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Short communication

The reductive mechanism of ethylene sulfite as solid electrolyte interphase film-forming additive for lithium ion battery

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ABSTRACT

The reduction mechanism of ethylene sulfite (ES) in propylene carbonate (PC) based electrolyte is investigated using density functional theory in gas phase. Based on the electron affinity energy and lowest unoccupied molecular orbital (LUMO) energy, it can be known that free ES is reduced most easily compared with ES-Li$^+$ and ES-Li$^+$-PC, generating SO_2 and propanal. However, the binding energy of ES-Li$^+$ and ES-Li$^+$-PC is quite negative, indicating that both of them are more possible in electrolyte solution than the free ES. The reductive decomposition products of ES-Li$^+$ and ES-Li$^+$-PC are OSO_2Li, OSO_2Li-R and ethylene. OSO_2Li and OSO_2Li-R are the main compositions of the solid electrolyte interphase film on the anode of lithium ion battery, which inhibits the reductive decomposition of PC. These calculations provide a detailed explanation on the experimental phenomena.

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1. Introduction

Lithium ion battery is a useful power source, either in small size for portable electronic devices or in large size for electric vehicles, but its performance such as safety and cyclic stability needs to be improved [1]. Much effort has been made in order to improve the battery performance. The most attracting approach is to develop functional electrolyte additives that limit the degradation of electrodes by stabilizing the interface between electrolyte and electrode, especially the anode [2]. Graphite is used as anode material for lithium ion batteries due to its low cost, high capacity and low and flat potential plateau with respect to lithium metal [3]. It has been widely accepted that ethylene carbonate (EC) can produce a protective solid electrolyte interphase (SEI) on the surface of the graphite anode through its reductive reaction. Thus a protective SEI film can be formed in an EC-based electrolyte. This SEI film can suppress to some extent the further decomposition of solvents [4]. However, graphite is highly sensitive to propylene carbonate (PC) based electrolyte. PC is important for its use in lithium ion batteries due to its advantages of high dielectric constant, wide temperature range for its liquid state, wide electrochemical stability window [5,6]. When graphite electrodes are negatively polarized in PC based electrolyte, Li ions solvated by PC molecules cointercalate with PC into graphite layers at around 0.8 V vs. Li/Li$^+$, resulting in the severe exfoliation of the graphite layers [7]. A stable SEI film cannot be formed in PC based electrolyte, unless a suitable film-forming additive is used. Several additives have been reported to be effective for the formation of a stable SEI film, including vinylene carbonate, vinyl acetate and chloroethylene carbonate [4,8]. Ethylene sulfites (ES) have been found to be an effective SEI film-forming additives, because small amount of sulfite added into PC based electrolyte could improve the anode behavior significantly [9–12]. Unfortunately, the mechanism on the formation of SEI film by ES as a film-forming additive is not well understood.

A good understanding of the reaction mechanism of electrolyte additives can provide significant guidance for searching new effective additives and forecasting the performance of the additives [13,14]. In this paper, high level density functional theory calculation was carried out to understand the formation mechanism of SEI film by ES.

2. Computational details

All the calculations were performed using the Gaussian 03 package [15]. The equilibrium and transition state structure was optimized by B3LYP method in conjunction with the 6-311++G(d,p) basis set [13]. To confirm each optimized stationary point and

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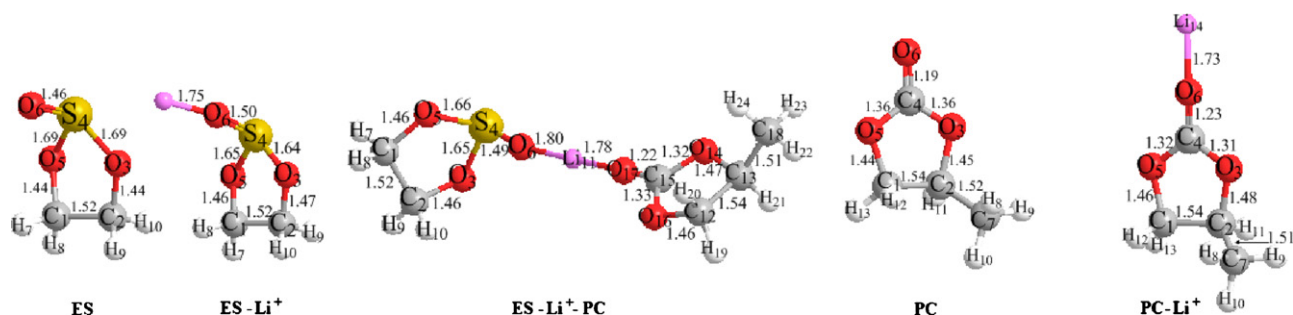*E-mail address:* liwsh@scnu.edu.cn (W. Li).

