



Short communication

Theoretical study on reduction mechanism of 1,3-benzodioxol-2-one for the formation of solid electrolyte interface on anode of lithium ion battery

L.D. Xing^a, C.Y. Wang^a, M.Q. Xu^{a,b}, W.S. Li^{a,b,c,*}, Z.P. Cai^a^a School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China^b College of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China^c Key Lab of Electrochemical Technology on Energy Storage and Power Generation in Guangdong Universities, Guangzhou 510006, China

ARTICLE INFO

Article history:

Received 21 June 2008

Received in revised form 23 August 2008

Accepted 28 August 2008

Available online 3 September 2008

Keywords:

Lithium ion battery

Propylene carbonate

1,3-Benzodioxol-2-one

Reduction mechanism

DFT

ABSTRACT

The geometric parameters of 1,3-benzodioxol-2-one (BO) and propylene carbonate (PC) was optimized at the B3LYP/6-311++G(d,p) level of density functional theory (DFT) with the polarized continuum models (PCM). The obtained frontier molecular orbital energies and vertical electron affinities indicate that BO is reduced more easily than PC. The transition state (TS) of ring-opening reaction $\text{BO}^{-1} \rightarrow \text{BO}^{\bullet-1}$ was optimized and confirmed by vibrational frequency analysis and intrinsic reaction coordinate (IRC) method. The bond orders and atomic charge distribution of the stable points along the minimum energy path (MEP) were analyzed using the natural bond orbital (NBO) method at the B3LYP/6-311++G(d,p) level of DFT. With these calculated results, the reduction mechanism of BO for the formation of solid electrolyte interface (SEI) film on anode of lithium ion battery can be inferred as: $\text{BO} + e \rightarrow \text{BO}^{-1} \rightarrow \text{BO}^{\bullet-1} \rightarrow \dots \rightarrow \text{SEI Film}$.

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1. Introduction

Li-ion battery is becoming a popular power source not only for electronic device but also for electric vehicle, due to its high-energy density, low self discharge rate and long cycle life [1,2]. Its successful application depends to great extent on the existence of solid electrolyte interface (SEI) film on the anode, which forms from additives during the first charge–discharge cycle and prevents the solvents from decomposition [3]. Propylene carbonate (PC) is an attractive solvent composition for Li-ion battery electrolyte because it provides the electrolyte with high ionic conductivity over a wide temperature range. However, PC is easy to be reduced on the anode, usually graphite, and co-intercalated into the graphite with lithium ions in electrolyte, resulting in the exfoliation of the graphite [4]. The reduction and the co-intercalation of PC can be suppressed by the SEI film and several effective additives for the SEI formation have been developed [5–7]. One of them is 1,3-benzodioxol-2-one (BO) [6]. It was believed that PC radical is generated first from the one electron reduction of PC and BO reacted with PC radical, forming stable film to suppress the co-intercalation of PC. However, this explanation lacks supports of experimental or theoretical results.

The purpose of this work is to understand the formation mechanism of SEI from BO by comparing the reduction process of BO and PC using density functional theory (DFT) calculations.

2. Computational details

The calculations were performed using the Gaussian 03 program package. The geometric parameters of stationary points were optimized at the B3LYP/6-311++G(d,p) level of DFT [8]. All the computations were carried out with the polarized continuum models (PCM) in an assumptive solvent whose dielectric constant is 78, which is between 64.4 (PC) and 89.2 (ethylene carbonate) [9]. The frontier molecular orbital energies and the electron affinities of BO and PC were obtained by calculating at B3LYP/6-311++G(d,p) level of DFT. The charge distribution and bond orders of BO and its anion (BO^{-1}) were analyzed by the natural bond orbital (NBO) theory. The vibrational frequency and intrinsic reaction coordinate (IRC) analyses were employed to confirm the transition state of ring-opening reaction at the same level.

3. Results and discussion

3.1. Geometric optimization

The optimized geometric parameters of PC, BO and their anions as well as the transition state structure of the anion radical ($\text{BO}^{\bullet-1}$) formation reaction from anion (BO^{-1}) are shown in Fig. 1. Results on

* Corresponding author at: School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China. Tel.: +86 20 39310256; fax: +86 20 39310256.

E-mail address: liwsh@scnu.edu.cn (W.S. Li).

