode so far. In order to demonstrate thoroughly the evolution mechanism of pillar-quinone cathode materials during charging and discharging processes, the electrochemical properties of P5Q as the cathode material for LIBs are studied by using DFT calculations. This work aims at providing insight into the following issues: (1) geometry structures and electronic properties of P5Q accepting electrons or binding lithium atoms, (2) the influence of solvent on the redox potential of P5Q cathode, (3) the relationship between pillar-quinone molecules and their electrochemical behavior, (4) the comparison of theoretical predicted results with the experimental data.

2. Theoretical and computational details

All calculations presented in this paper are performed using the Gaussian 09 software [16] at the M06-2X/6-31G(d,p) level of theory [17,18]. This method can provide good descriptions in redox potential, main group thermochemistry, and non-covalent interactions [19]. All of the optimized geometry structures in this way are calculated without imaginary frequency. To understand the electronic features, the natural bond orbital (NBO) analysis is carried out at the M06-2X/6-31G(d,p) level of theory for all the optimized structures [20]. To estimate the solvation contributions, single point energy calculations are carried out using the polarizable continuum model (PCM) [21,22]. The solvent mixture commonly used in LIBs [23] of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (1:1:1 by volume) is selected as the solvent phase. The dielectric constant of the mixed solvent is obtained by the following equation.

$$\varepsilon_{\mathrm{mix}} = \varepsilon_{\mathrm{EC}} \times (\mathrm{EC})\% + \varepsilon_{\mathrm{DMC}} \times (\mathrm{DMC})\% + \varepsilon_{\mathrm{EMC}} \times (\mathrm{EMC})\% \tag{1}$$

where ε is the dielectric constant, (EC)% is molar volume percentage of EC, and so on. The solvation free energy term (ΔG_{solv}) is the difference in the single-point energy of a solute molecule in solvent (E_{solv}) and in the gas phase (E_{gas}). ΔG_{solv} is added to the gas phase free energy (G_{gas}) to calculate the Gibbs free energy (G_{solu}) of the molecule in the electrolyte solution [24].

$$G_{\mathrm{solu}} = G_{\mathrm{gas}} + \Delta G_{\mathrm{solv}} \tag{2}$$

To calculate the average intercalation voltage, here, we construct a rechargeable lithium ion battery using a P5Q cathode. When this battery works, the redox reaction of P5Q is shown below.

$$\mathrm{P5QLi}_{x1} + (x_2 - x_1)\mathrm{Li} = \mathrm{P5QLi}_{x2} \quad (x_2 > x_1) \tag{3}$$

where x_1 and x_2 are the number of lithium atoms intercalated into P5Q cathode. Based on this reaction, the change in Gibbs free energy ($\Delta_r G_m$) and the average voltage ($\overline{V}$) are obtained using the following equations, respectively.

$$\Delta_r G_m = G_{\mathrm{P5QLi}_{x2}} - (x_2 - x_1)G_{Li} - G_{\mathrm{P5QLi}_{x1}} \tag{4}$$

$$\overline{V} = \frac{-\Delta_r G_m}{(x_2 - x_1)F} \tag{5}$$

where $(x_2 - x_1)$ is the number of electrons transferred, and F is the Faraday constant [25,26]. This method for calculating the average voltage using Eqs. (2)–(5) has been well described and verified in the research field of lithium-ion batteries [11,27,28].

3. Results and discussion

According to the work principle of a LIB, when discharging, the electrons transfer from anode to cathode through an external circuit. At the same time, Li^+ ions pass through the separator to cathode. As shown in Scheme 2, the P5Q cathode performance greatly depends on the capability to accept electrons and combine with Li^+ ions. In the following section, two aspects are considered in detail: one is the electron-accepting ability of P5Q, i.e. the properties of $P5Q^{n-}$ anions (n is the number of electrons accepted); the other is to explore the properties of P5Q interacting with Li^+ ions. As a known anion host compound [29], it is difficult for P5Q to combine with Li^+ directly. The Li^+ insertion process must be accompanied by the electron injecting into the cathode. The net result is that, at the cathode, P5Q interacts with Li atoms to form $P5QLi_n$ (n is the number of Li atoms). Therefore, as the second consideration, the interactions between P5Q molecule and Li atoms, in fact, are discussed systematically.

3.1. Geometric Structures, electronic properties and stabilities of $P5Q^{n-}$ anions

Based on the proposed redox mechanism of P5Q (Scheme 1), P5Q can accept a number of electrons to form $P5Q^{n-}$ anions. From a purely theoretical point of view, all of ten $P5Q^{n-}$ (n = 1–10) anion structures are optimized at the M06-2X/6-31G(d,p) level of theory. Similar to P5Q, all $P5Q^{n-}$ possess D_5 symmetry. Due to the repulsive interactions between adjacent electron-rich benzoquinone units, especially between two carbonyl oxygen atoms, the cavity diameter of $P5Q^{n-}$ becomes larger with the increasing number of extra electrons. As representatives, $P5Q^{5-}$ and $P5Q^{10-}$ are given in Fig. 1 as well as some selected atomic distances. As shown in Fig. 1, the distances between two adjacent oxygen atoms in $P5Q^{5-}$ and $P5Q^{10-}$ are 9.35% and 21.89% longer, respectively, than that in the parent compound P5Q molecule. The bridging C—C