Fig. 1. The optimize geometry of the possible compounds existing in the PC based electrolyte containing ES, Å for bond length.

make zero point energy (ZPE) corrections, frequency analyses were done with the same basis set. In order to confirm transition state (TS) connected with corresponding products (or intermediates) and reactants (or intermediates), intrinsic reaction coordinate (IRC) calculation was also performed at the same level. Enthalpies and Gibbs free energy was obtained at 298.2 K. The charge distribution was analyzed by the natural bond orbital (NBO) theory.

3. Results and discussion

3.1. Reductive activity of ES and PC in gas phase

The optimize geometry of ES, ES-Li$^+$, ES-Li$^+$-PC, PC, and PC-Li$^+$, the possible compounds existing in PC based electrolyte containing ES, is shown in Fig. 1. It should be noted that the bond length of Li-O in ES-Li$^+$ (1.75 Å) is slightly longer than in PC-Li$^+$ (1.73 Å), indicating that the association strength of the former is smaller than the latter. This result can be confirmed by the binding energy (Table 1), including the calculated binding energy of the solvent-Li$^+$ (ΔE), lowest unoccupied molecular orbital (LUMO) energy and electron affinity. E_n is the neutral geometry energy; E_n^- is the anion geometry energy gaining one electron. Both ES and PC are easy to associate with Li$^+$ by the oxygen of sulfo and carbonyl group. The lowest ΔE indicates ES-Li$^+$-PC is the most favorable association form among the calculated compounds, followed by PC-Li$^+$ and ES-Li$^+$. The LUMO energy of ES (−1.25 eV) is significantly lower than that of PC (−0.62 eV), indicating that ES is reduced more easily than PC. The data ΔE_1 indicates that the ability of the calculated forms to gain the first electron is as follows: ES-Li$^+$ > ES-Li$^+$-PC > PC-Li$^+$ > ES > PC. It is obvious that both ES and PC are more easily reduced after associating with Li$^+$. The positive ΔE_1 shows that free PC is difficult to reduce. Furthermore, the reductive mechanism of PC and PC-Li$^+$ has been reported [16]. Therefore, ES, ES-Li$^+$ and ES-Li$^+$-PC were considered in this work.

3.2. Reduction mechanism of free ES

The one electron reduction mechanism of ES was considered. The optimized geometry of ES anion (ES+e) shows that the initial reduction is accompanied with the cleavage of S_4–O_5 bond, as shown in Fig. 2. Based on the structure of ES+e, it can be known that it is possible for the reaction to generate SO_2, involving one transition state (TS1) and initial product (ES-1). The calculated relative energy (ΔE in kJ mol^{-1}), enthalpy (ΔH in kJ mol^{-1}) and free energy (ΔG in kJ mol^{-1}) of the stationary points are listed in Table 2.
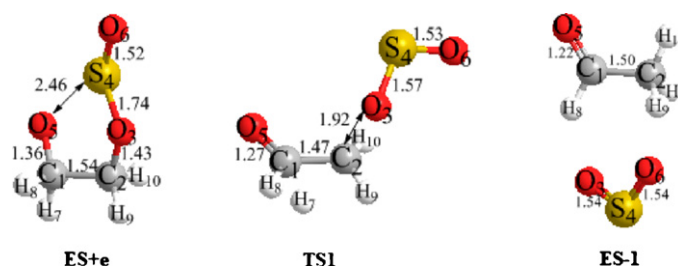

Fig. 2. The optimized geometry of the reductive products of free ES.