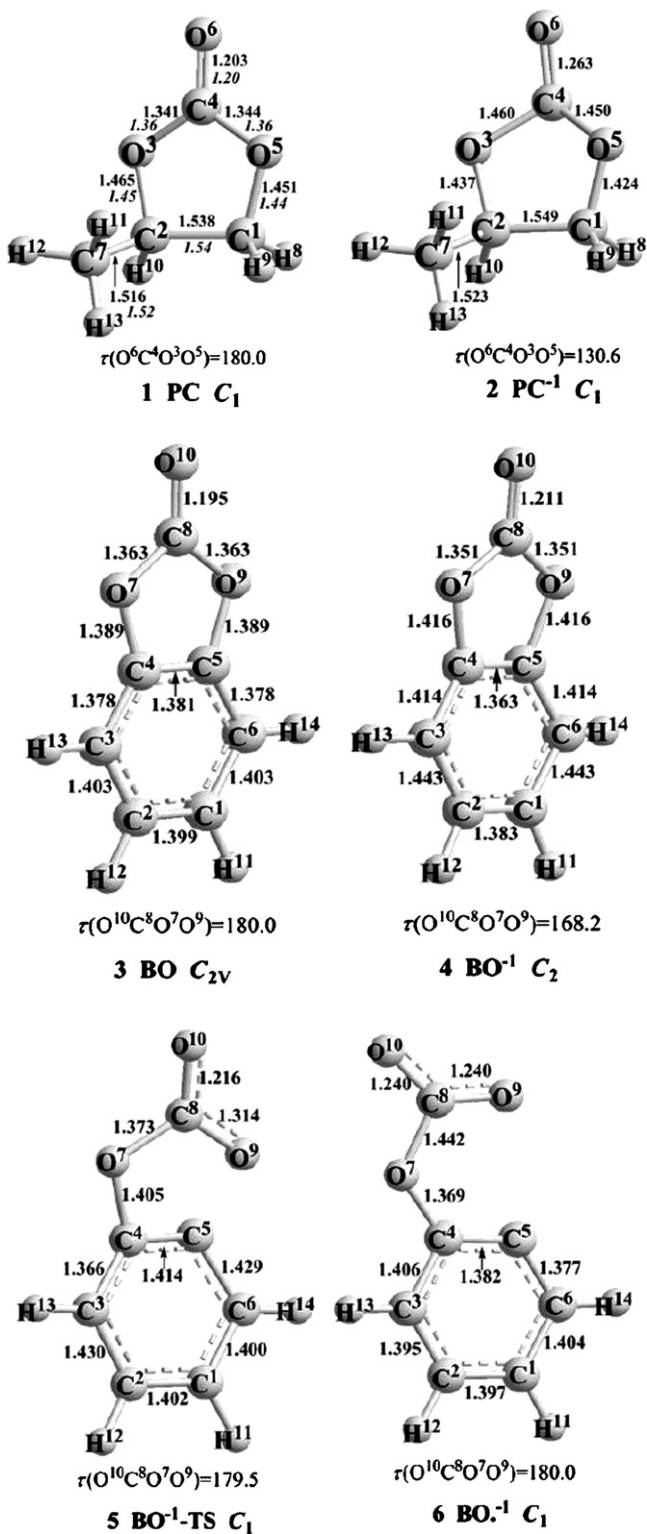


Fig. 1. Optimized geometric parameters (Å for bond lengths and deg for angles) at PCM-B3LYP/6-311++G(d, p) level. The italic data in PC is taken from Ref. [9].

PC from reference (italic data) [9] are also presented in Fig. 1 for a comparison. It can be seen that the calculated geometric parameters of PC is close to those from the reference. For the PC, the bond lengths of C⁴–O³, C⁴–O⁵, C²–O³, and C¹–O⁵ in PC are 1.341 Å, 1.344 Å, 1.465 Å, and 1.451 Å, respectively. After PC accepts one electron, C⁴–O³ and C⁴–O⁵ are markedly lengthened (1.460 Å and

Table 1

Frontier molecular orbital energy and electron affinity (eV) of PC and BO in solvent

Molecular	Frontier molecular orbital energy		EA _{vert}	EA _{ad}
	E_{HOMO}	E_{LUMO}		
PC	-8.795	-0.217	0.739	1.556 (1.523 ^a)
BO	-7.014	-0.999	1.201	1.423

^a Taken from Ref. [2], which was calculated at B3LYP/6-311+G(2d, p) level using CPCM model.

1.450 Å, respectively) but C²–O³ and C¹–O⁵ are shortened (1.437 Å and 1.424 Å, respectively). The dihedral of –CO₃ group changes from 180.0° in PC (1 PC in Fig. 1) to 130.6° in PC anion (2 PC⁻¹ in Fig. 1). It seems that the hybridization orbital type for the atomic C⁴ changes from sp² in PC to inequitable sp³ in PC⁻¹ [10], due to the enhance charge on C⁴ (1.0302 in PC and 0.6478 in PC⁻¹). For the BO, the bond lengths of C⁴–O⁷ (C⁵–O⁹) and C⁸–O⁷ (C⁸–O⁹) are 1.389 Å and 1.363 Å, respectively. After BO accepts an electron, the bond C⁴–O⁷ (C⁵–O⁹) is lengthened by 0.027 Å but C⁸–O⁷ (C⁸–O⁹) is shortened by 0.012 Å. The structure of –CO₃ group also changes but the changed degree is different, from 180° in BO (3 BO in Fig. 1) to 168.2° in BO⁻¹ (4 BO⁻¹ in Fig. 1), which is smaller than that in PC. This difference can be implied by their adiabatic electron affinities as shown in Table 1. The structures of both PC⁻¹ and BO⁻¹ are unstable and prone to a spontaneous rearrangement to form a near flat plane in the open cyclic anion radicals [2,10].

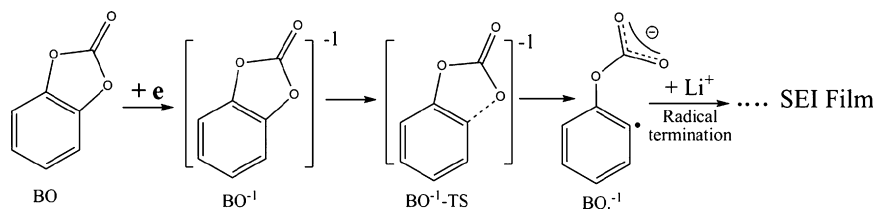
3.2. Reduction ability of PC and BO in solvent

The calculated frontier molecular orbital energies, vertical electron affinities (EA_{vert}) and adiabatic electron affinities (EA_{ad}) of BO and PC in solvent are listed in Table 1. Here, EA_{vert} = $E_n - E_n^-$ and EA_{ad} = $E_n - E_c$. E_n is the neutral geometry energy, E_n^- is the anion energy with optimized neutral geometry and E_c is the anion energy [11]. Based on the molecular orbital theory, the ability of one molecular to lose or gain an electron depends on the energy level of the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) [12,13]. The LUMO energy of BO (-0.999 eV) is obviously lower than that of PC (-0.217 eV), indicating that BO gain an electron in solvent more easily than PC. The calculated results on EA_{vert} of BO (1.201 eV) and PC (0.739 eV) also imply that BO accepts electron prior to PC in solvent. On the other hand, the fact that the EA_{ad} of PC (1.556 eV) is larger than that of BO (1.423 eV), showing that the change of structural parameters of the PC is larger than that of BO after gaining an electron. Apparently, BO is reduced in solvent prior to PC. Therefore, the proposed mechanism that PC radical is generated first from the one electron reduction of PC and BO reacted with PC radical for the SEI formation is not correct.

3.3. Reduction process of BO

3.3.1. Change of bond orders

To clarify the mechanism of bond breaking in BO reduction process, bond orders of BO and BO⁻¹ were calculated using the natural population analysis with natural localized molecular orbitals (NLMO/NPA). The obtained results are listed in Table 2. Bond orders of the adjacent atoms reflect the interaction of atoms, i.e. the bond strength is proportional to the bond orders. The bond orders in Table 2 follow the trend of bond lengths very well (3 BO and 4 BO⁻¹ in Fig. 1). The bond orders of C⁴–C⁵, C⁷–O⁸ and C⁸–O⁹ increase from 1.2471, 0.7253 and 0.7253 to 1.5006, 0.7581 and 0.7581, respectively, and those of C⁴–O⁷ and C⁵–O⁹ decrease from 0.6720 to 0.6301, which is the lowest. These results indicate that C⁴–C⁵, C⁷–O⁸ and C⁸–O⁹ are strengthened, while C⁴–O⁷ and C⁵–O⁹ are



Scheme 1. Possible mechanism on the formation process of SEI on anode from BO.

Table 2
NLMO/NPA bond orders in BO and BO^{-1}

Bond	BO	BO^{-1}
R(1, 2)	1.7480	1.7747
R(1, 6)	1.2488	1.1648
R(2, 3)	1.2488	1.1648
R(3, 4)	1.6406	1.2993
R(4, 5)	1.2471	1.5006
R(5, 6)	1.6406	1.2993
R(4, 7)	0.6720	0.6301
R(5, 9)	0.6720	0.6301
R(7, 8)	0.7253	0.7581
R(8, 9)	0.7253	0.7581
R(8, 10)	1.3141	1.2528

weakened after BO gains an electron. Based on the structures and bond order analyses, it is known that BO^{-1} experiences the breaking of C^4-O^7 or C^5-O^9 to form a stable open cyclic anion radical ($BO^{\bullet-1}$).