Table 2
Relative energy, enthalpy, and free energy (in kJ mol^{-1}) of the stationary points, and imaginary frequency (ω in cm^{-1}) of the transition state for the reductive decomposition of free ES.

Structure	ΔE	$\Delta E + \Delta$ZPE	ΔH	ΔG	ω
ES+e	0.0	0.0	0.0	0.0	
TS1	87.8	73.5	74.9	66.9	752 i
ES-1	−170.0	−175.3	−169.9	−188.8	

In order to confirm the geometry of transition states, frequency analyses and IRC calculations were carried out. The results are also included in Table 2. The SO_2 generating from ES-1 has been detected in PC based electrolyte containing ES by temperature programmed desorption or decomposition-gas chromatography/mass spectrometry (TPD-GC/MS) [2].

3.3. Reduction mechanism of ES-Li$^+$ and ES-Li$^+$-PC in gas phase

The one electron reduction of ES-Li$^+$ and ES-Li$^+$-PC was considered. Fig. 3 presents the optimized geometry of ES-Li$^+$ anion (ES-Li$^+$+e), ES-Li$^+$-PC anion (ES-Li$^+$-PC+e) and the selected structure parameters. The structure of ES changes obviously after gaining one electron, both in ES-Li$^+$ and ES-Li$^+$-PC forms. O_3–S_4 bond of ES breaks with the forming of O_3–Li_{11} bond of a seven membered ring. It can be noted that the structure of PC changes slightly during the reductive reaction of ES-Li$^+$-PC+e. Table 3 presents the charge distribution on ES, PC and Li$^+$ in ES-Li$^+$ and ES-Li$^+$-PC before and after gaining one electron, which was obtained by natural population analysis (NPA) calculation. It should be noted from Table 3 that the charge on PC keeps essentially constant, and the electron is mainly distributed on ES. This result indicates that PC is not involved in the decomposition of ES-Li$^+$-PC+e.

Table 1
The LUMO energy (in eV), binding energy and electron affinity of the calculated compounds (in kJ mol^{-1}), in gas phase.

	ES	ES-Li$^+$	ES-Li$^+$-PC	PC	PC-Li$^+$
ΔE	–	−199.94	−372.63	–	−224.33
LUMO	−1.25	–	–	−0.62	–
ΔE_1	−79.37	−605.75	−506.81	26.29	−370.50

Table 3
Atomic charges based on NPA for ES-Li$^+$, ES-Li$^+$-PC and their anions.