3.3.2. Charge distribution

The charge distributions on atoms in BO, BO^{-1} and $BO^{\bullet-1}$, obtained by using natural population analysis (NPA), are listed in Table 3. It can be seen from Table 3 that the charge distributions on atoms in BO, BO^{-1} and $BO^{\bullet-1}$ are quite different. The charges on $-CO_3$ group are -0.5852 , -0.7386 and -1.1664 , while those on the carbon atoms in benzene ring are -0.3806 , -1.0907 and -0.7404 for BO, BO^{-1} and $BO^{\bullet-1}$, respectively. This indicates that the breaking of C^4-O^7 or C^5-O^9 bond is ascribed to the weakened conjugation effect between benzene ring and $-CO_3$ group, due to the increase of the electron density on benzene ring. After the breaking of C^5-O^9 bond, the charges mainly transfer from the benzene ring to $-CO_3$ group in $BO^{\bullet-1}$, which is a relatively stable structure because the $-CO_3$ group and benzene ring return to the near planar structure.

3.3.3. Potential energy surface of BO reduction process

According to the above analysis, the BO^{-1} experiences a reaction of bond breaking, either C^4-O^7 or C^5-O^9 , to form $BO^{\bullet-1}$. The transition states (TS) are optimized for this reaction in the solvent and gas phase, and confirmed by vibrational frequency analyses and

Table 3
Atomic charges based on NPA for BO, BO^{-1} and $BO^{\bullet-1}$

Atom	BO	BO^{-1}	$BO^{\bullet-1}$
1 C	-0.2042	-0.2676	-0.2355
2 C	-0.2042	-0.2676	-0.2207
3 C	-0.2365	-0.4649	-0.2470
4 C	0.2504	0.1871	0.1991
5 C	0.2504	0.1872	0.0777
6 C	-0.2365	-0.4649	-0.3140
7 O	-0.4981	-0.5265	-0.6103
8 C	1.0259	0.9965	0.9897
9 O	-0.4981	-0.5265	-0.7499
10 O	-0.6149	-0.6821	-0.7959

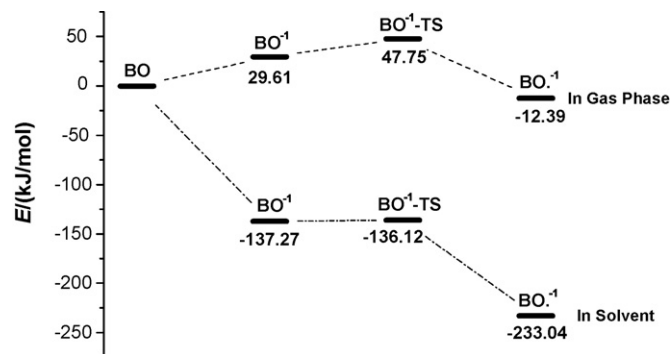


Fig. 2. Potential energy surface of BO reduction process.

IRC method. The calculated frequencies indicate that the BO^{-1-TS} possesses one and only one imaginary frequency, $268i$ and $367i$ in solvent and gas phases, respectively. The results from IRC calculation show that the BO^{-1-TS} in solvent or gas phase are connected with BO^{-1} and $BO^{\bullet-1}$. The potential energy surfaces of BO reduction reaction in solvent and gas phases are shown in Fig. 2. It can be seen from Fig. 2 that the transformation process of BO^{-1} to $BO^{\bullet-1}$ is similar in gas and solvent phase. However, the barrier height (1.15 kJ mol^{-1}) in solvent is much lower than that ($18.14 \text{ kJ mol}^{-1}$) in gas phase. This implies that solvent greatly decreases the barrier height for the reaction $BO^{-1} \rightarrow BO^{\bullet-1}$. On the other hand, from the potential energy surface in solvent it can be found that $BO^{\bullet-1}$ is far more stable than BO^{-1} .

Based on the results above, it can be concluded that the negative charge is mostly distributed on $-CO_3$ group in $BO^{\bullet-1}$, so that the combination of $-CO_3$ group with dissolved Li^+ and the termination of the radical respond for the formation of SEI. Therefore, the formation process of SEI on anode from BO can be inferred as Scheme 1.

4. Conclusion

The mechanism for the reduction of 1,3-benzodioxol-2-one (BO) on anode of lithium ion battery was understood by theoretical calculation at the B3LYP/6-311++G (d, p) level of density functional theory. It is found that BO in solvent is reduced prior to PC to form BO^{-1} . The structure of BO^{-1} is unstable, and prone to a spontaneous rearrangement to form a near flat plane of $BO^{\bullet-1}$ by the breaking of C^4-O^7 or C^5-O^9 . The negative charge is mostly distribution on $-CO_3$ group in $BO^{\bullet-1}$, thus the film formation mechanism of $BO^{\bullet-1}$ involves the combination of the $-CO_3$ group with the dissolved Li^+ and the radical termination.

Acknowledgement

This work was financially supported by National Natural Science Foundation of China (NSFC20873046).

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