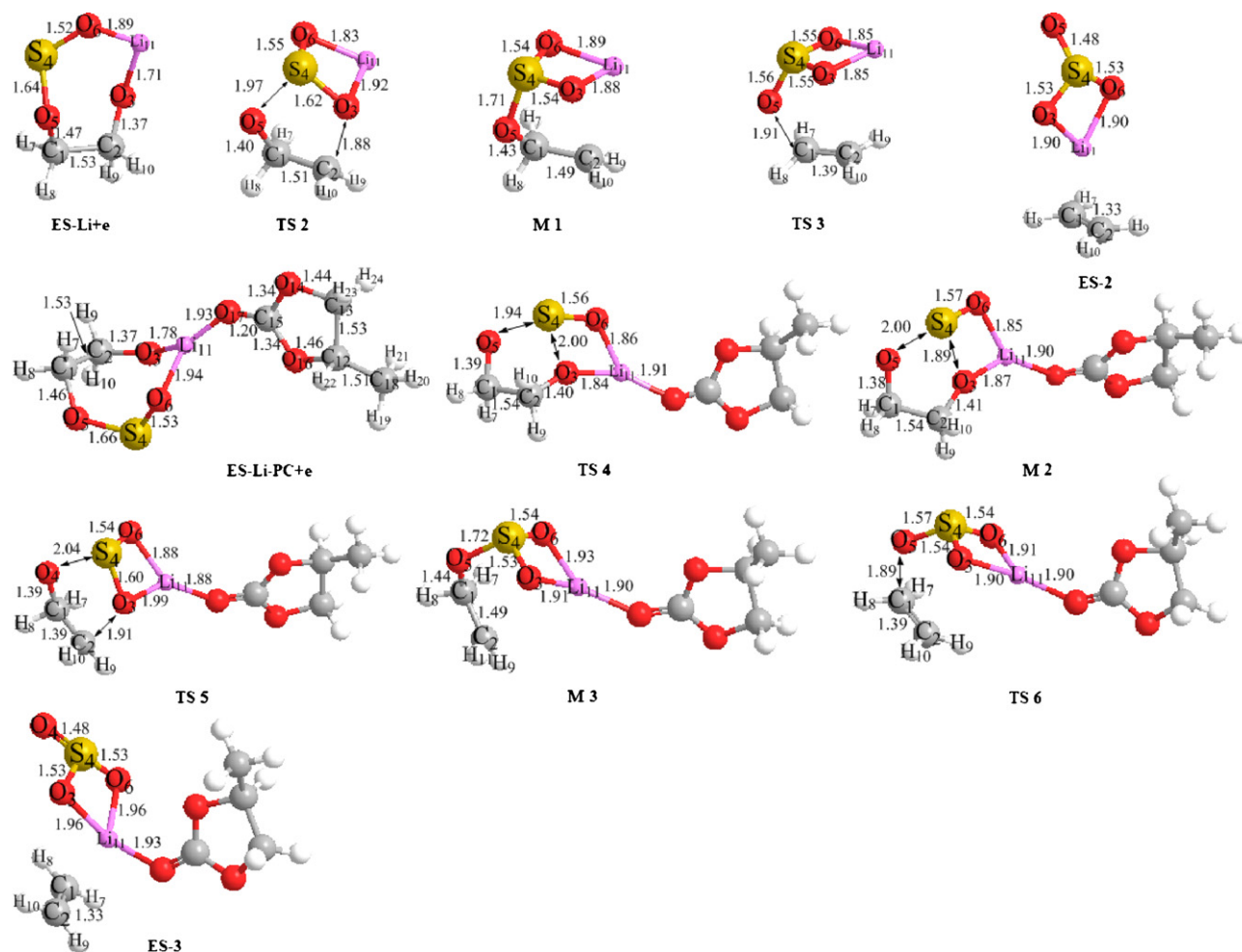| Total charge	ES-Li$^+$		ES-Li$^+$-PC		
	ES	Li$^+$	ES	Li$^+$	PC
1	0.01	0.99	0.02	0.96	0.02
0	−0.94	0.94	−0.93	0.90	0.03

Fig. 3. The optimized geometry of the reductive products of ES-Li⁺ and ES-Li⁺-PC.

The reductive reaction paths of ES-Li⁺+e and ES-Li⁺-PC+e are also presented in Fig. 3. The calculated relative energy (ΔE in kJ mol^{-1}), enthalpy (ΔH in kJ mol^{-1}) and free energy (ΔG in kJ mol^{-1}) of the stationary points are listed in Table 4. In order to confirm the geometry of transition states, frequency analyses and IRC calculations were carried out. The calculated imaginary frequency (ω in cm^{-1}) of the transition states is also included in Table 4. ES-Li+e converts into intermediate M1 via TS2, with the cleavage of O_5–S_4 and C_2–O_3. Subsequently, M1 could dissociate to form ES-2, which would release ethylene and LiSO$_3$, with a lower energy barrier transition state TS3. Both ethylene and LiSO$_3$ have been reported as the reductive products of the electrolyte containing ES

[9]. For ES-Li-PC+e, the structure of PC changes slightly during the reductive reaction. ES-Li-PC+e converts into ES-3 via three transition states TS4, TS5 and TS6, two intermediates M2 and M3. The structure of ES-3 is similar with ES-2, except one PC associating with Li⁺. OSO$_2$Li-R has also been detected by X-ray photoelectron spectroscopy (XPS) and TPD-GC/MS [9].

Table 4
Relative energy, enthalpy, and free energy (in kJ mol^{-1}) of the stationary points, and imaginary frequency (ω in cm^{-1}) of the transition state for the reductive decomposition of ES-Li⁺ and ES-Li⁺-PC.

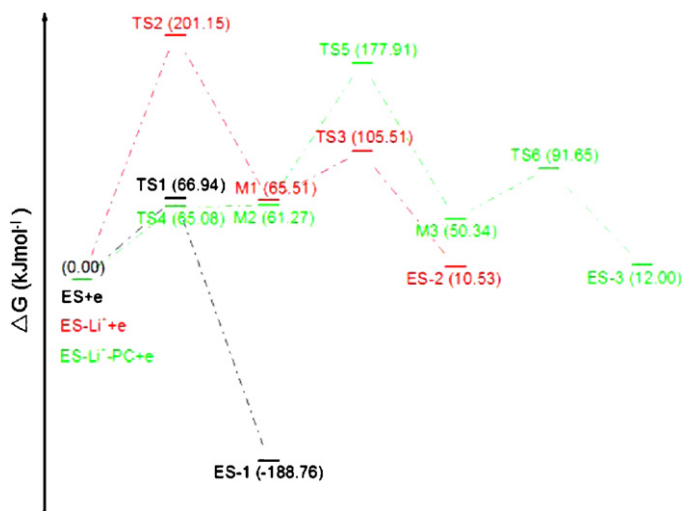| Structure	ΔE	$\Delta E + \Delta$ZPE	ΔH	ΔG	ω
ES-Li⁺+e	0.00	0.00	0.00	0.00	
TS 2	209.37	199.41	199.07	201.15	895 i
M1	72.33	64.46	65.30	65.51	
TS 3	118.31	107.74	108.79	105.51	485 i
ES-2	34.29	25.26	30.20	10.53	
ES-Li⁺-PC+e	0.00	0.00	0.00	0.00	
TS 4	66.90	65.78	64.46	65.08	190 i
M2	65.54	65.25	65.51	61.27	
TS 5	189.87	179.64	179.74	177.91	855 i
M3	61.85	52.55	54.70	50.34	
TS 6	105.68	95.30	96.71	91.65	517 i
ES-3	35.55	26.07	31.49	12.00	

Fig. 4. Potential energy profile for the decomposition process of ES in the forms of free ES, ES-Li⁺ and ES-Li⁺-PC.

The reaction potential free energy (ΔG) profile of free ES+e, ES-Li$^+$+e and ES-Li$^+$-PC+e is given in Fig. 4. It can be found that free ES+e is the most easy to decompose with the low energy barrier (66.94 kJ mol^{-1}) and lowest relative energy (-188.76 kJ mol^{-1}). Due to the highest energy barrier of TS2 (201.15 kJ mol^{-1}) in the reaction path of ES-Li$^+$+e, it must be the most difficult to decompose in the three forms of ES. Hence, the reaction activity of the three models should be as follows: ES+e > ES-Li$^+$-PC+e > ES-Li$^+$+e. ES-Li$^+$ and ES-Li$^+$-PC are the main compounds in PC based electrolyte containing ES as discussed above. Therefore, OSO$_2$Li and R-OSO$_2$Li are the main reductive products and the main compositions of the solid electrolyte interphase film on the anode of lithium ion battery.

4. Conclusions

The one electron reduction mechanism of ethylene sulfite (ES) in the forms of free ES, ES-Li$^+$, and ES-Li$^+$-PC, have been investigated by theoretical calculation at the B3LYP/6-311++G(d,p) level of density functional theory in gas phase. ES-Li$^+$ and ES-Li$^+$-PC are more possible in electrolyte solution than the free ES, due to their higher association strength. When these compounds are reduced, the electron is mainly distributed on ES, while the charge on PC keeps essentially constant. Furthermore, the O$_3$–S$_4$ bond of ES breaks with the forming of O$_3$–Li$_{11}$ bond of a seven membered ring in ES-Li$^+$ and ES-Li$^+$-PC, but the structure of PC changes slightly. PC is not involved in the reductive reaction of ES-Li$^+$-PC. The reductive products of ES-Li$^+$ and ES-Li$^+$-PC are OSO$_2$Li, OSO$_2$Li-R and ethylene. OSO$_2$Li and OSO$_2$Li-R are responsible for the formation of the solid electrolyte interphase film on the anode of lithium ion battery, which inhibits the reductive decomposition of PC.

Acknowledgments

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